Supporting Information

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Combination of Highly Efficient Electrocatalytic Water Oxidation with Selective Oxygenation of Organic Substrates using Manganese Borophosphates

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Chemicals

All chemical reagents (analytical grade) were used as received without any further purification. Deionized water was used to carry out all the experiments. Commercially available manganese(II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O), lithium tetraborate (Li₂B₄O₇), sodium tetraborate (Na₂B₄O₇), phosphoric acid (H₃PO₄, 85%), potassium hydroxide (1 M KOH, Fe < 0.05 ppm determined by ICP-AES) and 20% Pt on Vulcan XC72 were obtained from Sigma Aldrich. Selected manganese oxides (Mn₃O₄, Mn₂O₃, MnO₂), ruthenium oxide (RuO₂) and iridium oxide (IrO₂), cobalt oxide (Co₃O₄) were purchased from Alfa Aesar. The electrode substrates, nickel foam (NF), and fluorine-doped tin oxide (FTO, resistivity 8–12 Ω/sq) were obtained from Recemat BV and Sigma Aldrich, respectively.

Synthesis of the catalysts

Synthesis of LiMn(H₂O)₂[BP₂O₈]·H₂O (LiMnBPO). The single crystals of LiMn(H₂O)₂[BP₂O₈]·H₂O were prepared by a mild hydrothermal approach. A mixture of 2.003 g of Mn(CH₃COO)₂·4H₂O and 2.718 g Li₂B₄O₇ were first taken in a beaker, and the mixture was stirred after the addition of 20 mL of distilled water. To this mixture, 5.558 g of H₃PO₄ (85%) was added, and the pH was adjusted to 1 by addition of 2 mL HCl (37%). The mixture was then transferred into a 50 mL Teflon–lined autoclave (filling degree ~50%), kept under autogenous pressure at 180 ºC. After four days of reaction time, the autoclave was cooled down naturally to ambient temperature. The obtained reaction product was isolated by centrifugation, washed with deionized water (5–50 mL), and acetone (2–50 mL) several times and dried overnight in air at 60 ºC. The product consisted of colorless hexagonal bipyramid crystals with dimensions ranging from 0.1 mm to 0.5 mm.

Synthesis of NaMn(H₂O)₂[BP₂O₈]·H₂O (NaMnBPO). For NaMn(H₂O)₂[BP₂O₈]·H₂O, a mixture of 2.002 g of Mn(CH₃COO)₂·4H₂O, 3.227 g Na₂B₄O₇ were placed in 20 mL of distilled water. To this mixture, 5.553 g of H₃PO₄ (85%) was added to the mixture and the pH was adjusted to 1 by addition of 2 mL HCl (37%). The mixture was then transferred into a 50 mL Teflon–lined autoclave (filling degree ~50%), kept under autogenous pressure at 180 ºC. After four days of reaction time, the autoclave was cooled down naturally to ambient temperature. The obtained reaction product was isolated by centrifugation, washed with deionized water (5–50 mL), and acetone (2–50 mL) several times and dried overnight in air at 60 ºC. The product consisted of colorless hexagonal bipyramid crystals with dimensions ranging from 0.1 mm to 0.5 mm.

Synthesis of Mn₃N₂.¹ According to the previous literature, 500 mg of bis(cyclopentadienyl)manganese(II) was carefully weighed in a glove box and transferred into argon flushed tube furnace under a protective atmosphere. The furnace was then flushed with ammonia for 2 h prior to the annealing process. Afterward, the temperature was increased with a heating rate of 6 Kmin⁻¹ to 700 ºC and maintained at that
temperature for 12 h followed by naturally cooling down to room temperature. Dark grey metallic gleaming crystals of Mn$_3$N$_2$ were attained.

**Synthesis of Mn$_2$O$_3$-O$_2$.**[1] 500 mg of bis(cyclopentadienyl)manganese(II) was carefully weighed in a glove box and transferred into argon flushed tube furnace under a protective atmosphere. The furnace was first flushed with argon for 2 h and then switched to an oxygen atmosphere before the annealing process was started. The temperature was increased with 6 K min$^{-1}$ to 700 °C and maintained at that temperature for 12 h followed by cooling down to room temperature. The obtained dark brown particles represent the as-synthesized Mn$_2$O$_3$

**Synthesis of Mn$_2$O$_3$-SSP.**[2] Micro-emulsions containing cetyltrimethylammonium bromide (CTAB, 2.0 g) as a surfactant, 1-hexanol (20 mL) as co-surfactant and hexane (35 mL) as the lipophilic phase were synthesized and were mixed separately with an aqueous solution of 0.1 M Mn(CH$_3$COO)$_2$·4H$_2$O and (NH$_4$)$_2$C$_2$O$_4$·2H$_2$O. Both micro-emulsions were mixed slowly and stirred overnight. The white precipitate then obtained was then centrifuged and washed with 1:1 mixture of chloroform and methanol (200 mL) and subsequently dried at 60 °C for 12 hours to form manganese oxalate (MnC$_2$O$_4$·2H$_2$O). The as-prepared MnC$_2$O$_4$·2H$_2$O precursor was taken in an alumina crucible and heated in dry synthetic air (20% O$_2$, 80% N$_2$) at 400 °C for 8 hours (2 °C/min) and cooled down naturally to ambient temperature to form pure Mn$_2$O$_3$ phase.

**Synthesis of Co(OH)$_2$.**[3] 50 mL of 0.1 mol L$^{-1}$ NaOH solution was added dropwise into 80 mL of 0.05 mol L$^{-1}$ Co(NO$_3$)$_3$ solution. The solution was stirred and maintained at 45 °C for two hours which forms a pink precipitate, which was then washed with deionized water (3×50 mL) and dried in air at 60 °C.

**Synthesis of CoOOH.**[3] The as-synthesized Co(OH)$_2$ was dispersed in 30 mL 4 M KOH solution which was then slowly heated up to 45 °C. To this, 2 mL of 30% H$_2$O$_2$ solution was then added dropwise and was kept at the same temperature for 18 h. The final brown precipitate was filtered and washed with deionized water three times (3×50 mL), then dried at 60 °C overnight in air.

**Synthesis of Ni(OH)$_2$.**[4] 291 mg of Ni(NO$_3$)$_2$·6H$_2$O was dissolved in 10 mL of deionized water and to this solution, 15 mL of NaOH (0.1 M) was added dropwise and stirred for 30 min. A bright green solid was separated out which was then washed and centrifuged three times with deionized water (3×50 mL), once with acetone (1×50 mL) before drying at 60 °C overnight in air.

**Synthesis of NiOOH.**[3] The as-prepared Ni(OH)$_2$ was dispersed in 30 mL 4 M KOH solution which was then heated slowly up to 45 °C. 2 mL of 30% H$_2$O$_2$ solution was then added dropwise
and maintained at the same temperature for 18 h. The solid was washed and centrifuged 3 times with deionized water three times water (3×50 mL), once with acetone (1×50 mL), then dried at 60 °C overnight in air

**Synthesis of Fe(OH)$_3$.** Amorphous iron(III) hydroxide ((Fe(OH)$_3$) was prepared by a precipitation method. To an aqueous solution of Fe(NO$_3$)$_3$·9H$_2$O (205 mg in 10 mL), 1.6 mL of KOH (1 M) was added dropwise, and the solution was stirred at room temperature. A dark brown precipitate was separated by centrifugation and washed with deionized water (3×50 mL) and dried in air at 60°C.

**Synthesis of FeOOH.** The as-synthesized Fe(OH)$_2$ was first dispersed in 30 mL (4 M) KOH solution which was then heated slowly up to 45 °C. 2 mL of 30% H$_2$O$_2$ solution was then added dropwise and was kept at the same temperature for 18 h. The final brown precipitate was filtered and washed with deionized water three times (3×50 mL), then dried at 60 °C overnight in air.

**Synthesis of Amorphous Manganese Oxide (AMO).** First of all 1.58 g of KMnO$_4$ was dissolved in distilled water (60 mL). The solution was then slowly added dropwise to 100 mL of oxalic acid solution (contains 2.28 g of oxalic acid). The resultant mixture was stirred for 3 h at room temperature. Subsequently, the resultant slurry was filtered, and the obtained product was washed with water (5×50 mL) and dried at 90 °C overnight.

**Characterization of the catalysts**

**X-ray Diffraction.** Identification of the as-prepared and the transformed phases during catalysis were evaluated using powder X-ray diffraction pattern (PXRD), which was conducted on a Bruker AXS D8 advanced automatic diffractometer equipped with a position-sensitive detector (PSD) and curved germanium (111) primary monochromator. The radiation used for the measurement was Cu-Ka ($\lambda = 1.5418$ Å) and subsequently, the PXRD patterns were recorded in the 2 theta range of 5° < 2θ < 80°. The diffraction pattern fitting was carried out using the STOE WinxPow program. The Rietveld analysis of the as-prepared materials was performed by the FullProof program. The Rietveld method is a refinement technique that has the ability to determine the precise structural parameter of a crystalline phase, using the construction of a theoretical model that fits the experimental PXRD using the least-squares approach. The structural models of as-prepared products were constructed using the DIAMOND program version 3.0. The PXRD of the FTO deposited electrodes were measured using Bragg-Brentano geometry under air, using a Rigaku SmartLab 3 kW diffractometer (Rigaku Corporation, Japan) with Cu-Ka ($\lambda = 1.5418$ Å) radiation. Data acquisition was carried out using the SmartLab Guidance software package (Rigaku Corporation, Japan; Version 2.1.0.0).
**Elementary Analysis.** The chemical composition of the as-prepared materials and the materials post electrocatalysis were determined from the inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses. The materials were digested in aqua regia HCl: HNO₃ 3:1 v/v (nitric acid, SUPRA-Qualität ROTIPURAN® Supra 69% and hydrochloric acid, SUPRA-Qualität ROTIPURAN® Supra 30%) and the average of three independent experiments have been presented. The digestion volume (2.5 mL) was diluted with Milli-Q water up to 15 mL. The calibration curves were prepared for all manganese, phosphorus, boron, lithium, and sodium with concentrations between 1 mgL⁻¹ and 100 mgL⁻¹ from standard solutions (1000 mgL⁻¹ Single-Element ICP-Standard Solution ROTI®STAR).

**Electron Microscopy.** The details on the texture, morphology, and surface characteristics were examined by scanning electron microscopy (SEM) and the energy dispersive X-ray (EDX) analysis was used to semi-quantitatively identify the presence of manganese, phosphorus, sodium, potassium, and nickel. The elements with lower atomic numbers, such as lithium and boron could not be precisely determined due to the detection limits. The materials were placed on a silicon wafer, and the measurements were conducted on an LEO DSM 982 microscope integrated with EDX (EDAX, Appollo XPP). Data handling and analysis were performed with the software package EDAX. The more detailed microstructure analysis of the as-prepared materials and the materials post electrochemical investigations were investigated by transmission electron microscopy (TEM). A small amount of the material powder was kept on a TEM-grid (carbon film on 300 mesh Cu-grid, Plano GmbH, Wetzlar, Germany) and the microstructure (particle size, morphology, crystallinity, phase composition) of the materials were inspected by an FEI Tecnai G² 20 S-TWIN transmission electron microscope (FEI Company, Eindhoven, Netherlands) equipped with a LaB₆-source at 200 kV acceleration voltage. The EDX analysis was assessed with an EDAX r-TEM SUTW Detector (Si (Li)-detector). Images were recorded with a GATAN MS794 P CCD-camera. Both SEM and TEM experiments were conducted partially at the Zentrum für Elektronenmikroskopie (ZELMI) of the TU Berlin.

**Fourier transform infrared (FT-IR) spectroscopy.** The presence of different modes of vibrations of the as-prepared materials was studied using a BIORAD FTS 6000 FTIR spectrometer under attenuated total reflection (ATR) conditions. The data were collected in the range of 400–4000 cm⁻¹ with an average of 32 scans at 4 cm⁻¹ resolution. Further, the presence of −OH groups and H₂O in the crystal structures of the investigated BPOs and transformed materials were directly compared with the literature reported examples.[7]

**Brunauer–Emmett–Teller (BET) specific surface area.** The surface areas of the as-prepared materials were determined on a Quantachrome Autosorb-1 apparatus. Nitrogen adsorption/desorption isotherms were measured at -196°C after degassing the sample at 120°C overnight. The BET surface areas (S_BET) were calculated from the adsorption data in a relative pressure ranging from 0.01 to 0.1. The S_BET of LiMnBPO and NaMnBPO was 1.36 and 1.10 m²g⁻¹, respectively.
Gas chromatography (GC). An Agilent 7890A gas chromatograph (GC) was used to determine the FE of oxygen evolution reaction (OER). The GC was equipped with a carboxen-1000 column and a thermal conductivity detector (TCD), where the carrier gas used was argon (Ar). The electrodes were first immersed in the 53 mL closed electrolyzer set-up and bubbled with Ar for 1 h. Subsequently, the produced O₂ gas in the headspace was collected with a syringe and injected into the GC. Post OER experiment, the amount of O₂ collected in the head-space was determined. The aerial O₂ contribution during sampling was corrected by estimating O₂ before and post electrochemical reaction.

X-ray photoelectron spectroscopy (XPS). To understand the chemical state, bonding situation and surface structure of the synthesized catalysts, as well as post electrocatalysis, the XPS measurements were performed using a Kratos Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, UK) with an Al Kα (1486.7 eV) monochromatic radiation source with 90° takeoff angle (normal to analyzer). The vacuum pressure in the analyzing chamber was kept at 2 x 10⁻⁹ Torr. The high-resolution XPS spectra were collected for C 1s, O 1s, Mn 2p, Mn 3p, P 2p, B 1s, and Li 1s levels with a pass energy of 20 eV and step size of 0.1 eV. The binding energies were then calibrated relative to the C 1s peak energy position as 285.0 eV. Analyses of the data were conducted using Casa XPS (Casa Software Ltd.) and Vision data processing program (Kratos Analytical Ltd.).

Raman spectroscopy. To gain further insight into the structure of the as-prepared and active catalysts, Raman spectroscopy was performed using a Renishaw in-Via (serial number: 37x207) Raman microscope with a 532nm laser (Renishaw RL-532-08, serial number: 17GU77). The objectives used were a 50x (HC PL FLUOTAR 20x/0.80) and 63x (HC PL FLUOTAR 63x/0.70) “long-range” (1 cm focal length) from LEICA. In-situ Raman spectroscopy on the samples was performed in combination with electrochemical measurements. The electrochemical cell was fabricated by depositing the catalyst film onto an FTO anode, and Pt coated on FTO was used as the cathode. The top of the cell contained two small holes through which 1 M KOH electrolyte was injected prior to the OER experiments. The potential required for OER to reach 10 mA was applied using a Metrohm Potentiostat/Galvanostat (Autolab PGSTAT302N) and maintained until the end of the electrochemical measurements. For in-situ time-resolved Raman measurements, measurements were performed repeatedly with a 10-second exposure for one acquisition, three acquisitions were combined to one accumulation (spectrum).

Quasi in-situ X-ray absorption spectroscopy (XAS). To get insights on the local atomic and electronic structure, extended X-ray absorption fine-structure (EXAFS), and near-edge structure (XANES) studies were carried out under quasi in-situ conditions. The XAS spectra (XANES/EXAFS) were recorded at the BESSY II synchrotron radiation source operated by the Helmholtz-Zentrum Berlin. The measurements were performed at the KMC-3 bending-magnet beamline at 20 K in a helium-flow cryostat (Oxford-Danfysik). The incident beam energy was selected by a Si(111) double-crystal monochromator. The measurements at the manganese K-
edge were performed in fluorescence mode (\(K\) fluorescence energy region selected) using a 13-element energy-resolving Ge detector (Canberra) cooled with liquid nitrogen (\(N_2\)). The extracted spectra were weighted by \(k^3\) and simulated in \(k\)-space (\(E_0 = 6547\) eV). All EXAFS simulations were performed using in-house software (SimXLite, programmed by Dr. Petko Chernev) after calculation of the phase functions with the FEFF program (version 8.4, self-consistent field option activated). The data range used in the simulation of the EXAFS spectra was \(k = (3-14)\) \(\text{Å}^{-1}\). The EXAFS simulation was optimized by a minimization of the error sum obtained by the summation of the squared deviations between measured and simulated values (least-squares fit). The fit was performed using the Levenberg-Marquardt method with numerical derivatives. The error ranges of the fit parameters were estimated from the covariance matrix of the fit. Cosine windows covering 10% of the low \(k\)-side and 10% of the high \(k\)-side of the spectra were applied for the calculation of the Fourier transforms. Further details are given elsewhere.\(^8\) LiMnBPO samples for XAS experiments were prepared on FTO substrates (including the powder sample) in analogy to the electrochemical experiments. The samples were electrochemically treated in OER chronoamperometric conditions (CA, 24 h) at 1.56 V vs. RHE in 1 M KOH solution. After the desired electrochemical measurement, the samples were immediately freeze-quenched using liquid \(N_2\) under vigorous argon gas flow and stored in liquid \(N_2\) until XAS measurements were conducted.

**Electrophoretic deposition (EPD) of catalysts**

The EPD process is based on the suspension of particles in a solvent where the migration and the deposition of charged particles in suspension occur that is initiated by applying an electric field between two electrodes (the anode and the cathode).\(^9\) It is a binder-free coating approach and has the benefits of faster deposition, easy, cost-effective, and suitable for mass production.\(^10\) In the presented work, the as-synthesized (catalyst) materials were deposited on both NF and FTO electrophoretically by applying a potential of -10 V in a mixture of iodine and acetone on a 1 \(\times\) 1 cm\(^2\) area. Before deposition, the electrodes (cathode and anode) were fixed 1 cm apart from each other.\(^11\) The detailed mechanism involving electrophoretic deposition has been discussed elsewhere.\(^12\) The electric charge on the catalyst surface in acetone is insufficient to carry out the EPD process as very small amounts of free ions exist in acetone; hence, large potentials are necessary. However, when iodine is used as the dispersant, it can rapidly react with acetone through the keto-enol tautomerism to produce protons as per the following equation.\(^12\)

\[
\begin{align*}
\text{CH}_3\text{C}\equiv\text{CH}_2 & \quad \overset{\text{OH}}{\rightleftharpoons} \quad \text{CH}_3\text{C}\equiv\text{CH}_2 \quad + \quad \text{I}_2 \quad \overset{\text{Fast}}{\rightarrow} \quad \text{CH}_3\text{C}\equiv\text{CH}_2\text{I} & + & \quad \text{I}^- & + & \quad \text{H}^+ \\
\text{Keto} & & \text{Enol}
\end{align*}
\]

The protons formed from the reaction are adsorbed on the surface of the suspended catalyst particles by creating a positive charge. Subsequently, the applied electric field induces the
positively charged particles to migrate towards and deposit on the cathode.\[11,13\] To have a better dispersion in acetone and smooth deposition of the catalyst on the electrode substrates, the LiMn(H$_2$O)$_2$[BP$_2$O$_8$]·H$_2$O (LiMnBPO) and NaMn(H$_2$O)$_2$[BP$_2$O$_8$]·H$_2$O (NaMnBPO) crystals were first grounded for 15 min to reduce the particle size. Other nanostructured oxides or nitride catalysts were used directly without additional grinding.\[7\] In order to conduct EPD, typically, 30 mg of the desired catalyst powder was suspended in 10 ml acetone, and 3 mg of iodine was then added. The solution was agitated in an ultrasonic bath for 30 min. Before EPD, the empty electrodes were weighed using an analytical balance, and the weights were noted. The EPD was conducted by applying a potential at -10 V for 1 minute with stirring the solution continuously at room temperature. After each EPD, the increase in weight of the electrodes was monitored carefully. The catalyst loading on each FTO was \(\sim 0.5\) and \(\sim 1.3\) mgcm$^{-2}$, respectively. The mass loading was reproducible up to the first 7 films within the margins of an experimental error (\(\pm 0.05\) mg), and only films with similar mass loading were chosen for electrochemical tests. The bare NF was also subjected without a catalyst to same EPD conditions and measured as a reference.\[14\]

**Electrochemical measurements.** A typical electrocatalytic run was carried out in a standard three-electrode (working, counter, and reference) electrochemical cell in 1 M aqueous KOH with a potentiostat (SP-200, BioLogic Science Instruments) controlled by the EC-Lab v10.20 software package. The electrodes (NF/FTO) with samples deposited served as the working electrodes, Pt wire (0.5 mm diameter × 230 mm length; A-002234, BioLogic) as a counter and Hg/HgO as the reference electrode (CH Instruments, Inc.). Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out with an applied iR compensation of 85%. The uncompensated resistance \(R_u\) was obtained by an electrochemical impedance measurement at 100 MHz and a potential of 1.175 V vs. RHE prior to each experiment. The obtained values for \(R_u\) ranged between 13 and 17 \(\Omega\) consistent with the \(R_s\) values from the presented impedance spectra over a wider frequency range. 85% of \(R_u\) was used for the iR compensation. The compensation was performed by the software of the electrochemical workstation. The potentials presented in this work were referenced to the reversible hydrogen electrode (RHE) through calibration in 1 M aqueous KOH,

\[
E(\text{RHE}) = E(\text{Hg/HgO}) + 0.098\ V + (0.059 \times \text{pH})\ V.
\]

The chronoamperometric measurements (CA) were performed in 1 M aqueous KOH at selected constant potentials with respect to RHE. Tafel plots were determined by potentiostatic measurements between 1.44 and 1.54 V vs. RHE, employing stepwise changes of the potential by 10 mV. The current density at each potential was measured for a stable potential for 600 s and the average current values were used for the determination of Tafel plots. The Tafel slope was calculated according to the Tafel equation

\[
\eta = b \log j + a
\]
where $\eta$ represents the overpotential (V), $j$ is the current density (mA cm$^{-2}$), and $b$ is the Tafel slope (mVdec$^{-1}$).

The electrochemically active surface areas (ECSAs) of LiMnBPO and NaMnBPO was obtained both on FTO and NF by determining their double-layer capacitance ($C_{dl}$) from the CV at a potential range, where no apparent faradaic process occurred. The anodic charging currents measured at a particular potential and were plotted as a function of the scan rate and from the slope, and the double layer capacitance $C_{dl}$ was attained. The ECSA of the catalysts were then calculated using the equation

$$\text{ECSA} = \frac{C_{dl}}{C_s}$$

where $C_s$ is the specific capacitance of the material for a standard with 1 cm$^2$ of the real surface area under identical electrolyte conditions.$^{[15]}$ However, the exact ECSA of our material is difficult to measure due to the unknown capacitive behavior ($C_s$) of borophosphates. Therefore, we estimated the relative surface area as the $C_{dl}$ is expected to be linearly proportional to effective active surface area for material with similar composition and has been widely used in previous OER studies.$^{[16]}$

The electrochemical impedance spectroscopy (EIS) was recorded at 1.55 V vs. RHE for FTO and 1.5 V vs. RHE for NF to obtain the Nyquist plots. The amplitude of the sinusoidal wave was determined in a frequency range of 100 kHz to 1 mHz. The charge transfer resistance ($R_{ct}$) was attained from the diameter of the semicircle in the Nyquist plots.$^{[17]}$ In addition to this, the variation of charge transfer as a function of applied potentials (at. 1.4 V, 1.5V, 1.55 V and 1.6 V vs. RHE) were also been measured for LiMnBPO/FTO and bare FTO substrate.

The overall alkaline water-splitting reaction was performed in a two-electrode system on materials using Pt/C as cathode and LiMnBPO as an anode on both FTO and NF substrates. The long-term durability was also tested at a selected potential, where the current reached 10 mAcm$^{-2}$ and 120 mAcm$^{-2}$.

**Turnover frequencies (TOFs).** The TOF can be defined as moles of O$_2$ per moles of total metal content (Mn in this case) evolved per second (s$^{-1}$). The TOF of electrocatalysts were calculated from the equation

$$\text{TOF (s}^{-1}) = \frac{(j \times A)}{(z \times F \times n)}$$

where $j$ is the OER current density, which was achieved from CV with a low scan rate of 5 mV s$^{-1}$, $A$ is the geometrical surface area of the electrode, $F$ is the Faraday constant (96500 C mol$^{-1}$), $z = 4$ electron transfer for the overall reaction, $n$ (mol) is mole number of transition metal loaded on the electrode, which was determined by ICP-AES analysis (here all metal cations were assumed to be catalytically active, representing the lower limits of TOF). Similarly, the TOF was
also derived using the amount of electroactive Mn sites that were also obtained by integration of the area under the metal redox peaks (see Figure S20) as described elsewhere.[18]

**Bulk Electrolysis of organic substrate.** Bulk electrolysis was performed under constant current (10 mA) in a two-electrode cell set-up. The electrochemical cell was assembled by using a T-type two-compartment glass cell where the cathode and anode compartments are separated by a porous g-4 glass frit. Electrophoretically deposited LiMnBPO on Ni foam (0.5 x 2 cm), as described for OER reaction, was used as a working electrode, and a platinum wire was used as the counter electrode. In each compartment, 4 mL of 1 M aqueous KOH was used as the electrolyte, the desired amount of organic substrate was added to the working electrode compartment. Similarly, to investigate the extent to which electro-oxidation is favored, the experiments were also performed in a three-electrode set-up (similar to the OER process), and the corresponding LSVs were recorded.

**Organic product analysis by ¹H NMR.** ¹H nuclear magnetic resonance (¹H NMR). The reactivity and the corresponding organic product formation during the electro-oxidation reaction of different substrates were analyzed by ¹H NMR spectroscopy in a 200 MHz JEOL NMR instrument. Organic products formed during the electro-oxidation reaction were analyzed by ¹H NMR spectroscopy in a 200 MHz JEOL NMR instrument. During the reaction, 100 µL of the reaction solution was taken out of the working electrode compartment and diluted with 400 µL D$_2$O. All the spectra were analyzed in MestReNova software. Each spectrum consisted of a sharp peak 4.7 ppm appeared for residual H$_2$O (aqueous solution of 1 M KOH) in the reaction solution is used as a reference, and chemical shift values of the protons of the organic compounds were assigned accordingly and compared with literature values of the known compounds. The organic compounds are quantified (chemical conversion) by calculating the relative intensity of the proton signals.

Chemical conversion and FE were calculated following equations:

\[
\text{Chemical conversion (\%) = } \frac{n(\text{product})}{n(\text{reactant initial conc.})} \times 100
\]

\[
\text{FE (\%) = } \frac{n(\text{product formed}) \cdot n_e \cdot F}{Q} \times 100
\]

where F is the Faraday constant (96 485 C mol$^{-1}$), n the mol of reactant quantified from ¹H NMR, $n_e$ no electron needed for the oxidation process and Q is the charge (coulombs) passed through the solution.
Figure S1. Rietveld refinement patterns of high-resolution powder X-ray diffraction (PXRD) of the NaMnBPO with respective crystal system, space group, and unit cell parameters.\textsuperscript{[7,19]} Red dots: experimental data points; black line: calculated powder pattern; blue ticks: Bragg positions; blue line: the difference between the observed and calculated patterns.
Figure S2. Optical microscopic images of (a) LiMnBPO and (b) NaMnBPO. From the images, it was observed that colorless crystals of hexagonal bipyramids were produced.
Figure S3. The scanning electron microscopic (SEM) images of the single crystals of (a, b) LiMnBPO and (c, d) NaMnBPO. Well-defined crystals of hexagonal bipyramids were attained.
Figure S4. The helical LiMn(H$_2$O)$_2$[BP$_2$O$_8$]·H$_2$O (LiMnBPO) and NaMn(H$_2$O)$_2$[BP$_2$O$_8$]·H$_2$O (NaMnBPO) crystallize in the chiral space groups $P6_522$ or $P6_122$, and the crystal structure here can be termed as one-dimensional infinite loop-branched borophosphate helices $\propto[\text{BP}_2\text{O}_8]^{3-}$ built of alternate BO$_4$ (blue) and PO$_4$ (purple) tetrahedra.$^{[19\text{a},20]}$ The borate groups share all their oxygen apices with the next PO$_4$ tetrahedra. The PO$_4$ is connected to only two BO$_4$ units. The resulting structural motif can be described as a spiral ribbon of four-membered rings of tetrahedra where the PO$_4$ occupy the borders of the ribbons with two terminal oxygen atoms (see main text for more detailed structural aspects). The crystal water is located within these helical channels.$^{[21]}$
**Figure S5.** The crystals structure of helical LiMnBPO and NaMnBPO in the [001]. The helices \[\alpha_1[BP_2O_8]^{3-}\] built of alternate BO\(_4\) (blue) and PO\(_4\) (purple) tetrahedra are further interconnected through MnO\(_4\)(OH\(_2\)) coordination octahedra (green spheres) and the free threads of helices are occupied by alkali metal cations (yellow spheres; Li or Na) which are in an irregular surrounding of oxygen atoms.\[19b\] The hydrate water (red spheres) is located within the running helical channels (red spheres), and the overall structure can be depicted as the arrangement of helical chains in a dense rod-packing.\[19a,20-21\]
Figure S6. The SEM image of LiMnBPO used for elemental mapping. For details, see Figure 1e-g, main text.
Figure S7. The SEM image (a) and the EDX mapping analysis of NaMnBPO. The distribution of Na (b), Mn (c), P (d), and O (e) is shown in green, orange, yellow, and red, respectively. The element boron was difficult to analyze due to its low photon energy and owing to its detection limit (hence, ICP-AES was conducted). The resultant NaMnBPO hexagonal bipyramids display a homogeneous distribution of elements that confirms the phase purity of the product.
Figure S8. The EDX (mapping) spectra of LiMnBPO (top) and NaMnBPO (bottom).
Figure S9. The transmission electron microscopy (TEM) images of LiMnBPO (a, b) and NaMnBPO (c, d). The corresponding selected area electron diffraction (SAED) patterns showing crystallinity in both materials is shown in the inset. The single crystals were ground before measuring TEM to reduce the size of the particles.
Figure S10. The presence of heavy elements such as manganese, phosphorus, and sodium in LiMnBPO (top) and NaMnBPO (bottom) was determined by the EDX. The appearance of peaks for carbon and copper is due to the TEM grid (carbon film on 300 mesh Cu-grid).

Table S1. Determination of chemical composition in LiMnBPO and NaMnBPO was obtained by EDX, X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis.

| Chemical Formula          | Li/Na:Mn:B:P (Theo.) | Mn:P (EDX) | Li/Na:Mn:B:P (XPS) | Li/Na:Mn:B:P (ICP-AES) |
|---------------------------|----------------------|------------|---------------------|------------------------|
| LiMn(H$_2$O)$_2$[BP$_2$O$_8$]·H$_2$O (LiMnBPO) | 1:1:1:2             | ~1:2.08    | 1:1.04:0.94:2.1     | 1:1.01:0.99:2          |
| NaMn(H$_2$O)$_2$[BP$_2$O$_8$]·H$_2$O (NaMnBPO) | 1:1:1:2             | ~1:2.1     | 1:1.1:0.91:2.03     | 0.98:1:1:2.03         |
Figure S11. The Fourier transformed infrared (FT-IR) spectra of LiMnBPO and NaMnBPO, depicting the presence of water by characteristic absorption bands at about ~1647 cm\(^{-1}\) (H\(_2\)O deformation) and between 3000 and 3600 cm\(^{-1}\) (O\(^-\)H stretching).\(^{[7,20b]}\) Moreover, the spectrum in both cases is dominated by the strong P–O stretching modes in the region ranging from 800 to 1100 cm\(^{-1}\) and overlaps heavily with the strong B–O stretching vibrations in the range of 700–1200 cm\(^{-1}\).\(^{[7,20a,21a,21b]}\)
Figure S12. High-resolution XPS spectra of LiMnBPO in the regions containing (a) Mn 2p, (b) Mn 3p and Li 1s. The core-level spectrum centered on Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ was deconvoluted into a major and a minor peak.[22] The major peaks evolving at 640.3 eV and 652.2 eV can directly be correlated to the MnO confirming the main oxidation state the material is Mn$^{II}$.[23] Similarly, the minor peaks at 641.7 eV and 653.2 eV can be ascribed to Mn$^{III}$, which is due to the slight surface oxidation of the LiMnBPO. In addition, a satellite peak attained at 645.2 eV is typical for compounds containing Mn$^{II}$ (MnO).[24] The Mn 3p spectra also showed two peaks at ~47 and ~48.7 eV that could be corroborated to the Mn$^{II}$ and Mn$^{III}$.[25] The binding energies of Mn 2p and Mn 3p are in good accordance with the manganese-based materials.[26] Furthermore, the Li 1s binding energy peaks at ~55.5 eV could directly be compared to the other Li$^{I}$ containing compounds.[25b,27] As LiMnBPO and NaMnBPO were structurally analogs, the XPS measurement of NaMnBPO was not carried out.
Figure S13. Typical high-resolution XPS spectra of the regions containing the (a) B 1s, (b) P 2p, and (c) O1s of as-synthesized LiMnBPO. The B 1s XPS spectrum exhibited a peak at ~191.4 eV is attributed to the structure of boron linked to oxygen atoms with four coordination indicative of B\(^{III}\) (borate).\(^{[7,28]}\) High-resolution P 2p XPS spectrum was deconvoluted into two components, and every component was fitted in two peaks, namely 2p\(_{3/2}\) and 2p\(_{1/2}\), that are attributed to the phosphate (PO\(_4\))\(^{3-}\) on the surface, which is in good agreement with the literature reported phosphate materials.\(^{[7,29]}\) The O 1s spectrum was deconvoluted into broad O1 and O2 peaks. The peak at ~ 531.3 eV (O1) fits very well with the binding energy of oxygen present in borates and phosphates. The O2 peak ~ 532.3 eV could be assigned to the crystal water in the structure. The O1s values obtained here can be matched well with literature reported materials of phosphates and borates.\(^{[7,29a,29b]}\)
Figure S14. The SEM images (a, b) of LiMnBPO films deposited on FTO substrate at two magnifications.
Figure S15. The SEM image (a) and the EDX mapping analysis of LiMnBPO films deposited on FTO. The homogenous distribution of Mn (b), P (c), and O (d) are shown in orange, yellow, and red, respectively. The element boron was difficult to analyze due to its low photon energy and owing to its detection limit. This signifies that the deposited films detained their chemical identity (also see XAS section later).
Figure S16. The EDX (mapping) spectrum of LiMnBPO films deposited on FTO.

LiMnBPO/FTO
Figure S17. The LiMnBPO material was deposited on FTO electrode substrate and tested for water oxidation using a three-electrode set-up in aqueous 1M KOH. An immediate change of color was observed from colorless (left) to brown (right) under applied water oxidizing potentials suggesting the surface-structural changes.
Figure S18. Electrochemical double-layer measurements for the estimation of the relative electrochemical active surface area (ECSA) in a non-Faradaic potential range of 1.07 V to 1.12 V vs. RHE at different scan rates (10, 20, 50, 100 and 200 mVs⁻¹) for (a) LiMnBPO/FTO and (b) NaMnBPO/FTO in aqueous 1 M KOH solution. (c) Determination of double-layer capacitances ($C_{dl}$) by plotting the current density variation ($\Delta j = (j_a - j_c)/2$), obtained from the (a) and (b) at 1.095 V vs. RHE.¹⁵,³⁰ A $C_{dl}$ value of 0.079 mFcm⁻² was obtained for LiMnBPO, whereas a slightly lower value of 0.063 mFcm⁻² resulted in NaMnBPO.
Figure S19. Cyclic voltammograms (CV) normalized by (a) geometric area, (b) mass, (c) Brunauer–Emmett–Teller (BET) surface, and (d) ECSA (C \text{dl} \text{ is proportional to the ECSA for similar materials}) of LiMnBPO and NaMnBPO on FTO.
Figure S20. The amount of electroactive Mn site was obtained by integration of the area under the metal redox peaks and considered for the calculation of the number of redox-active sites. We estimated that the redox transition involves one electron per redox-active Mn center. The detailed calculations of determination of turnover frequencies (TOF) from redox-active metal centers have been described in the numerous previously reported literature.[18,31]
Figure S21. TOF determined from (a) Mn mass loading (from ICP-AES) and (b) the number of surface-active Mn sites by the integration of the area of the redox peaks (refer Figure S20) The attained TOFs here are the best among any Mn-based catalysts reported to-date.\cite{6,32}
The plot on the left top shows the EIS spectrum of LiMnBPO/FTO together with three different fits based on the three circuits, a, b, c, shown on the right top. In the circuits, $R$ represents a resistor and $Q$ a constant phase element (CPE). The table at the bottom summarized the parameters of the fits. All three circuits have been previously used to fit transition metal-based systems during OER reaction conditions.\cite{17,33} The plot on the left top shows that, for LiMnBPO, all three circuits can be applied to obtain reasonable fits. The magnified inset in the plot reveals that, for high frequencies, the simulated spectra based on circuit b and c agree better with the experimental data. However, these two models are based on significantly more fitting parameters and the assignment of the additional circuit elements to physically relevant phenomena is not straightforward. In this regard, $R_3$ was assigned to different phenomena already including an oxidation change resistance of Mn,$^{[33a]}$ the resistance of the relaxation of surface coverage of adsorbed intermediates,$^{[17a]}$ or the diffusion of intermediates in porous materials.$^{[33b]}$ There is no straightforward reason to exclude any of these phenomena for LiMnBPO. Therefore, no unambiguous assignment of the additional circuit elements can be done. Further, the dispersion parameter of the additional CPE in circuit b indicates that its physical meaning is that of a capacitor; while in circuit c, it indicates a Warburg element. Such a strong difference shows that the added complexity is not justified. Therefore, we decided to perform all the fits with the simple model a. The assignment of the of its elements is consistent in the literature and can be applied to our system: $R_1$ is the ohmic resistance of the solution and electrode ($R_s$), $R_2$ is the charge transfer resistance ($R_{ct}$), and the CPE element represent the double-layer capacitance ($C_{dl}$)$.^{[17,33]}$ The same assignment can be done for circuits b and c for these three elements and as the table at the bottom of this figure reveals, these parameters do not change strongly for all three circuits. Therefore, circuit a is sufficient for a meaningful interpretation of $R_s$ and $R_{ct}$.

**Figure S22.** The plot on the left top shows the EIS spectrum of LiMnBPO/FTO together with three different fits based on the three circuits, a, b, c, shown on the right top. In the circuits, $R$ represents a resistor and $Q$ a constant phase element (CPE). The table at the bottom summarized the parameters of the fits. All three circuits have been previously used to fit transition metal-based systems during OER reaction conditions.\cite{17,33} The plot on the left top shows that, for LiMnBPO, all three circuits can be applied to obtain reasonable fits. The magnified inset in the plot reveals that, for high frequencies, the simulated spectra based on circuit b and c agree better with the experimental data. However, these two models are based on significantly more fitting parameters and the assignment of the additional circuit elements to physically relevant phenomena is not straightforward. In this regard, $R_3$ was assigned to different phenomena already including an oxidation change resistance of Mn,$^{[33a]}$ the resistance of the relaxation of surface coverage of adsorbed intermediates,$^{[17a]}$ or the diffusion of intermediates in porous materials.$^{[33b]}$ There is no straightforward reason to exclude any of these phenomena for LiMnBPO. Therefore, no unambiguous assignment of the additional circuit elements can be done. Further, the dispersion parameter of the additional CPE in circuit b indicates that its physical meaning is that of a capacitor; while in circuit c, it indicates a Warburg element. Such a strong difference shows that the added complexity is not justified. Therefore, we decided to perform all the fits with the simple model a. The assignment of the of its elements is consistent in the literature and can be applied to our system: $R_1$ is the ohmic resistance of the solution and electrode ($R_s$), $R_2$ is the charge transfer resistance ($R_{ct}$), and the CPE element represent the double-layer capacitance ($C_{dl}$)$.^{[17,33]}$ The same assignment can be done for circuits b and c for these three elements and as the table at the bottom of this figure reveals, these parameters do not change strongly for all three circuits. Therefore, circuit a is sufficient for a meaningful interpretation of $R_s$ and $R_{ct}$. 

|       | $R_1$ [Ω] | $R_2$ [Ω] | $Q_2$ [$F \times s^{0.5}$] | $n_2$ | $R_3$ [Ω] | $Q_3$ [$F \times s^{0.5}$] | $n_3$ |
|-------|-----------|-----------|---------------------------|-------|-----------|---------------------------|-------|
| Circuit a | 13.5      | 17.2      | 0.048                     | 0.90  | -         | -                         | -     |
| Circuit b | 13.3      | 15.9      | 0.050                     | 0.96  | 0.83      | 0.093                     | 0.84  |
| Circuit c | 13.1      | 16.8      | 0.046                     | 0.98  | 2.2       | 0.22                      | 0.51  |
Figure S23. The plots (a), (b), (c), show the EIS spectra of LiMnBPO/FTO (squares, dots, triangles) at four different potentials together with the respective fits (straight lines) at different magnifications. The table presents the parameters of the performed fits based on the circuit a of Figure 22 with the assignment of the circuit elements described in the caption. For the measurement at 1.40 V, only the beginning of the arc was obtained experimentally, which led to a worse fit. Therefore, we also performed a fit based on circuit b (dashed purple line), which resulted in a better agreement with the experimental data, but the $R_{ct}$ (4165 $\Omega$) and $R_s$ (15.3 $\Omega$) values changed only marginally. In all cases, $R_{ct}$ represents the total charge transfer resistance for the overall rate of the OER. It decreases with increased applied potential revealing increased electron transfer kinetics for higher potentials. This dependency is consistent with a Faradaic process such as the OER.\[17a]\] The $R_{ct}$ values can also be used to estimate the Tafel slope ($b$) using the relation

$$\log \left( \frac{1}{R_{ct}} \right) = \frac{\eta}{b} + \log \left( 2.303 \frac{i_0}{b} \right)$$

where $\eta$ is the overpotential and $i_0$ is the exchange current density.\[34] Consistent with the steady-state Tafel analysis, a Tafel slope of 49 mV/dec could be obtained for the potential range 1.4 V to 1.5 V. For the range 1.5 to 1.6 V, the Tafel slope is larger (125 mV/dec) caused by additional mass transport limitations, a change in the reaction mechanism, or/and a different surface coverage.\[35]
Figure S24. The plot shows the EIS of bare FTO, LiMnBPO/FTO, and NaMnBPO/FTO. The table presents the parameters of the performed fits based on the circuit a of Figure 22 with the assignment of the circuit elements described in the caption. The $R_{ct}$ decreases dramatically when Li/NaMnBPO has been deposited on the FTO unveiling its excellent catalytic properties towards the OER. The $R_{ct}$ of LiMnBPO/FTO is smaller than the one of NaMnBPO/FTO revealing better electron transfer kinetics for LiMnBPO/FTO, which is consistent with the other electrochemical data.

|         | FTO  | LiMnBPO | NaMnBPO |
|---------|------|---------|---------|
| $R_s$ [Ω] | 13.0 | 13.5    | 11.9    |
| $R_{ct}$ [Ω] | 1.2×10^{15} | 17.2    | 51.1    |
| $Q$ [F×s^{0.1}] | 10^6 | 0.048   | 0.055   |
| $n$      | 0.95 | 0.90    | 0.92    |
Figure S25. The plot shows the EIS of bare FTO obtained through variation of charge transfer as a function of applied potentials (at 1.4 V, 1.5 V, 1.55 V and 1.6 V vs. RHE).\textsuperscript{56,57}
Figure S26. The chronoamperometric (CA) response of LiMnBPO/FTO and NaMnBPO/FTO measured in water oxidation conditions at 1.56 and 1.58 V vs. RHE in 1 M aqueous KOH solution for 24 h. The broken red line is a guide to the eye at 10 mA cm$^{-2}$. 
Figure S27. The PXRD patterns and the respective Miller indices of commercially obtained Mn$_2$O$_3$ (JCPDS 24-508), Mn$_3$O$_4$ (JCPDS 24-734), and MnO$_2$ (JCPDS 30-820) (Figure top). Similarly, the PXRD of various single-source precursor derived manganese-based materials such as Mn$_2$O$_3$-SSP (JCPDS 24-508), Mn$_2$O$_3$-O$_2$ (JCPDS 24-508) as well as Mn$_3$N$_2$ (JCPDS 1-1158) is shown at the bottom (preparation details are given in the synthetic section).
Figure S28. The SEM (a, d, g), TEM (b, e, h) and SAED (c, f, i) patterns of commercially obtained Mn$_2$O$_3$ (JCPDS 24-508), Mn$_3$O$_4$ (JCPDS 24-734) and MnO$_2$ (JCPDS 30-820) showing their morphological, structural aspects and crystallinity.
Figure S29. The SEM (a, d, g), TEM (b, e, h) and SAED (c, f, i) patterns of synthesized Mn$_2$O$_3$-SSP (JCPDS 24-508), Mn$_2$O$_3$-O$_2$ (JCPDS 24-508) and Mn$_3$N$_2$ (JCPDS 1-1158) showing their morphology, structure, and crystallinity.
Figure S30. The EDX pattern of commercial Mn$_2$O$_3$, Mn$_3$O$_4$, MnO$_2$, and prepared Mn$_2$O$_3$-SSP and Mn$_2$O$_3$-O$_2$. The appearance of peaks for copper is due to the TEM grid (carbon film on 300 mesh Cu-grid).
Figure S31. Comparison of water oxidation polarization curves of LiMnBPO and NaMnBPO with Mn$_2$O$_3$, Mn$_3$O$_4$, MnO$_2$, Mn$_2$O$_3$-SSP, Mn$_2$O$_3$-O$_2$, and Mn$_3$N$_2$ deposited on FTO at a sweep rate 1 mVs$^{-1}$ in aqueous 1M KOH (with the same mass loading). The attained overpotentials ($\eta$) for presented BPO materials were significantly lower compared to other highly active manganese oxide or nitride-based catalysts (see Table S3).
Figure S32. The PXRD (JCPDS 42-1467), Co(OH)$_2$ (JCPDS 30-433), CoOOH (JCPDS 7-169), FeOOH (JCPDS 27-713) and Ni(OH)$_2$ (JCPDS 24-2075) patterns. The synthetic procedures are given in the synthetic section. The Fe(OH)$_3$ and NiOOH were X-ray amorphous.
Figure S33. The PXRD patterns and the respective Miller indices of noble RuO$_2$ (JCPDS 43-1027), IrO$_2$ (JCPDS 43-1029), and Pt/C (JCPDS 4-802).
**Figure S34.** Comparison of water oxidation polarization curves of LiMnBPO and NaMnBPO with (a) Co$_3$O$_4$, Co(OH)$_2$, CoOOH, Ni(OH)$_2$, NiOOH, Fe(OH)$_3$, FeOOH and, (b) on noble IrO$_2$ and RuO$_2$ deposited on FTO at a sweep rate $1 \text{ mVs}^{-1}$ in aqueous 1M KOH (with the same mass loading). Bar graph showing overpotentials ($\eta$) required to drive a current density of $10 \text{ mAcm}^{-2}$ is shown in (c) and (d). The attained overpotentials of presented BPO materials were indeed substantially lower compared to the as-synthesized highly active transition metal-based or noble metal-based catalysts (see Table S4 and S5).
Table S2. The comparison of water oxidation overpotentials $\eta$ (mV) of BPO’s with other benchmark catalysts synthesized and tested using our three-electrode set-up in aqueous 1 M KOH.

| Catalyst     | $j$ (mAcm$^{-2}$) | $\eta$ (mV) on FTO | $\eta$ (mV) on NF |
|--------------|-------------------|---------------------|-------------------|
| LiMnBPO      | 10                | 322±2               | 228±3             |
| NaMnBPO      | 10                | 338±2               | 262±5             |
| Mn$_3$N$_2$  | 10                | 395±3               | 320±3             |
| Mn$_2$O$_3$-O$_2$ | 10     | 460±8               | 332±5             |
| Mn$_2$O$_3$-SSP | 10          | 700±10              | 338±8             |
| Mn$_2$O$_3$  | 10                | -                   | 352±3             |
| Mn$_3$O$_4$  | 10                | -                   | 381±9             |
| MnO$_2$      | 10                | -                   | 342±8             |
| Co$_3$O$_4$  | 10                | 378±4               | 265±6             |
| Co(OH)$_2$   | 10                | 383±5               | 270±3             |
| CoOOH        | 10                | 406±4               | 319±5             |
| Fe(OH)$_3$   | 10                | 570±3               | 258±3             |
| FeOOH        | 10                | 610±7               | 317±7             |
| Ni(OH)$_2$   | 10                | 380±6               | 278±5             |
| NiOOH        | 10                | 444±6               | 289±5             |
| IrO$_2$      | 10                | 400±3               | 310±4             |
| RuO$_2$      | 10                | 354±5               | 292±8             |
| NF           | 10                | -                   | 490±9             |
Table S3. The comparison of OER overpotentials of BPO’s with literature reported the best active manganese oxide catalysts in aqueous alkaline solution known to-date.

| Catalyst                | $j$ (mA·cm$^{-2}$) | Substrate | Stability (h) | $\eta$ (mV) | Reference |
|-------------------------|--------------------|-----------|---------------|--------------|-----------|
| LiMnBPO                 | 10                 | NF        | 3850          | 228±3        | This work |
| NaMnBPO                 | 10                 | NF        | 24            | 262±5        | This work |
| LiMnBPO                 | 10                 | FTO       | 96            | 322±2        | This work |
| NaMnBPO                 | 10                 | FTO       | 24            | 338±2        | This work |
| LiMnBPO                 | 10                 | NF        | 160           | 270          | [1]       |
| NaMnBPO                 | 10                 | NF        | 1             | 270          | [1]       |
| Mn$_3$N$_2$             | 10                 | NF        | 10            | 287          | [37]      |
| MnO$_x$/CNT             | 10                 | SS        | 10            | 291          | [38]      |
| MnGa$_4$                | 10                 | NF        | 120           | 291          | 17        |
| MnS$_2$                 | 10                 | SS        | -             | 302          | [38]      |
| Mn$_3$(PO$_4$)$_2$ micro| 10                 | -         | -             | 332          | [39]      |
| Mn-NG                   | 10                 | GP        | 120           | 337          | [40]      |
| Mn$_2$O$_3$             | 10                 | FTO       | 3             | 340          | [1]       |
| Mn$_3$O$_2$             | 10                 | FTO       | 2             | 340          | [41]      |
| Mn$_2$O$_3$ (at 450°C)  | 10                 | FTO       | 5             | 387          | [45]      |
| MnO$_2$-Mn$_2$O$_3$     | 10                 | CC        | 10            | 400          | [46]      |
| Mn$_2$O$_3$ (at 550°C)  | 10                 | FTO       | -             | 407          | [45]      |
| MnGa$_4$                | 10                 | FTO       | -             | 410          | 17        |
| Mn$_3$O$_2$             | 10                 | ITO       | -             | 410          | [47]      |
| Li-MnO$_x$              | 10                 | CFP       | 1             | 410          | [23a]     |
| MnO$_x$/NCNT            | 10                 | GC        | 2             | 410          | [43]      |
| MnO$_x$-5               | 10                 | FTO       | -             | 417          | [44]      |
| e-MnO$_2$               | 10                 | GC        | -             | 420          | [48]      |
| Mn                      | 10                 | NF        | 24            | 425          | 17        |
| Mn$_2$O$_3$ (at 350°C)  | 10                 | FTO       | -             | 426          | [45]      |
| Mn-380                  | 10                 | ITO       | -             | 427          | [49]      |
| Mn                      | 10                 | Ti        | -             | 428          | [50]      |
| Mn$_3$O$_4$             | 10                 | GC        | -             | 430          | [51]      |
| MnO$_x$-1               | 10                 | FTO       | -             | 439          | [44]      |
| a-(K)MnO$_2$-water      | 10                 | GC        | -             | 440          | [52]      |
| b-MnO$_2$-porous        | 10                 | CP        | 0.69          | 450          | [53]      |
| Cs/MnO$_x$              | 10                 | FTO       | 1             | 450          | [15a]     |
| a-MnO$_2$               | 10                 | GC        | -             | 450          | [54]      |
| a-(K)MnO$_2$-He         | 10                 | GC        | -             | 450          | [52]      |
| Mn$_x$O$_y$/NC          | 10                 | GC        | 2             | 460          | [55]      |
| Material                          | Layer(s) | Support | Reference |
|----------------------------------|----------|---------|-----------|
| α-(K)MnO2-O2                     | 10       | GC      | [52]      |
| Mn-450                           | 10       | ITO     | [49]      |
| Na-MnOx                          | 10       | CFP     | [23a]     |
| Mn2O3                            | 10       | NF      | [1]       |
| Mn3O4@G-Ph-SN                    | 10       | GC      | [56]      |
| Mn3O4                            | 10       | FTO     | 10        | 480       | [42] |
| MnCO3                            | 10       | SS      | 10        | 480       | [38] |
| Mn3O8                            | 10       | FTO     | 10        | 490       | [42] |
| α-MnO2                           | 10       | GC      | 3         | 490       | [6]  |
| β-MnO2                           | 10       | FTO     | 1         | 500       | [57] |
| MnO2                             | 10       | GC      | -         | 500       | [51] |
| α-(K)MnO2                        | 10       | GC      | 2         | 500       | [52] |
| α-MnO2/β-MnO2                    | 10       | GC      | -         | 510       | [54] |
| MnO                              | 10       | GC      | -         | 510       | [51] |
| MnOx                             | 1      | ITO     | -         | 513       | [58] |
| Mn3Oy/NCNT                       | 10       | GC      | 5         | 520       | [59] |
| Mn3O4@G-SN                       | 10       | GC      | -         | 527       | [56] |
| Mn3Oy/OCNT                       | 10       | GC      | -         | 530       | [59] |
| Mn2O3                            | 10       | GC      | -         | 530       | [51] |
| γ-MnOOH                          | 10       | GC      | 0.2       | 530       | [32a]|
| Mn3O4@graphite                   | 10       | GC      | -         | 542       | [56] |
| K-MnOx                           | 10       | CFP     | -         | 560       | [23a]|
| Mn-575                           | 10       | ITO     | -         | 570       | [49] |
| α-Mn2O3                          | 10       | FTO     | 1         | 570       | [60] |
| Mn2O3-ALD                        | 10       | GC      | -         | 580       | [61] |
| β-MnO2                           | 10       | GC      | -         | 600       | [54] |
| Rb-MnOx                          | 10       | CFP     | -         | 600       | [23a]|
| Cs-MnOx                          | 10       | CFP     | -         | 610       | [23a]|
| MnO-ALD                          | 10       | GC      | -         | 610       | [61] |
| MnO2 (KIT-6)                     | 10       | GC      | 2.2       | 610       | [62] |
| MnO2-ALD                         | 10       | Si      | -         | 619       | [63] |
| Li/MnOx                          | 1        | FTO     | -         | 680       | [15a]|
| Mn2O3                            | 10       | CC      | 10        | 700       | [42] |
| Mn                               | 10       | FTO     | -         | 730       | 17   |
| Mn2O3-ALD                        | 10       | Si      | -         | 801       | [63] |
| MnOx                             | 10       | Si      | -         | 880       | [64] |

GC = glassy carbon, GP = graphite plate, CFP = carbon fiber paper, CP = carbon paper, CC =carbon cloth, ITO = indium tin oxide, FTO = fluorine doped tin oxide, NF = nickel foam; SS = stainless steel.
**Table S4.** The comparison of water oxidation ($\eta$) overpotentials of BPO’s with other highly active selected Mn incorporated non-noble transition metal-based catalysts in 1 M KOH.

| Catalyst             | $j$ (mA·cm$^{-2}$) | Substrate | Stability (h) | $\eta$ (mV) | Reference |
|----------------------|--------------------|-----------|---------------|--------------|-----------|
| LiMnBPO              | 10                 | FTO       | 96            | 322±2        | This work |
| LiMnBPO              | 10                 | NF        | 3850          | 228±3        | This work |
| NaMnBPO              | 10                 | NF        | 24            | 262±5        | This work |
| NaMnBPO              | 10                 | FTO       | 24            | 338±2        | This work |
| Ni-MnO$_2$           | 10                 | NF        | 10            | 232          | [65]      |
| Co$_3$MnO$_2$        | 10                 | GC        | 10            | 340          | [66]      |
| MnCo$_2$O$_4$        | 10                 | NF        | 25            | 360          | [67]      |
| Mn$_3$Co$_{3-x}$O$_4$ | 10                 | NF        | 8             | 320          | [68]      |
| LiMn$_{0.25}$Co$_{0.75}$O$_4$ | 10 | GC | - | 430 | [69] |
| Mn$_3$O$_4@Co$_x$Mn$_{3-x}$O$_4$ | 20 | NF | 20 | 284 | [70] |
| CoMnP                | 10                 | GC        | 20            | 350          | [71]      |
| Mn$_{25}$Ru$_{75}@450$ | 10 | Ti | - | 259 | [50] |
| CoMnP                | 10                 | GC        | -             | 330          | [72]      |
| MnCo$_2$O$_4$/N-rmGO | 10                 | GC        | -             | 340          | [73]      |
| Ni$_6$MnO$_8$        | 1                 | FTO       | 16            | 480          | [74]      |
| CoMnOOH              | 10                 | NF        | 18            | 320          | [75]      |
| K$_2$Fe[$Co_{0.16}$Mn$_{0.84}$O$_2$] | 10 | GC | - | 375 | [76] |
| MnNiO$_3$/Mn$_3$O$_4$ | 10                 | NF        | 24            | 340          | [77]      |
| Co-MnO$_2$           | 10                 | GC        | 12            | 279          | [78]      |
| Mn-Cd-S@Ni$_3$S$_2$  | 10                 | NF        | -             | 333          | [79]      |
| Ni$_3$S$_2$/MnS      | 10                 | NF        | 50            | 310          | [80]      |
| CeOMS2)Ce@MnO$_2$    | 10                 | GC        | -             | 760          | [81]      |
| Mn-Co-P              | 50                 | CC        | 24            | 355          | [82]      |
| Mn$_{1.5}$Ni$_{1}$   | 10                 | GC        | 2.5           | 360          | [83]      |
| Ni$_{1.5}$$[Co_{0.75}$Mn$_{0.75}]$O$_4$ | 10 | GC | - | 540 | [84] |
| MoP$_4$@MnP$_y$      | 20                 | GC        | 0.7           | 301          | [85]      |
| Mn$_{1.5}$V$_{1.5}$O$_4@N-rGO$ | 10 | GC | 5 | 320 | [86] |
| Ce$_{0.2}$MnFe$_{1.8}$O$_4$ | 10 | Pt | 10 | 310 | [87] |
| CoMnAl-LDH           | 10                 | GC        | 1             | 300          | [88]      |
| (Co$_4$Mn$_1$)Se$_2$ | 10                 | GC        | 7             | 274          | [89]      |
| Co-Ni–Mn LDH         | 10                 | GC        | 5.5           | 310          | [90]      |
| Fe–Mn–O NSs          | 10                 | CC        | 12            | 273          | [91]      |
| Pd–Mn$_3$O$_4/C$     | 5                  | Graphite rod | 0.5    | 430          | [92]      |
| Mn-CoP               | 10                 | GC        | 30            | 356          | [93]      |
| CoMnON               | 10                 | GC        | -             | 470          | [94]      |
| 0.61NiMnO$_3$/NiMn$_2$O$_4$ | 10 | GC | 24 | 380 | [95] |
| Cs–MnO$_x@450$       | 10                 | Graphite rod | 28    | 420          | [96]      |
| CoMn$_2$O$_4$        | 10                 | GC        | 0.5           | 610          | [97]      |
| MnCo$_2$O$_4$        | 10                 | GC        | 0.5           | 510          | [97]      |

GC = glassy carbon, Ti = titanium wire, NF = nickel foam, gold, CC =carbon cloth, Pt = platinum, FTO = fluorine doped tin oxide
Table S5. The comparison of water oxidation ($\eta$) overpotentials of BPO’s with other established selected non-noble transition metal-based catalysts in aqueous 1 M KOH.

| Catalyst              | $j$ (mA·cm$^{-2}$) | Substrate | Stability (h) | $\eta$ (mV) | Reference |
|-----------------------|--------------------|-----------|---------------|-------------|-----------|
| LiMnBPO               | 10                 | FTO       | 96            | 322±2       | This work |
| LiMnBPO               | 10                 | NF        | 3850          | 228±3       | This work |
| NaMnBPO               | 10                 | NF        | 24            | 262±5       | This work |
| NaMnBPO               | 10                 | FTO       | 24            | 338±2       | This work |
| LiMnBPO               | 10                 | NF        | 50            | 240         | [98]      |
| LiMnBPO               | 10                 | NF        | 18            | 215         | [99]      |
| NiFe LDH              | 10                 | NF        | 13            | 300         | [100]     |
| Fe-O–Ni(OH)$_2$/NF   | 10                 | NF        | 50            | 185         | [101]     |
| Ni$_3$Fe$_{0.5}$V$_{0.5}$ | 10             | CFP       | 60            | 200         | [102]     |
| NiFe LDH              | 10                 | NF        | 100           | 184         | [103]     |
| FeCoW-oxyhydroxide    | 10                 | Au        | 550           | 223         | [104]     |
| NiFe LDH              | 10                 | GC        | 1             | 210         | [105]     |
| Co$_x$Fe(OH)$_y$      | 10                 | GC        | 3             | 295         | [106]     |
| ZnCo$_2$O$_4$         | 10                 | FTO       | -             | 390         | [107]     |
| CoO-MoO$_2$           | 10                 | NF        | 1             | 270         | [108]     |
| CoS$_4$:O$_{0.6}$     | 10                 | GC        | 2             | 290         | [109]     |
| FeOOH/Co/FeOOH        | 10                 | NF        | 50            | 245         | [110]     |
| Fe$_7$:S$_8$          | 10                 | GC        | 24            | 270         | [111]     |
| Co$_4$N               | 10                 | CC        | 12            | 257         | [112]     |
| Ni$_2$P               | 10                 | NF        | 12            | 240         | [113]     |
| Ni$_2$P$_5$           | 10                 | NF        | 12            | 260         | [113]     |
| MoO$_2$               | 10                 | NF        | 24            | 250         | [114]     |
| NiFe LDH              | 10                 | HOPG      | 5             | 260         | [115]     |
| Ni$_3$S$_2$           | 10                 | NF        | 200           | 260         | [116]     |
| CoFeH                 | 10                 | GC        | 40            | 280         | [117]     |
| CoFeP                 | 10                 | NF        | 10            | 244         | [118]     |
| NiFe-LDH              | 10                 | NF        | 3             | 240         | [119]     |
| FeP                   | 10                 | NF        | 15            | 227         | [13b]     |
| CoP amorphous         | 10                 | NF        | 24            | 284         | [120]     |
| CoSn$_2$              | 10                 | NF        | 14            | 230         | [11a]     |
| Co$_3$(OH)$_2$(HPO$_4$)$_2$ | 10     | FTO       | 24            | 292         | [121]     |
| CoP                   | 10                 | FTO       | 24            | 360         | [120]     |
| Ni$_2$P               | 10                 | FTO       | 16            | 330         | [113]     |
| Ni$_2$P$_5$           | 10                 | FTO       | 16            | 295         | [113]     |
| FeNiO$_3$:H$_y$       | 10                 | NF        | 50            | 206         | [122]     |
| CuO@NiFeOH$_x$        | 10                 | Cu        | 16            | 230         | [123]     |
| NiFe-MOF              | 10                 | CP        | 100           | 275         | [124]     |
| NiFe-LDH              | 10                 | CW        | -             | 260         | [125]     |
| NiFe-LDH              | 10                 | NW        | 1.5           | 300         | [126]     |

GC = glassy carbon, CFP = carbon fiber paper, Au = gold, CC = carbon cloth, FTO = fluorine doped tin oxide, HOPG = highly-ordered pyrolytic graphite, NF = nickel foam, CW = carbon wire, NW = nickel wire
Figure S35. PXRD of LiMnBPO, post-CV (3 cycles), and post-CA (24 h) films along with bare FTO as a reference. Only a marginal difference in terms of diffraction pattern was observed after water oxidation by preserving its crystallinity at least for 24 h, whereas the surface of the particles transformed into the amorphous structure (which couldn’t be identified by PXRD and thus, evidenced by HR-TEM analysis). In addition to this, the loss of elements during CA was identified by the ICP-AES analysis and given in Table S6.

Table S6. Determination of the chemical composition of as-synthesized LiMnBPO and post-CA catalysis (24 h) was carried out using ICP-AES. Although the PXRD pattern showed only a marginal difference preserving its crystallinity, a substantial loss of Li was observed, including a certain amount of B and P.

| Li:Mn:B:P as-prepared | Li:Mn:B:P (post-CA 24 h) |
|------------------------|--------------------------|
| LiMn(H_2O)_2[BP_2O_8]·H_2O (LiMnBPO) | 1:1:1:2 | 0.26:1:0.74:1.65 |
Figure S36. SEM images (a-b) of the LiMnBPO film post-CA (24 h) shown at different magnifications. The particles displayed corrosion at the surface. More insights on the particles were attained by TEM analysis.
Figure S37. The SEM image (a) and the respective EDX mapping of a selected LiMnBPO particle after 24 h CA (b-e). The manganese (b, orange), phosphorous (c, yellow), and oxygen (d, red) were still found to be homogeneously distributed on the LiMnBPO particles (Note that the element boron and lithium was difficult to analyze due to its low photon energy). In addition to this, some amount of potassium (e, violet) was also present on the particle surface, strongly suggesting its intercalation into the active structure through KOH electrolyte to form K-/Li-birnessite type $\delta$-MnO$_2$ structure (see *in-situ* Raman and *in-situ* XAS) under electrochemical conditions.
Figure S38 The SEM image (a) and the respective EDX mapping of LiMnBPO film after 24 h CA (b-e). The manganese (b, orange), phosphorous (c, yellow), and oxygen (d, red) were found to be homogeneously distributed on the LiMnBPO film. The presence of potassium (e, violet) on the particle surface was due to the intercalation of K from the KOH electrolyte to form K-/Li-birnessite type δ-MnO₂ structure (see in-situ Raman and XAS) under electrochemical process.
Figure S39. The EDX (mapping) spectrum of LiMnBPO on (a) particles and (b) film after CA (24 h). The presence of K is due to the electrolyte (in the form of KOH) as well as the intercalation of K into the MnOₓ structure (K-/Li-birnessite type δ-MnO₂) during the electrochemical process. The higher amount of K in the film (b) is due to the overlapping signals of Sn from FTO.
Figure S40. TEM (a) and HRTEM (b,c) images of the surface of the thin films of LiMnBPO after 24 h CA measured in aqueous 1 M KOH solution. A very thin amorphous shell (~10 nm) started growing on the surface of the LiMnBPO particles indicating the surface structural change during water oxidation. The presence of an amorphous shell on the surface is due to the formation of the K-/Li-birnessite type $\delta$-MnO$_2$ structure (see *in-situ* Raman and *in-situ* XAS)\textsuperscript{[1,127]} The SAED (d, e) show the respective amorphous surface and crystalline core.
Figure S41. The EDX analysis of LiMnBPO after CA (24 h) in aqueous 1M KOH solution. The presence of heavy elements such as manganese and phosphorus was identified by the EDX. The presence of K is due to the electrolyte (in the form of KOH) as well as the intercalation of K into the MnOₓ structure (K-/Li-birnessite type δ-MnO₂) under the electrochemical process, and the peaks for copper can be unambiguously correlated to the TEM grid (carbon film on 300 mesh Cu-grid).
**Figure S42.** The FTIR-spectra of as-prepared LiMnBPO and the films after CA (24 h). After the CA, a broad band was observed at ~3330 cm\(^{-1}\) which is due to stretching vibrations of interlayer water molecules whereas the band at ~1640 cm\(^{-1}\) could be assigned to the bending vibration of H\(_2\)O and structural OH groups.\(^{[7,128]}\)
Figure S43. High-resolution XPS spectra of LiMnBPO after CA measurements (24 h) in the regions containing (a) Mn 2p (b) Mn 3p and Li 1s. The core-level spectrum centered on Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ was deconvoluted into two dominant and a minor peak.$^{[23a]}$ The peaks at 642.5 and 654.2 eV belong to the Mn oxidation state of Mn$^{IV}$, while the peaks at 641.4 and 653 eV can be ascribed to Mn$^{III}$.\cite{129} Furthermore, the minor peaks obtained at 640.2 and 651.9 eV can directly be correlated untransformed Mn$^{II}$ from the as-synthesized LiMnBPO.$^{[23c]}$ Besides, two satellite peaks are also present at the binding energies of 644 and 656 eV. The Mn 3p spectra showed two peaks at ~49.3 eV and 50.7 eV that could be corroborated to the Mn$^{III}$ and Mn$^{IV}$.$^{[129b,130]}$ The binding energies of Mn 2p and Mn 3p attained here are consistent with the literature reported manganese-based materials.$^{[25,131]}$ The Li 1s binding energy peaks at ~55 eV could directly be compared to the remaining Li$^{+}$ from LiMnBPO.$^{[25b,27]}$
**Table S7.** The distribution of the area in the region of Mn 2p\(\frac{3}{2}\) and Mn2p\(\frac{1}{2}\) XPS with respect to Mn\(^{II}\), Mn\(^{III}\), and Mn\(^{IV}\) oxidation states and satellites for as prepared LiMnBPO and after OER (24 h) experiments.

| Binding Energy (eV) | LiMnBPO in % | OER (24 h) area in % |
|---------------------|--------------|----------------------|
| Mn 2P\(\frac{3}{2}\) Mn(II) | ~640.2 | 40.97 | 5.84 |
| Mn 2P\(\frac{1}{2}\) Mn(II) | ~652 | 20.41 | 2.91 |
| Mn 2P\(\frac{3}{2}\) Mn(III) | ~641.5 | 22.70 | 17.76 |
| Mn 2P\(\frac{1}{2}\) Mn(III) | ~653.2 | 11.31 | 8.85 |
| Mn 2P\(\frac{3}{2}\) Mn(IV) | ~642.5 | - | 36.66 |
| Mn 2P\(\frac{3}{2}\) Mn(IV) | ~654.2 | - | 18.27 |
| Mn 2P Satellite 1 | ~645 | 4.61 | 5.66 |
| Mn 2P Satellite 2 | ~656 | - | 4.04 |
Figure S44. High-resolution XPS spectra of the regions containing the (a) B 1s, (b) P 2p, and (c) O1s of LiMnBPO after electrocatalytic CA (24 h). The B 1s XPS spectrum exhibited a peak at ~191.4 eV is attributed to the structure of boron linked to oxygen atoms with four coordination indicative of B$^{III}$ (borate).[7,28] High-resolution P 2p XPS spectrum was deconvoluted 2p$_{3/2}$ and 2p$_{1/2}$, at binding energies of 133.5 and 134.4 eV, that is attributed to the formation of phosphate (PO$_4$)$^{3-}$ on the surface, which is in good agreement with the literature reported phosphate materials.[7,29] The O 1s spectrum was deconvoluted into broad O1, O2, and O3 peaks. The intense peak at ~530.1 eV (O1) corresponds to metal-oxygen bonds (MnO$_x$) in the metal oxide, whereas the peak at 531.6 eV (O2) is due to the surface hydroxides.[1,11a,13b,14,21a] The O3 peak ~533 eV could be assigned to the chemisorbed oxygen or associated crystal water in the structure.[7] The attained O 1s values fits very well with literature reported metal oxides and hydroxide materials, suggesting that a structural transformation at the surface resulted under prolonged treatment of LiMnBPO films under electrochemical treatment in aqueous 1 M KOH solution.
Figure S45. (a) Ex-situ Raman spectrum of bare FTO film. (b) Raman spectra of LiMnBPO/FTO film measured ex-situ, after placing in the electrochemical device and after in contact with KOH electrolyte prior to electrochemical measurements.
Note S1: Ex-situ Raman spectroscopy

The ex-situ Raman spectra of LiMnBPO/FTO film in the electrochemical device and after in contact with KOH electrolyte prior to electrochemical measurements are shown in Figure S43. Here, we focus on specific assigned Raman lines to deduce the structure of LiMnBPO. In the as-prepared LiMnBPO/FTO film, the Raman line at 270 cm\(^{-1}\) could be associated with the stretching mode of Li-O\(^{[132]}\), while the line at 380 cm\(^{-1}\) can be ascribed to Mn-O stretching.\(^{[133]}\) The lines between 537 and 638 cm\(^{-1}\) correspond to the out of plane bending modes of the PO\(_4\) groups as well and could be ascribed to Mn-O vibrations of MnO\(_4\)(OH\(_2\))\(_2\) in BPO\(^{[132-134]}\). Furthermore, the peak at 948 cm\(^{-1}\) is associated with symmetric stretching of PO\(_4\)\(^{[135]}\) while the small band at 1005 cm\(^{-1}\) is due to B-O stretching.\(^{[136]}\) The highly intense band at 1055 cm\(^{-1}\) could arise from the symmetric stretching vibration of non-bridging phosphate atoms in PO\(_4\) units as well as asymmetric B-O vibration.\(^{[134,136-137]}\) The Raman spectra obtained here are consistent with literature reported metal phosphates or borates.\(^{[133-135,136,138]}\) After placing the LiMnBPO/FTO films in the electrochemical cell as well as when the films come into contact with KOH, the most intense bands were still preserved.

After the electrochemical CA measurements (maintaining the current density of 10 mAc cm\(^{-2}\)) of 24 h, the bands of as-prepared LiMnBPO/FTO disappeared, and new Raman lines appeared corresponding to a K intercalated birnessite structure (Figure 4a, main text).\(^{[139]}\) The birnessite \(\delta\)-MnO\(_2\) structure comprises of edge-sharing octahedral MnO\(_2\) layers, accompanied by typical interlayer (the usual distance of ~7 Å) randomly distributed interstitial disordered water/cationic (such as water or alkali metals) and due to this reason, some of the Mn cations within the layers are reduced from Mn\(^{IV}\) to Mn\(^{III}\).\(^{[6,140]}\) Usually, for a birnessite \(\delta\)-MnO\(_2\) structure, three most prominent Raman lines are found in the region of ~500 and 650 cm\(^{-1}\).\(^{[33a,132,139,141]}\) In the present case, the most intense band at 578 cm\(^{-1}\) is associated with Mn–O vibration in the basal plane of the [MnO\(_6\)] sheets of \(\delta\)-MnO\(_2\), whereas the bands at 510 and 637 cm\(^{-1}\) are correlated to out-of-plane Mn–O vibrations perpendicular to the layers.\(^{[47,141a]}\) Notably, the out-of-plane Mn–O stretching vibrations at 637 cm\(^{-1}\) is red-shifted while 510 cm\(^{-1}\) is blue-shifted compared to ideal birnessite \(\delta\)-MnO\(_2\) structure, and match perfectly with K intercalated amorphous \(\delta\)-MnO\(_2\) (a-\(\delta\)-MnO\(_2\)).\(^{[139]}\) A similar Raman shift was also observed for activated \(\delta\)-MnO\(_2\) reported by Nocera and co-workers in water oxidation conditions.\(^{[141a]}\) This is also in line with results obtained from ICP-AES and EDX analysis. The line associated with symmetric stretching of PO\(_4\) units at 948 cm\(^{-1}\) decreased significantly, further confirming the surface transformation of LiMnBPO to K-/Li-intercalated a-\(\delta\)-MnO\(_2\),\(^{[139]}\) which is an active phase for the water oxidation with profound stabilized Mn\(^{III}\) species.
Figure S46. *In-situ* Raman spectrum of LiMnBPO/FTO film where the transformation of PO$_4^{3-}$ vibration (PO$_4$ leaching) was monitored (~948 cm$^{-1}$) over time under CA conditions in aqueous 1 M KOH solution.$^{[135b,135c,138]}$
X-ray absorption spectroscopy

Table S8. Edge positions and corresponding oxidation states deduced from the XANES spectra. To determine the XANES edge energy position the step-integral method described in Ref.\textsuperscript{[142]} was used, and the averaged Mn oxidation state was calculated from a calibration line constructed from spectra of several reference Mn oxides, as described in Ref.\textsuperscript{[143]}

| LiMnBPO                | Edge position (eV) | Oxidation state        |
|------------------------|--------------------|------------------------|
| As prepared            | 6546.79            | 2.1 (±0.1)             |
| As-deposited           | 6546.74            | 2.1 (±0.1)             |
| Post CA                | 6546.86            | 2.1 (±0.1)             |

Figure S47. $k^3$-weighted experimental EXAFS spectra of as-prepared (powder), as-deposited, and post-CA LiMnBPO on FTO substrate. Thin black lines represent the simulation of the experimental data. The simulation parameters are given in Tables S9 and S10.
Table S9. Parameters obtained by the simulation (curve-fitting) of $k^3$-weighted EXAFS spectrum of the as-synthesized LiMnBPO (N, coordination number; R, absorber-backscatter distance; $\sigma$, Debye-Waller parameter). Debye-Waller parameters were all fixed to 0.063 Å. Only single-scattering paths were included. The amplitude-reduction factor $S_0^2$ was 0.65. Fitting was performed using in-house software (SimXLite) after calculation of the phase functions with the FEFF program (version 8.4, self-consistent field option activated).[144] The phase functions have been calculated using a fragment of the crystal structure of LiMnBPO. The error ranges of the fit parameters were estimated from the covariance matrix of the fit and represent the 68% confidence intervals (error calculations as described in Ref.[145]).

|            | N, XRD | R, from simulations (Å) | R, XRD (Å) |
|------------|--------|-------------------------|-------------|
| Mn-O       | 6      | 2.12                    | 2.12        |
| Mn-Li      | 2      | 3.13                    | 3.13        |
| Mn-P       | 4      | 3.31                    | 3.30        |
| Mn-O       | 6      | 3.69                    | 3.72        |
| Mn-O       | 8      | 4.14                    | 4.22        |
| Mn-O       | 8      | 4.64                    | 4.66        |
| Mn-B       | 3      | 4.75                    | 4.43        |
| Mn-P       | 2      | 5.01                    | 4.93        |
| Mn-Mn      | 4      | 5.46                    | 5.47        |

Table S10. Simulation of the material after exposure to oxidizing potentials as a linear combination of the spectrum of as-synthesized LiMnBPO and a calculated spectrum where two interatomic vectors were considered (Mn-O and Mn-Mn) as it would be expected for the birnessite structure $\delta$-MnO$_2$. The distances of these two shells were freely varied during the simulation, and the determined values Mn-O (1.87 Å) and Mn-Mn (2.82 Å) agree well with the values predicted for the birnessite.[146]

| Catalyst    | LiMnBPO, % | birnessite, % |
|-------------|------------|---------------|
| As-deposited | 100%       | 0             |
| Post-CA     | 83 ± 2.4   | 17 ± 2.4      |
Figure S48. Mn$^{III/IV}$ reduction peak integration of a CV after 24 h OER of LiMnBPO. The area indicates that around 50% of the Mn sites of the newly formed α-δ-MnO$_2$ phase are redox-active.
Figure S49. The SEM images (a-d) of the LiMnBPO film deposited on NF with different magnifications.
Figure S50. The SEM image (a) and the mapping analysis of the LiMnBPO film deposited on NF. The mapping distribution of Ni (b), Mn (c), P (d), and O (e) is shown in blue, orange, yellow, and red, respectively. The element boron was difficult to analyze due to its low photon energy and owing to its detection limit (hence ICP-AES was conducted). The uniformly distributed elements on the films were obtained confirming the phase purity of the LiMnBPO on NF substrate.
**Figure S51.** The EDX (mapping) spectrum of LiMnBPO deposited on NF.
Figure S52. The CV curves of bare NF at a sweep rate 1 mVs$^{-1}$ in aqueous 1M KOH showing limited activity for water oxidation.
Figure S53. Electrochemical double-layer measurements for the estimation of the ECSA in a non-Faradaic potential range of 1V to 1.1 Vs. RHE at different scan rates (10, 20, 50, 100 and 200 mVs⁻¹) for (a) LiMnBPO and (b) NaMnBPO and (c) NF in aqueous 1M KOH solution. (d) Determination of the double-layer capacitances ($C_{dl}$) by plotting the current density variation ($\Delta j = (j_a - j_c)/2$), which was 6.27, 5.06 and 0.8 mFcm⁻² for LiMnBPO, NaMnBPO and NF, respectively. The results show that the LiMnBPO and NaMnBPO provide more electrochemical catalytic active surface area and probably favor the efficient adsorption and transfer of reactants to enhance the electrochemical reaction. [15,30,147]
Figure S54. Cyclic voltammograms (CV) normalized by (a) geometric area, (b) mass, (c) BET surface, and (d) ECSA of LiMnBPO and NaMnBPO on NF.
Figure S55. The Nyquist plot of (a) LiMnBPO/NF, NaMnBPO/NF, and NF at an anodic polarization potential of 1.5 V vs. RHE attained from EIS and (b) the magnified image of (a).
Figure S56. (a) CA of LiMnBPO/NF and NaMnBPO/NF measured in the water oxidizing conditions at a potential of 1.47 V and 1.50 V vs. RHE in aqueous 1 M KOH solution for 24 h. The broken red line is a guide to the eye at 10 mAcm$^{-2}$. (b) CA of LiMnBPO/NF measured at 1.49V vs. RHE for nearly 96 h.
Figure S57. Comparison of water oxidation polarization curves of LiMnBPO and NaMnBPO with Mn₂O₃, Mn₃O₄, MnO₂, Mn₂O₃-SSP, Mn₂O₃-O₂, and Mn₃N₂ deposited on NF at a sweep rate 1 mVs⁻¹ in aqueous 1M KOH. The bar diagram showing overpotentials (η) required to drive a current density of 10 mAcm⁻² is shown in Fig.4 of the main text. For comparison of the overpotentials refer to Table S3.
Figure S58. (a) Comparison of water oxidation polarization curves of LiMnBPO and NaMnBPO with Co$_3$O$_4$, Co(OH)$_2$, CoOOH, Ni(OH)$_2$, NiOOH, Fe(OH)$_3$, FeOOH and NF measured at a sweep rate 1 mVS$^{-1}$ in aqueous 1M KOH. The bar diagram showing overpotentials ($\eta$) required to drive a current density of 10 mAcm$^{-2}$ is shown in (b). The overpotential comparison with literature reported catalysts is shown in Table S4.
**Figure S59.** (a) Comparison of water oxidation polarization curves of LiMnBPO and NaMnBPO with noble IrO$_2$ and RuO$_2$ on NF measured at a sweep rate 1 mVs$^{-1}$ in aqueous 1M KOH. The bar diagram showing overpotentials ($\eta$) required to drive a current density of 10 mAcm$^{-2}$ is shown in (b). The overpotential comparison with literature reported catalysts is shown in Table S5.
Figure S60. (a) The polarization curve of Pt/C(-)║(+LiMnBPO, Pt/C(-)║(+NaMnBPO, Pt/C(-)║(+RuO₂, Pt/C(-)║(+IrO₂, Pt/C(-)║(+Ni(OH)₂, and Pt/C(-)║(+NiOOH on FTO substrate fabricated via a two-electrode setup in aqueous 1 M KOH at a scan rate of 1 mVs⁻¹. For comparison, Pt/C(-)║(+FTO was also measured in the same conditions. (b) The long-term stability test of Pt/C(-)║(+LiMnBPO at a cell potential of 1.68 V for nearly 4 days. The broken red line is a guide to the eye at 10 mAcm⁻².
Figure S61. (a) The polarization curve of Pt/C(-)||(+LiMnBPO, Pt/C(-)||(+NaMnBPO, Pt/C(-)||(+RuO₂, Pt/C(-)||(+IrO₂, Pt/C(-)||(+Ni(OH)₂ and Pt/C(-)||(+NiOOH on NF substrate fabricated via a two-electrode setup in aqueous 1 M KOH at a scan rate of 1 mV s⁻¹. For comparison, Pt/C(-)||(+NF was also measured in the same conditions.
Calculation of Faradaic efficiency

The Faradaic efficiency (FE) of LiMnBPO in 1M KOH towards oxygen evolution reaction was measured with LiMnBPO on NF as anode in a closed electrochemical cell. The cell and the electrolyte were first degassed with Argon for 30 min under stirring. Afterward, the constant current density of 10 mA cm\(^{-2}\) was applied for a specified period. At the end of electrolysis, the gaseous samples were taken out of the headspace by a gas-tight syringe and analyzed by a GC calibrated for O\(_2\). Every injection step was repeated at least three times, and the average value is presented.

The Faradaic efficiency (FE) is calculated based on:

\[
FE(O_2, \%) = \frac{V_{O_2} \times 4 \times F}{V_m \times j \times t} \times 100\%
\]

\(V_{O_2}\) is the evolved volume of oxygen, \(F\) is the Faraday constant (96485.33289 C/mol), \(V_m\) is the molar volume of the gas, \(j\) is the current density (10 mA cm\(^{-2}\)), and \(t\) is the period of electrolysis.

Table S11: Calculation of Faradaic efficiency

|          | \(j\) (mA cm\(^{-2}\)) | \(t\) (sec) | \(V_{O_2}\) (mL) | FE \((O_2,\%)\) |
|----------|--------------------------|-------------|------------------|-----------------|
| LiMnBPO  | 10                       | 300         | 0.169            | 97±1%           |
| LiMnBPO (160 d) | 10                       | 300         | 0.165            | 95±2%           |
**Figure S62.** The SEM images of the LiMnBPO/NF film after long-term durability tests of 160 days shown at different magnifications. The particles displayed complete transformation and change in morphology.

**Table S12.** ICP-AES and EDX analysis of the anode after 160 days of electrolysis were carried out to determine the compositional changes of LiMnBPO. The almost complete loss of Li, B, and P was observed, forming an active MnOₓ structure.

|          | Theoretical Ratio (Li: Mn : B : P) | Ratio by ICP (Li: Mn : B: P:K) | Ratio by EDX (Mn : P : K) |
|----------|-----------------------------------|-------------------------------|---------------------------|
| LiMnBPO  | 1 : 1 : 1 : 2                     | 1:1.01:0.99:2                | ~1:2.08:0                 |
| Anode (160 d) | -                               | 0.06:1:0.1:0.12:1.4         | ~1:0.08:1.52              |
Figure S63. The SEM image (a) and the respective EDX mapping spectra of the LiMnBPO/NF film (used as the anode) after a long-term durability test of 160 days. Notably, the EDX mapping on the film also ruled out the Ni incorporation (b) in the transformed active material, whereas K (c), Mn (d), and O (f) were homogeneously distributed. The P (e) mostly disappeared from the structure, indicating a complete transformation of the particles into (K intercalated-a-δ-MnO$_2$ structure (as revealed from Raman and XAS measurements).
Figure S64. The EDX mapping analysis of the LiMnBPO/NF film (used as the anode) after a long-term durability test of 160 days. The presence of K is due to the electrolyte (in the form of KOH) as well as the incorporation of K into the MnO$_x$ structure (K intercalated-a-$\delta$-MnO$_2$).
Figure S65. The TEM (a, b) and HR-TEM images (c, d) and SAED pattern (inset d) of LiMnBPO deposited on NF after the durability test of 160 days. The LiMnBPO/NF films were first sonicated in acetone for 30 min, and the acquired particles were used for the TEM measurements. A complete transformation of particles was observed after the stability test in comparison to the initial phase. A closer look at the nanostructures revealed an amorphous nature of the transformed active MnO\textsubscript{x} material (K intercalated-a-\(\delta\)-MnO\textsubscript{2} structure) under oxidizing conditions, which is also consistent with the SAED image.
Figure S66. The EDX analysis of the particles (obtained from sonication of films) of LiMnBPO deposited on NF after the durability test of 160 days in aqueous 1 M KOH. The phosphorous peaks mostly disappeared with the concomitant increase in K peaks. The presence of K is due to the electrolyte (in the form of KOH) as well as the incorporation of K forming K intercalated-a-δ-MnO₂ structure. The peaks for copper can be unambiguously correlated to the TEM grid (carbon film on 300 mesh Cu-grid).
Figure S67. High-resolution XPS spectra of the LiMnBPO/NF film after the water oxidation durability test of 160 days in aqueous 1 M KOH in the regions containing (a) Mn 2p (b) P 2p, (c) B 1s and (d) O 1s. The core-level spectrum of LiMnBPO/NF (160 d) centered at Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ revealed a drastic change in the surface oxidation state of Mn from Mn$^{II}$ to Mn$^{III}$/Mn$^{IV}$ over time (in comparison to as-synthesized and 24 h CA treated material (a)).$^{[6,148]}$ However, phosphorous and boron were absent on the surface (b, c). The O 1s spectrum exhibited peaks corresponding to metal-oxygen bonds (MnO$_x$) as well as hydroxylation of the material. (For detailed XPS see Figures S43, and S44). From the XPS results, we could conclude that under alkaline electrochemical CA (24 h), the LiMnBPO particles are oxidized to phosphate and borate-like species, which then dissolve in the electrolyte, converting the catalyst surface to higher valent Mn-oxide/hydroxides. Under prolonged water oxidation conditions (160 d), the conversion process goes deeper beyond the particle surface thereby transforming the original LiMnBPO structure to a highly active K intercalated-a-δ-MnO$_2$ structure (consistent with SEM, ICP-AES, EDX, elemental mapping, and TEM).$^{[140a,140b,141a]}$
Figure S68. High-resolution Mn 3P XPS spectra of the LiMnBPO/NF films after the durability test of one day and 160 days in aqueous 1 M KOH. Similar to the Mn 2p spectrum, a severe change in the Mn oxidation state was observed by transforming most of its Mn$^{II}$ to Mn$^{III}$/Mn$^{IV}$ and matches necessarily well with the K intercalated-a-δ-MnO$_2$ structure.$^{[25,140a,140b,141a]}$
Figure S69. PXRD powder pattern of birnessite-type amorphous manganese oxide (AMO) synthesized by a literature reported procedure.
Figure S70. (a, b) The SEM images and (c) the EDX mapping spectrum of AMO. The ratio K:Mn:O = 0.25:1:2 obtained from EDX matches very well with the synthetically obtained amorphous birnessite type structure. The silicon peak arises from the substrate.
Figure S71. The SEM image (a) and the respective EDX mapping spectra of the AMO film where Mn (b), O (c) and K (d) are homogeneously distributed.
Figure S72. Comparison of water oxidation polarization curves of LiMnBPO and NaMnBPO with AMO on FTO (a) and NF (b) at a sweep rate 1 mVs$^{-1}$ in aqueous 1M KOH (with the same mass loading). The attained overpotentials of synthetically prepared AMO on both substrates were much lower compared to the BPOs. This demonstrates that in-situ formed K intercalated-a-δ-MnO$_2$ structure from the BPO precatalysts by anion leaching are more active than the synthetic amorphous K-birnessite-type structure. This could be attributed to the different size of the particle, specific and electrochemical surface area, defects as well as abundant available surface-stabilized Mn$^{III}$ sites, which are inevitable to enhance the catalytic OER activity.
Scheme S1. The formation of the O–O bond in the OER reaction of Mn-borophosphates can proceed through two different mechanisms.[40,149] In the acid-base mechanism, the first water molecule is dissociated on the Mn^{II} site forming Mn^{III}-OH intermediate species through proton-coupled electron transfer (PCET) followed by further oxidation to Mn^{IV}=O. In the next step, the second water molecule (in alkaline conditions probably a hydroxide) then acts as a nucleophile and attacks the Mn^{IV}=O to form a Mn^{III}-OOH intermediate species after the coupling of oxygen (Figure top).[40] Finally, the oxidation of Mn^{III}-OOH evolves molecular O_{2} by closing the catalytic cycle. In contrast, in the direct-coupling (or radical coupling) mechanism, two high-valent Mn oxo species (Mn^{IV}=O) on the surface form radicals leading to O-O bond formation provided that they are relatively close (Figure bottom).[149b]
**Note S2: Oxygenation of organic compound**

Owing to the outstanding catalytic performance for water oxidation, LiMnBPO/NF electrocatalyst was used as a promising anode for oxygenation of organic substrates such as 5-hydroxymethylfurfural (HMF) and acetaldehyde (CH₃CHO). First of all, the oxidation reaction was conducted in 1 M KOH solution using a three-electrode set-up where LiMnBPO/NF (mass loading 0.5 mg, 0.5 x 2 cm) was directly used as a working electrode, Hg/HgO as reference electrode and Pt wire as a counter electrode. The most common competing reaction during oxygenation reaction is water oxidation to oxygen. The Fig. 5b (main text) shows an LSV of LiMnBPO/NF in KOH as well as after the addition of 30 mM HMF to KOH. A sharp oxidation peak at 1.35 V vs. RHE indicated the oxidation of Mn followed by HMF oxidation, whereas only a weak redox peak was observed in the absence of HMF, indicating for the oxidation of Mn. Besides, the catalytic current increased substantially beyond 1.35 V vs. RHE, indicating selective oxidation of HMF to 2,5-furandicarboxylic acid (FDCA). The bare NF has deficient activity both for HMF and water oxidation. Based on these results, the electrochemical cell in two-electrode configuration (separated by a membrane) was constructed using LiMnBPO/NF as the anode and Pt as the cathode, and the formation of the product was monitored through ¹H NMR spectroscopy (see Fig. 5b and c in the main text).

![Diagram](image)

**Scheme S2.** Possible pathways for the electrocatalytic oxidation of HMF to FDCA
The electrocatalytic oxidation of HMF to FDCA is shown in Scheme S2 and follows two pathways, (a) the hydroxymethyl group of HMF is first oxidized to form 2,5-diformylfuran (DFF), and consequently, its two aldehyde groups are further oxidized to yield 5-formyl-2-furancarboxylic acid (FFCA) and (ii) the aldehyde group of HMF is oxidized to form 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), comply with the oxidation of the hydroxymethyl group to form FFCA and then FDCA.

Similar to HMF, biomass-derived furfural to furoic acid was studied by electroxidation in alkaline solution (Scheme S3). Furfural can be oxidized selectively to furoic acid with a high conversion rate as shown in the $^1$H NMR spectroscopy (Fig. S73).

**Scheme S3.** Possible pathway for the electrocatalytic oxidation of furfural to 2-furoic acid

The electrocatalytic oxidation of CH$_3$CHO to acetic acid (CH$_3$COOH) was investigated similarly to that of HMF and furfural (Fig. S74). The product formation and progress of the reaction was monitored from the $^1$H NMR spectroscopy. The possible oxidation pathway is depicted in Scheme S4.

**Scheme S4.** Possible pathway for the electrocatalytic oxidation of CH$_3$CHO to CH$_3$COOH
Figure S73. $^1$H NMR spectra of the reaction solution before (0 h, bottom) and after (1.0 h, top) electrochemical oxidation of furan-2-carboxaldehyde (30 mM) using the LiMnBPO/NF as working electrode in a two electrochemical set-up. The –CHO and aromatic proton resonances of furan-2-carboxaldehyde disappeared with the concomitant formation of a new peak of furan-2-carboxylic acid. After a 36 coulomb charge passed through the solution leads to 86 % conversion and 52 % Faradaic efficiency.
Figure S74. $^{1}$H NMR spectra of the reaction solution before (0 h, bottom) and after (1.5 h, top) electrochemical oxidation of acetaldehyde (CH$_3$CHO) using the LiMnBPO/NF as working electrode in a two electrochemical set-up. The sharp signal at 1.9 ppm is for the methyl protons of acetic acid formed after a 54 coulomb charge passed through the solution. Quantification gives a 66 % conversion and 84 % Faradaic efficiency.
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