Supplementary Figure 1 | XRD characterization. XRD pattern of Mn₅O₈ nanoparticles (black) and Mn₃O₄ (blue) impurity phase.
Supplementary Figure 2 | XPS characterization of Mn$_5$O$_8$ nanoparticles. (a) XPS survey spectrum, (b) Mn 2p, (c) Mn 3s and (d) O 1s chemical states of Mn$_5$O$_8$ nanoparticles. (e) The fitting of Mn 3s spectra shows the Mn$^{2+}$ and Mn$^{4+}$ with an integrated intensity ratio of 1:2.
Supplementary Figure 3 | Electrochemical half-cell measurements of carbon black. (a) The CVs of carbon black, and (b) calculated capacitance of carbon black showing that the Mn$_5$O$_8$ materials contributed to the majority of the capacitance in the mixture of Mn$_5$O$_8$ and carbon black.

Supplementary Figure 4 | TAFEL plots of HER and OER. (a, b) Mn$_5$O$_8$ nanoparticles, and commercial (c, d) Mn$_3$O$_4$, and (e, f) Co$_3$O$_4$ nanopowders. The measurements were carried using a three-electrode half-cell in 0.1M Na$_2$SO$_4$ electrolyte with a rotating disc working electrode (500 rpm).
Supplementary Figure 5 | TAFEL slopes analysis. TAFEL slopes of (a) HER and (b) OER as function of scan rates for Mn$_5$O$_8$ nanoparticles and commercial Mn$_3$O$_4$ and Co$_3$O$_4$ nanopowders.

Supplementary Figure 6 | Electrochemical half-cell studies at various pH values. (a, b) CVs of 3.5 ug Mn$_5$O$_8$ and 1.5 ug carbon black measured at pH = 4 and pH = 10, and (c) calculated capacitance at various pHs.

Supplementary Figure 7 | Structural and electrochemical half-cell studies of bulk Mn$_5$O$_8$. (a) Scanning electron microscopy (SEM) image, (b) XRD spectra, and (c) CVs of bulk Mn$_5$O$_8$ materials with an average diameter of 2 μm. Scale bars, 5 μm (a).
Supplementary Figure 8 | Electro-kinetics analysis. Electro-kinetics studies of (a) Mn₅O₈ nanoparticles, (b) bulk Mn₅O₈, (c) Mn₃O₄ nanoparticles and (d) Mn₃O₄ bulk materials, showing the ratio between total current and diffusion-limited redox current. The integrated curves provide the contribution from diffusion-limited redox process and capacitive process to the overall charge stored as shown in Fig. 2c.
**Supplementary Figure 9 | Galvanostatic change/discharge studies.** Electrode capacities of Mn$_5$O$_8$ during galvanostatic charging and discharging at current densities of (a) 10 A g$^{-1}$, (b) 20 A g$^{-1}$, and (c) 50 A g$^{-1}$.

**Supplementary Figure 10 | Mn$_5$O$_8$ full cell performance at low/high current densities.** (a) Electrode capacities as a function of cycling number of Mn$_5$O$_8$ cells at current densities from 0.5 to 50 A g$^{-1}$; (b) electrode capacities at current densities from 0.5 to 50 A g$^{-1}$ after 2,000 cycles.

**Supplementary Figure 11 | Galvanostatic charge/discharge studies at low current densities.** Electrode capacities of Mn$_5$O$_8$ during galvanostatic charging and discharging at (a) 0.5 A g$^{-1}$ and (b) 1 A g$^{-1}$ ($2^{nd}$ cycle data).
Supplementary Figure 12 | Electrode capacities and cell resistances analysis. Electrode capacities and electrical resistances of Mn₃O₈ full cell calculated from i-R drop during the discharge process as functions of cycle number at current densities of (a) 0.5 A g⁻¹, (b) 1 A g⁻¹, (c) 5 A g⁻¹, (d) 10 A g⁻¹, (e) 20 A g⁻¹ and (f) 50 A g⁻¹.
Supplementary Figure 13 | Pre-soaked Mn₅O₈ full cell performance. Electrode capacities as a function of cycle number for Mn₅O₈ cells at current densities from 0.5 to 50 A g⁻¹. The electrode materials are pre-soaked in the electrolyte before assembling.

Supplementary Figure 14 | STEM characterizations. STEM of Mn₅O₈ nanoparticles (a) before and (b) after cycling. No hydroxylated coating is discernable on surface after cycling. Scale bars, 5 nm (a, b).
Supplementary Figure 15 | Neutron Scattering. (a) Neutron PDF of the Mn₅O₈ material soaked in D₂O and the Mn₅O₈ cycled ex-situ in Na₂SO₄ (light water). The PDFs showed little difference, notably both PDFs containing a strong negative peak at ~0.98 Å. (b) Simulated PDFs of a single D₂O and H₂O molecule, exhibiting the difference between water molecules with different isotopes of hydrogen. Because the neutron scattering length of Deuterium is positive the O-D correlation is positive, whereas the neutron scattering length of Hydrogen is negative the O-H correlation is negative. Both the D-D and H-H correlations of both the light and heavy water are positive. As the peak at ~0.98 Å in the PDF of both cycled and soaked Mn₅O₈ data is strongly negative, the D₂O substitution was unsuccessful, and is therefore the signal is due to light water in the sample. (c) Models containing Mn₅O₈ + O-H species and Mn₅O₈ + H₂O molecule were fit to the data of the cycle Mn₅O₈. The model containing O-H species was unable to fit the peak at ~1.5 Å, but the model with water was having the H-H correlation that the Mn₅O₈ + O-H model lacks.

Supplementary Figure 16 | Activation energies of HER/OER intermediate steps. The activation energies of intermediate reaction steps of (a) HER and (b) OER on the (100) surface of surface hydroxylated Mn₅O₈ (Mn₅O₈-OH) or as-made Mn₅O₈ and (101) surface of Mn₃O₄ (the asterisk symbol denotes the chemical species that are adsorbed on the surface).
Supplementary Figure 17 | Schematic Na-ion transport through hydroxylated Mn₅O₈. (a) Side view along <010> direction and (b) top view along <100> direction of Mn₅O₈ stacked lattice demonstrates the alternative arrangement of layered Mn⁴⁺ (purple) and Mn²⁺ (blue) atoms. Na-ion (grey) transport can be achieved from the pathway along empty sites along <100> direction as marked in black arrows, and can be achieved from electrostatic interaction with the hydroxylated interphase (-OH) which is marked with in a red arrow.
Supplementary Table 1. Structural parameters obtained from fitting of X-ray scattering PDF.

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Supplementary Table 2. Structural parameters obtained from fitting of neutron scattering PDF.

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Supplementary Table 3. Summarized electrochemical performance of various Mn based electrode materials for aqueous electrochemical energy storage.

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Supplementary Note 1. Capacitance and electro-kinetic analyses in half-cell.

The CV measurements were conducted in 0.1M Na₂SO₄ electrolyte at scans rates from 1 to 1000 mV s⁻¹ within a potential range from –1.7 V to 0.8 V (vs. MSE).

The mass-specific capacitance \( C_{MS} \) from CV measurement in half-cell was calculated from:

\[
C_{MS} = \frac{i}{(dv/dt) * m} = \int_{t_0}^{t_F} \frac{i}{\Delta V * m} dt
\]

Supplementary Eq. (1)

Where \( i \) (A) is the measured current at certain time of \( t \) (s), \( m \) (g) is the mass of active material loaded on working electrode, \( \Delta V \) (V) is potential window, \( t_0 \) (s) and \( t_F \) (s) are respective times at the initial potential and the final potential.

The current contributed from surface-controlled capacitive process can be represented by:

\[ i_1 = k_1 v \]

Supplementary Eq. (2)

Where \( i \) is the current (A) and \( v \) is the scan rate (mV s⁻¹).

While the current contributed from diffusion-limited redox process can be represented by:

\[ i_2 = k_2 v^{1/2} \]

Supplementary Eq. (3)

Therefore, the overall current can be represented by:

\[ i = k_1 v + k_2 v^{1/2} \]

Supplementary Eq. (4)

After rearrangement, it can be written as:

\[ \frac{i}{v^{1/2}} = k_1 v^{1/2} + k_2 \]

Supplementary Eq. (5)

By plotting \( i/v^{1/2} \) vs. \( v^{1/2} \) curves at a given potential, \( k_1 \) and \( k_2 \) values can be determined, and hence the contribution of capacitive charge and diffusion-limited redox charge during the CV measurements in half-cell can be analyzed quantitatively.

TAFEL analyses of HER and OER were conducted in half-cell. The TAFEL equation relates the HER and OER activities to their overpotentials \( \eta \) and is expressed as:

\[ \eta = A \times \log \left( \frac{i}{i_0} \right) \]

Supplementary Eq. (6)

where \( i \) is experimentally observed current density, \( i_0 \) is the exchange current density (the equilibrium current density when \( \eta = 0 \)) and \( A \) is the TAFEL slope. The TAFEL slope is calculated from the linear region of TAFEL plots (\( \eta \) vs. \( \log \frac{i}{i_0} \)), typically in the overpotential range from ~0.5 V to ~0.63 V.
Supplementary Note 2. Electrochemical full cell calculations.

The cell capacitance $C_{\text{cell}}$ (F), cell mass-specific capacitance $C_{\text{MS}}$ (F g$^{-1}$), electrode mass-specific capacitance $C_{\text{MS(electrode)}}$ (F g$^{-1}$), discharge cell capacity by mass $C_{\text{discharge}}$ (mAh g$^{-1}$), discharge electrode capacity by mass $C_{\text{discharge(electrode)}}$ (mAh g$^{-1}$), specific energy $E_{\text{MS}}$ (Wh kg$^{-1}$), specific power $P_{\text{MS}}$ (W kg$^{-1}$) and coulombic efficiency ($\eta$) and energy efficiency ($\gamma$) were calculated.

**Cell capacitance:**

$$C_{\text{cell}} = \frac{it}{U}$$  
Supplementary Eq. (7)

**Cell mass-specific capacitance:**

$$C_{\text{MS}} = \frac{it}{U+M} = \frac{it}{U+2m}$$  
Supplementary Eq. (8)

**Electrode mass-specific capacitance:**

$$C_{\text{MS(electrode)}} = 4C_{\text{MS}} = \frac{2it}{U+M/2} = \frac{2it}{U+m}$$  
Supplementary Eq. (9)

**Discharge cell capacity by mass:**

$$C_{\text{discharge}} = \frac{it}{3.6+M} = \frac{it}{3.6+2m}$$  
Supplementary Eq. (10)

**Discharge electrode capacity by mass:**

$$C_{\text{discharge(electrode)}} = 4C_{\text{discharge}} = \frac{2it}{3.6+M/2} = \frac{2it}{3.6+m}$$  
Supplementary Eq. (11)

**Specific energy:**

$$E_{\text{MS}} = \frac{1}{2}CU^2 = \frac{1}{2} \times \frac{itU}{3.6+M} = \frac{1}{2} \times \frac{itU}{3.6+2m}$$  
Supplementary Eq. (12)

**Specific power:**

$$P_{\text{MS}} = \frac{3600 \times E_{\text{MS}}}{t}$$  
Supplementary Eq. (13)

**Coulombic efficiency:**

$$\eta = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} = \frac{it_{\text{discharge}}}{t_{\text{charge}}} = \frac{t_{\text{discharge}}}{t_{\text{charge}}}$$  
Supplementary Eq. (14)

**Energy efficiency:**

$$\gamma = \frac{\int_{V_{\text{discharge}}}^{V_{\text{charge}}} \frac{V_{\text{discharge}}}{V} C_{\text{discharge(electrode)}}(V) dV}{\int_{V_{\text{charge}}}^{V_{\text{discharge}}} \frac{V_{\text{charge}}}{V} C_{\text{charge(electrode)}}(V) dV}$$  
Supplementary Eq. (15)

**Cell resistance:**

$$R = \frac{\Delta V}{i}$$  
Supplementary Eq. (16)

Where $i$ (A) is the applied constant current, $t$ (s) is discharge time of the cell device, $U$ (V) is potential window, $\Delta V$ (V) is the i-R drop during discharge curve, $M$ (g) is the total mass of active materials on both electrodes and $m$ (g) is the mass of active materials on one electrode.
Supplementary Methods:

**Structural characterization.** High resolution transmission electron microscopy (HRTEM) images were collected using aberration-corrected Hitachi HD 2700C equipped with a modified Gatan Enfina ER spectrometer at the Center for Functional Nanomaterials at the Brookhaven National Laboratory. Regular TEM images were obtained using a Zeiss/LEO 922 Omega TEM at the University of New Hampshire. Powder XRD spectra were obtained at beam line 17-BM (λ = 0.72768 Å) at Advanced Photon Source, Argonne National Laboratory. SEM images were collected by Lyra 3 GMU FIB SEM (Tescan, Inc.) at University of New Hampshire.

**Pair distribution function (PDF) analysis of neutron and X-ray scattering.** The neutron scattering experiments were conducted at the Nanoscale-Ordered Materials Diffractometer (NOMAD) beamline at Spallation Neutron Source at Oak Ridge National Laboratory, and X-ray scattering were conducted at the 11-ID-B beamline at Advanced Photon Source at Argonne National Laboratory. The PDF analysis was conducted using PDFgui software. The X-ray PDF was fit from 1 Å to 50 Å with using a Q_max value of 23.5 Å⁻¹ and the Neutron PDF was fit from 1.6 Å to 50 Å using a Q_max value of 25 Å⁻¹. The refinement of the X-ray and neutron PDFs resulted in lattice parameters that are in good agreement with one another. The PDF analysis also showed that the nanoparticles consisted of 80.8% of Mn₅O₈ and 19.2% of Mn₃O₄ by mass from neutron scattering, and 80.4% of Mn₅O₈ and 19.6% of Mn₃O₄ by mass from X-ray scattering experiments.

**Soft X-ray Absorption Spectroscopy (sXAS):** sXAS was performed at Beamline 8.0.1 at the Advanced Light Source (ALS) of the Lawrence Berkeley National Lab (LBNL). The undulator and spherical grating monochromator supply a linearly polarized photon beam with resolving power up to 6000. The experimental energy resolution is about 0.15eV. The electrode samples were loaded into the ultra-high vacuum sXAS characterization chamber from an Argon glove box through a sample transfer kit to avoid any air exposure. Experiments were performed at room temperature and with the linear polarization of the incident beam oriented at 45° to the electrode surface. The sXAS spectra were collected using total electron yield (TEY) mode with a probing depth of about 10 nm. All the spectra have been normalized to the beam flux that was measured simultaneously by an upstream gold mesh.

**Density Functional Theory (DFT) calculations:** The reaction free energies and activation energies for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) on the (100) surface of Mn₅O₈ with and without hydroxylated layer were calculated using the first principles. For the calculation of water splitting at various electrochemical potential windows (Fig. 5), the following steps were considered:

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \frac{1}{2}\text{OH}^+ + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}(\text{H}^+ + e^-) \\
\frac{1}{2}\text{OH}^+ & \rightarrow \frac{1}{2}\text{O}_2^+ + \frac{1}{2}\text{H}_2\text{O} + (\text{H}^+ + e^-) \\
\frac{1}{2}\text{OH}^+ & \rightarrow \frac{3}{2}(\text{H}^+ + e^-) \\
\frac{1}{2}\text{OH}^+ & \rightarrow \frac{1}{2}\text{O}_2 + 2(\text{H}^+ + e^-)
\end{align*}
\]  

Supplementary Eq. (17)

The reaction kinetics on the (100) surface of Mn₅O₈ with and without OH adsorption were investigated by calculating the reaction activation energy of each intermediate reaction step
On all the surfaces, we assume that the reaction mechanism of HER is surface hydrogen association while the reaction mechanism of OER is surface OOH intermediate reaction as shown in Fig. 5a and 5b, respectively. For both HER and OER, the activation energy of water adsorption was ignored since the negative adsorption energy of water -0.87 eV on both surfaces indicates that water can be easily adsorbed onto the surface. We also ignored the activation energy of the combination of surface hydrogen and the dissociation of OOH for these reactions are usually not rate determining.

All the spin-polarised DFT calculations were performed using Vienna Ab-initio Simulation Package (VASP)\textsuperscript{9,10}. Project augment wave (PAW) method was used to describe the interaction between the ion and valence electrons\textsuperscript{11}. The exchange-correlation functional developed by Perdew, Burke and Ernzerhof (PBE)\textsuperscript{12} was used. The energy cutoff of all the calculations was set to be 400 eV as suggested by Franchini \textit{et al.}\textsuperscript{13}. In addition, PBE+U method following the approach of Dudarev\textsuperscript{14} was used to describe the correlation between the d electrons of Mn. The U value was set as 4 eV as suggested by Wang \textit{et al.}\textsuperscript{15}. Furthermore, the transition state of all the relevant reactions on the surfaces were calculated by climb-image nudged-elastic band (CINEB) method\textsuperscript{16}, in which all the force components both along and perpendicular to the tangent of the reaction path were relaxed to be less than 0.05 eV Å\textsuperscript{-1}.

**Supplementary References**


