## **Electronic Supplementary Information**

## Water oxidation catalysis – role of redox and structural dynamics in biological photosynthesis and inorganic manganese oxides

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## **Materials and Methods**

**Freeze-quench X-ray absorption experiment.** Mn oxides deposited on thin glassy carbon were frozen after 3 min exposure to the selected potential (in 0.1 M phosphate buffer adjusted to pH 7). The electrolyte-exposed samples were frozen inside of an adapted electrochemical cell, which subsequently served as a sample holder in the low-temperature XAS measurements; during the freezing the voltage between the working and counter electrodes was kept constant. For details on this freeze-quench, *quasi-in situ* approach <sup>1</sup>, see Fig. S1.

**EXAFS Fourier-transforms and EXAFS simulations.** After transition from an energy to a wave-vector scale (*k*-scale) and weighting by  $k^3$ , the Fourier transforms shown in Fig. 2 in the main text and Fig. S5b were calculated for *k* ranging from 2.6 to 12.2 Å<sup>-1</sup> (same *k*-range for PSII and all oxide films). Cosine windows covering 10% at the low-*k* and high-*k* side of the spectra were applied before calculation of the Fourier transforms. The absolute value of the Fourier-transform amplitudes is shown.

Simulations of the  $k^3$ -weighted EXAFS spectra of the catalytically active Mn-only oxide (MnCat) and the inactive Mn oxide were performed as described in Refs.<sup>2, 3</sup> using the k-range from 2 to 14 Å<sup>-1</sup>. In order to minimize the number of free parameters and to improve the significance of the simulation results, a joint fit approach was used where the interatomic distances were kept the same for all spectra of one data set (the same oxide type at various potentials). In addition, the Debye-Waller parameters for all oxygen shells were kept the same for all potentials. The Debye-Waller parameters for all manganese shells were fixed to 0.063 Å. Also, the sum of the EXAFS coordination numbers in the two oxygen shells was fixed to 6. The EXAFS coordination numbers for the Mn-Mn vectors were varied freely. For the catalytically active oxide, the short Mn-Mn distance (~ 2.9 Å) was simulated with two separate shells. For the inactive material, only one shell was used because splitting of this distance into two shells did not result in significant improvement of the fit quality, but in an increased number of fit parameters and thus increased uncertainty in the parameter values. This observation suggests that the short Mn-Mn distances are more uniform in the inactive Mn oxide, as expected from the better ordered structure. The simulation results are presented in Table S1. The used amplitude reduction factor  $(S_0^2)$  was 0.7. For calculation of the Fourierfiltered error (described in Ref.<sup>4</sup>), the range from 1 to 3.5 Å on the reduced distance scale was used.

**Time-resolved** *in situ* **X-ray absorption measurements.** For an overview scheme of the timeresolved *in situ* experiment, see Fig. S9. The measurements were performed at 20 °C at the BESSY II synchrotron radiation source at beamline KMC-3. A silicon (111) double-crystal monochromator was used for selecting a fixed X-ray excitation energy (6553.3 eV). Manganese oxide deposited on thin glassy carbon was attached as a window to the wall of a home-made Teflon cell filled with 0.1 M phosphate buffer (adjusted to pH 7) and placed in the path of the X-ray beam. The size of the area illuminated by the X-ray beam was approximately 11 x 3 mm. All X-ray absorption signals were collected in fluorescence mode. The excited Mn X-ray fluorescence passed through the glassy carbon and then through a Cr foil (10  $\mu$ m) shielding against scattered X-rays. The fluorescence was monitored perpendicular to the incident beam by a scintillation detector (19.6 cm<sup>2</sup> active area, 51BMI/2E1-YAP-Neg, Scionix; shielded by 2  $\mu$ m Al foil against visible light). The detector consisted of a scintillating crystal (YAP) converting X-ray photons into visible light (~50% efficiency) detected by a fast photomultiplier operated at 1.1 kV. The current signal from the photomultiplier passed through a 1 M $\Omega$  resistor for current-to-voltage conversion and was fed into a low-noise amplifier (Stanford Research Systems, model SR560; 10 Hz low-pass filtering, 6 dB/oct; amplification factor of 20). The amplified signal was finally recorded with a time resolution of 10 ms by the potentiostat (Biologic SP-300) that also operated the electrochemical cell and recorded the signal from an ionization chamber monitoring the intensity of the incoming X-ray beam. Short-range Mn *K*-edge absorption spectra of the oxide film on the glassy carbon electrode were recorded immediately before and after each time-resolved experiment, in order to facilitate normalization of time-resolved data and to ascertain that there was no significant film dissolution. In separate X-ray scans, absorption spectra of KMnO<sub>4</sub> powder were measured for precise energy calibration, setting the maximum of the pre-edge absorption peak of the KMnO<sub>4</sub> to 6543.3 eV.



**Figure S1.** Freeze-quench (quasi-*in situ*) approach for investigation of Mn(Ca) oxide film by low-temperature X-ray absorption spectroscopy (XAS). (**A**) Sample cell made of transparent PVC (33 mm x 19 mm x 2 mm) with a window (14 mm x 14 mm) and two holes drilled for insertion of a platinum wire, which can serve as a counter electrode (CE). The window is closed by the working electrode (WE) consisting of a glassy carbon sheet (thickness of 100  $\mu$ m) supported by Kapton® tape. Copper tape was connected to the glassy carbon, facilitating electric contact by using crocodile clamps (not shown). (**B**) The Mn(Ca) oxide were electrodeposited on the working electrode as described in the Materials and Methods section of the main article. After electrodeposition of the Mn(Ca) oxide films, ~250  $\mu$ l of Mn-free electrolyte (0.1 M potassium phosphate, pH 7.0) were filled in the cell and a mercury sulfate

reference electrode (REF, Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> +650 mV vs. NHE) was immersed into the electrolyte as shown in the scheme. Then the desired potential was applied for 2 minutes and the voltage,  $V_{WE/CE}$ , between the working electrode and the counter electrode was measured. (C) The reference electrode was removed and  $V_{WE/CE}$  was applied between the working electrode and counter electrode (meaning operation in a two-electrode configuration). (D) After 1 minute the whole sample cell was quickly frozen by spilling liquid nitrogen over the cell assembly. Only after the whole cell had been frozen, the electrode clamps were detached and the copper tape was cut off (under liquid nitrogen). Finally, the platinum wire was removed and the samples were stored in liquid nitrogen until use in the XAS measurements.



**Figure S2.** Cyclic voltammograms (CVs) of catalytically active Mn oxide (MnCat, red line) and inactive Mn oxide (Inactive, blue line). Scan rate 20 mV/s; the second CV of a series is shown.



**Figure S3.** Calibration line relating Mn *K*-edge energy position and the formal Mn oxidation state. Edge energies of the commercial Mn compounds  $Mn^{II}O$ ,  $\alpha$ - $Mn^{III}_2O_3$  and  $\beta$ - $Mn^{IV}O_2$  were used for calibration. Using additional Mn oxide references results in a very similar calibration curve (see ref. 2). The linear regression line results in the following calibration equation for estimating the mean Mn oxidation state:  $z_{ox} = (E_{edge} - 6538.4 \text{ eV})/3.8$ . All edge energies were determined using an 'integral method', which is clearly less sensitive to edge-shape changes than other methods.<sup>4</sup>



**Figure S4.**  $k^3$ -weighted EXAFS spectra (top) and their Fourier transforms (bottom) of the catalytically active Mn oxide (MnCat, left) and the inactive oxide (right) equilibrated at different potentials (vs. NHE, pH 7). Black lines represent experimental data, red lines – simulated spectra. The simulation parameters are listed in Table S1.

**Table S1.** Simulation parameters for the EXAFS spectra of the catalytically active Mn-only oxide (MnCat) and of the inactive Mn oxide. The interatomic distances, *R*, for each shell are shown in bold (in Å) and were kept the same at all potentials. The rest of the values show the coordination numbers at the respective potential. The errors representing 68% confidence intervals of the respective fit parameters are shown in parentheses. For the MnCat, the Debye-Waller parameter ( $\sigma$ ) for the two oxygen shells was 0.065 ± 0.001 Å (at all potentials) and the filtered R-factor was 10.9%. For the inactive Mn oxide, the Debye-Waller parameter ( $\sigma$ ) for the two oxygen shells was 0.059 ± 0.001 Å and the filtered R-factor 11.4%. The asterisks indicate that the sum of the EXAFS coordination numbers of the two oxygen shells was forced to be equal to six; the error is indicated only for one of the two coordination numbers. The Debye-Waller parameters for all manganese shells were fixed to 0.063 Å.

|        | Mn-O                       | Mn-O        | Mn-Mn        | Mn-Mn          | Mn-Mn       | Mn-Mn       | Mn-Mn       |
|--------|----------------------------|-------------|--------------|----------------|-------------|-------------|-------------|
|        | catalytically active MnCat |             |              |                |             |             |             |
| all    | 1.90 (0.001)               | 2.28 (0.01) | 2.85 (0.01)  | 2.99<br>(0.01) | 3.16 (0.01) | 3.42 (0.01) | 3.81 (0.02) |
| 0.45 V | 4.7 (0.2)*                 | 1.3*        | 2.6 (0.4)    | 1.7 (0.6)      | 1.1 (0.5)   | 0.7 (0.4)   | 0.4 (0.5)   |
| 0.70 V | 5.0 (0.2)*                 | 1.0*        | 3.0 (0.4)    | 2.8 (0.7)      | 2.0 (0.6)   | 1.3 (0.4)   | 0.2 (0.5)   |
| 0.85 V | 5.3 (0.2)*                 | 0.7*        | 3.6 (0.4)    | 3.3 (0.7)      | 2.8 (0.7)   | 2.0 (0.5)   | 0.4 (0.5)   |
| 0.95 V | 5.4 (0.2)*                 | 0.6*        | 3.6 (0.4)    | 3.0 (0.7)      | 2.6 (0.6)   | 1.7 (0.4)   | 0.5 (0.5)   |
| 1.15 V | 5.4 (0.2)*                 | 0.6*        | 3.5 (0.4)    | 2.9 (0.7)      | 2.3 (0.7)   | 2.0 (0.4)   | 0.9 (0.5)   |
| 1.20 V | 5.5 (0.2)*                 | 0.5*        | 3.7 (0.4)    | 3.1 (0.7)      | 2.7 (0.7)   | 2.3 (0.5)   | 0.4 (0.5)   |
| 1.35 V | 5.4 (0.2)*                 | 0.6*        | 3.7 (0.4)    | 3.0 (0.7)      | 2.3 (0.7)   | 1.9 (0.4)   | 0.5 (0.5)   |
| 1.45 V | 5.6 (0.2)*                 | 0.4*        | 4.1 (0.4)    | 3.1 (0.7)      | 2.2 (0.7)   | 1.8 (0.4)   | 0.6 (0.5)   |
|        | inactive Mn oxide          |             |              |                |             |             |             |
| all    | 1.90 (0.001)               | 2.28 (0.01) | 2.87 (0.002) |                | 3.14 (0.01) | 3.49 (0.01) | 3.78 (0.01) |
| 0.45 V | 5.0 (0.2)*                 | 1.0*        | 4.6 (0.2)    |                | 0.7 (0.3)   | 1.7 (0.4)   | 0.4 (0.5)   |
| 0.70 V | 5.3 (0.2)*                 | 0.7*        | 4.8 (0.2)    |                | 0.9 (0.3)   | 1.7 (0.4)   | 0.7 (0.5)   |
| 0.85 V | 5.5 (0.2)*                 | 0.5*        | 4.9 (0.2)    |                | 0.9 (0.3)   | 1.3 (0.4)   | 0.1 (0.5)   |
| 1.15 V | 5.7 (0.2)*                 | 0.3*        | 4.9 (0.3)    |                | 1.5 (0.3)   | 1.5 (0.4)   | 1.3 (0.5)   |
| 1.35 V | 5.7 (0.2)*                 | 0.3*        | 4.6 (0.2)    |                | 0.8 (0.3)   | 1.6 (0.4)   | 0.9 (0.5)   |
| 1.45 V | 5.8 (0.2)*                 | 0.2*        | 4.8 (0.2)    |                | 0.7 (0.3)   | 1.4 (0.4)   | 1.1 (0.5)   |



**Figure S5.** Averaged Mn–O distances calculated from the simulation results presented in Table S1. Mn oxidation state calculated according to the bond-valence sum rules<sup>5</sup> is +3.48 for the MnCat and +3.61 for the inactive Mn oxide at 0.45 V and +3.86 for the MnCat and +3.95 for the inactive Mn oxide at 1.45 V.



**Figure S6.** Fourier-isolated EXAFS oscillations corresponding to the Mn–Mn peak (Fourier isolation from 2.1 Å to 2.9 Å on the reduced distance scale) of the data for the MnCat shown in Fig. S4. For clarity, only the positive amplitudes of the EXAFS oscillations are shown. In panel A, the experimental data is presented. In panel B, the simulated oscillations with fixed Debye-Waller parameter (using the simulation approach presented in Fig. S4 and Table S1) are shown. Panel C shows the results from simulations in which (i) the coordination numbers for the two short Mn-Mn distances (2.85 Å and 2.99 Å) were fixed to the values obtained at 0.45 V and (ii) the Debye-Waller factors for these two shells were freely varied. Only four potentials are shown for clarity. The experimental data is better modeled with fixed Debye-Waller parameter (in B), indicating that the observed potential-induced increase in the amplitude of the second peak is a result rather from an increase in the coordination number than from a decreased inhomogeneity in the length of the shortest Mn-Mn distances.



**Figure S7.** XANES spectra (**a**) and Fourier transformed EXAFS spectra (**b**) of the MnCa oxides equilibrated at the indicated potentials (vs. NHE, pH 7). The inset in (a) show the extracted pre-edge features. For each FT peak, the corresponding structural motif is schematically shown (Mn, magenta; O, red). In the MnCa oxide, the third FT-peak also contains contributions from Mn-Ca distances.



**Figure S8.** Absorption spectra of (**a**) the catalytically active Mn-only oxide (MnCat), (**b**) of the inactive Mn oxide and (c) the absorption 370 nm of the catalytically active Mn-only oxide (MnCat, red circles) and the inactive film (blue circles) as a function of the applied potential (vs. NHE at pH 7). The catalyst films were deposited on optically transparent ITO-covered glass slides and equilibrated at the indicated potentials (vs. NHE, pH 7) for 2 min before measuring the UV-vis spectra.



**Figure S9**. Estimation of the initial rate of Mn reduction from the UV-vis time courses of Fig. 4 in (**a**) active oxide (MnCat) and (**b**) inactive oxide. To obtain a rough estimate, the time period for an absorption change corresponding to  $\Delta I/I = 0.5 \ 10^{-3}$  was determined graphically. Values of about 20 ms and 3000 ms are obtained for active and inactive oxide, respectively. (In this estimation, it is assumed that equal  $\Delta I/I$  values correspond to roughly similar changes in the average Mn oxidation state, as suggested by comparison of Fig. S8c with Fig. 3.)



**Figure S10.** Time course of current and open-circuit potential (OCP) measured in parallel to the UV-vis experiment of Figure S9. *Top panels*: Time courses of the current for stepping the electrode working conditions from OCP top application of 1.4 V vs NHE (pH 7). *Bottom panels*: Time courses of the electrode potential for switching between application of 1.4 V (vs. NHE, pH 7 and OCP) conditions. The right panels show the respective time course in form of a double-logarithmic plot.



Figure S11. Time-resolved in situ X-ray absorption experiment. (a) Illustration of the experimental concept. Panel-a shows XANES spectra collected in freeze-quench experiments for the MnCat equilibrated at different electrode potentials. The X-ray absorption at 6553.3 eV (arrow) decreases (see inset) because the edge position shifts with increasingly positive potentials to higher energies, as a result of Mn oxidation. This absorption change at 6553.3 eV was traced in the time-resolved X-ray experiments. (b) Scheme of the experimental setup for time-resolved X-ray absorption measurements. Monochromatic synchrotron radiation (6553.3 eV) passes through an ionization chamber (IC, for recording the variations in the incoming beam intensity) and a photoshutter (PS) before hitting the Mn oxide film (Mn). The Mn oxide film deposited on a thin, X-ray-transparent glassy carbon (GC) electrode serves as the working electrode in a 3-electrode electrochemical setup, with reference electrode (RE) and a platinum mesh serving as counter electrode (CE). The cell is filled with 0.1 M phosphate buffer (pH 7). The excited Mn X-ray fluorescence passes through the glassy carbon and then through a 10 µm chromium foil (Cr), which absorbs a major fraction of the scattered X-ray photons. The fluorescence is monitored perpendicular to the incident beam by a scintillation detector consisting of a scintillating crystal and a fast photomultiplier operated at 1.1 kV. The signal from the photomultiplier passes through a 1 M $\Omega$  resistor for current-to-voltage conversion and is fed into an amplifier. The amplified signal is finally recorded by the same potentiostat device that also operates the electrochemical cell and records the IC signal. (c) Mn oxidation-state changes of catalytically active Mn oxide (red) and inactive oxide (blue) induced by stepping the electrode potential between 1.4 V and 0.6 V and tracked by recording the  $K_{\alpha/\beta}$  X-ray fluorescence intensity for excitation at 6553.3 eV (same data as in Fig. 5a, but with extended time window shown and estimated Mn oxidation states indicated). The Mn oxidation state estimates were derived from rapid XAS scans before and after the voltage-jump experiments; the corresponding numbers are less precise than in Figure 3.



**Figure S12.** Bode plots for electrochemical impedance spectra obtained at different potentials (vs. NHE, pH 7) for the catalytically active Mn-only oxide (MnCat, in a and b) and the inactive Mn oxide (c, d). The experimental data are presented by points, the simulation results according to the model in Fig. S14 are indicated by solid lines.



**Figure S13.** Nyquist plots for electrochemical impedance spectra obtained at different potentials for the catalytically active Mn-only oxide (MnCat, in a, b, and c) and the inactive Mn oxide (d, e f). In the different plots, different scales are used. The experimental data are presented by points; the simulations according to the model in Fig. S14, by solid lines. The simulations parameters are shown in Fig. S14.



**Figure S14.** Parameters for the simulation of the impedance spectra according the equivalent circuit shown bottom right.  $R_{Ohm}$  – summed Ohmic resistance of electrolyte and ITO electrode;  $C_{dl}$  – double-layer capacitance, modelled as a constant-phase element;  $C_{ox}$  – capacitance describing oxidation state changes of the catalyst film (in other contexts also denoted as pseudo-capacitance), modelled as a constant phase element;  $R_{ox}$  – resistance describing the oxidation state changes of the catalyst film;  $R_{cat}$  – catalytic resistance of the oxide (in other contexts also denoted as charge-transfer resistance). The values for the Ohmic resistance were fixed during the simulations (46.5  $\Omega$  for the MnCat and 53  $\Omega$  for the inactive Mn oxide). The double layer capacitance ( $C_{dl}$ ) and the oxidation capacitance ( $C_{ox}$ ) were calculated according to the given equation (following the Brug conversion rules<sup>6</sup>), where  $\alpha$  is the phase parameter of the constant phase element (with values between 0.75 and 1 in all simulations) and Q is the capacitance parameter of the constant phase element in units of  $Fs^{(\alpha-1)}$ . The formal uncertainty ranges for the fit parameters were below 4%.

## References

- 1. M. Risch, F. Ringleb, M. Kohlhoff, P. Bogdanoff, P. Chernev, I. Zaharieva and H. Dau, *Energy Environ. Sci.*, 2015, **8**, 661-674.
- 2. I. Zaharieva, P. Chernev, M. Risch, K. Klingan, M. Kohlhoff, A. Fischer and H. Dau, *Energy Environ. Sci.*, 2012, **5**, 7081-7089.
- 3. M. Wiechen, I. Zaharieva, H. Dau and P. Kurz, *Chem. Sci.*, 2012, **3**, 2330-2339.
- 4. H. Dau, P. Liebisch and M. Haumann, Anal. Bioanal. Chem., 2003, 376, 562-583.
- 5. I. D. Brown and D. Altermatt, *Acta Crystallographica Section B*, 1985, **41**, 244-247.
- 6. G. J. Brug, A. L. G. van den Eeden, M. Sluyters-Rehbach and J. H. Sluyters, *J. Elelectroanal. Chem.*, 1984, **176**, 275-295.