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Supporting Information to:

Electronic Structural Insights into Efficient MnO_x Catalysts

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Sample Preparation

All reagents and solvents were purchased from Sigma-Aldrich and used as received. Purity was as follows: $Mn(ClO_4)_2.6H_2O$ (99%, this is referred to as Mn(II) in the text), Nafion perflourinated resin solution (5 wt. % in lower aliphatic alcohols containing 15-20% water), acetonitrile (99.9%), perchloric acid ($HClO_4$, 0.1 M), and Na_2SO_4 (ACS reagent, 99%). The $[Mn_2O(OAc)_2L_2](ClO_4)_2$ complex, referred to as Mn(III) in the text where L = Me_3TACN (1,4,7-trimethyl-1,4,7-triazacyclononane), OAc = μ-CH_3COO^-) was prepared as described elsewhere.[1] Reference birnessite was prepared as described in the literature.[2] Solutions of the two compounds with concentrations of 8mM for $Mn(ClO_4)_2.6H_2O$ and 4mM for $[Mn_2O(OAc)_2L_2](ClO_4)_2$ in acetonitrile were prepared and acidified with an equimolar amount of perchloric acid. A known volume of Nafion solution (10 µL) was cast onto $1cm^2$ graphite electrodes, dried in air and then in an oven at 120 °C for 20 minutes. These Nafion coated electrodes were impregnated with the Mn compounds by dipping them in precursor solution for 20 minutes. The impregnated films were washed with deionized water and then air-dried. A potential of 1.0 V versus Ag/AgCl (3M NaCl, 0.200V vs. NHE) electrode was applied to the Mn-doped in nafion coated graphite films (anodes) using a platinum counter electrode in a conventional three-electrode electrochemical cell for 60 minutes. An aqueous solution containing 0.1M Na_2SO_4 (pH 6.5) was used as the electrolyte. The films were then washed with deionized water and air-dried. For the last step in the analysis, referred to as state 3, the films were irradiated for 16 hours with visible light of 20W, generated by a halogen lamp, whilst being dipped in a 0.1M Na_2SO_4(aq) electrolyte (without bias). After light exposure, the samples were rinsed with deionized water and air-dried.

To address the possibility that the samples may be changing over time when either exposed to air or under high vacuum during measurement, the following steps were followed. After electrochemical generation of the samples or treatment in solution, the samples were carefully air-dried. This step was not expected to have any effect on the Mn^{2+} samples as Mn^{2+} is stable in Nafion and does not react with oxygen. If it did, the resultant species of the oxidation process would have been seen in previous XAS studies. For the oxidised species, the stability was predicted to be an issue only if the samples were kept as wet films or films which have electrolyte and water in the Nafion channels. In that case, light would cause partial reduction of the oxide and the release of oxygen, changing the sample. From our experience the films containing the oxides are stable and show no evidence of converting/reducing to Mn^{2+} when left as dry films. For the possibility of the samples being changed over time in the high vacuum environment of the soft X-ray chamber, spectra were collected at multiple spots on the same sample, one after another. The spectra obtained were reproducible. As the second spot analysed has been subjected to the vacuum for a longer duration without changing, it can be concluded that the samples are stable under the analysis conditions. This is not surprising, as once the samples are dry, there will not be any species present that are able to evaporate under the conditions in use.

Experimental Methods

XAS and RIXS experiments were performed in the LIXEdrom experimental station at U41-PGM beamline, at BESSY II synchrotron facility. Details of the LIXEdrom end-station have been described somewhere else[3]. Mn-doped nafion films deposited on graphite anodes were mounted on a sample holder with adhesive copper tapes. The incoming synchrotron beam was impinging the sample at 45º angle, and the emitted (RIXS) photons were detected with an x-ray emission spectrometer (XES) mounted normal to the synchrotron beam. X-ray absorption spectra, were measured in total electron yield, with the conventional method of sample drain current. Each measurement was repeated several times at different spots on the same sample and on several identically prepared samples to test for sample homogeneity and to assure experimental reproducibility. Rapid scans of 1 sec per point were employed to avoid any radiation damage of active catalyst caused by soft X-rays. Birnessite samples showed radiation damage and the synchrotron flux was strongly reduced until the damages were minimized.

Radiation Damage Study

It is well known that the manganese oxide samples undergo photo-reduction under the intense flux of the soft X-rays[4]. Therefore, we carried out a systematic study to check for any possible radiation damage for all Mn catalysts in all states (doped, as biased and light shined). In order to reduce radiation damages we recorded the XAS spectra in electron yield mode which allowed us to drastically reduce the photon flux on the sample (in the soft X-ray range electron yield method has a cross section of ~95%, compared to 1-5% of fluorescence yield). The photon flux was reduced by closing the primary beam line baffles (the one located directly after the undulator) from the 1.2x1.2, 1.0x1.0 conventional values up to 0.1x 0.2, 0.1x 0.0. The beam flux reduces linearly with the closing of the baffles. The XAS spectra of catalysts and some of the reference oxides samples are shown in Figure S1-S3. To test for radiation damages the spectra were measured at least twice at the same spot and then to a fresh illuminated spot for each sample. For all the catalysts we observed no intensity change or energy shift of the XAS spectral features measured at different spots and at the same spot (see Figure S1). We explained it with the fact that the MnO_x catalysts are doped inside the nafion layer which itself absorbs and therefore attenuate further X-rays. In opposite, for the oxide reference powders we observed a change in intensity of spectral features upon reducing the synchrotron beam flux. Radiation damages were severe in case of MnO_2 and synthetic birnessite, where manganese is in high oxidation state Mn^{2+}, Mn^{3+} and Mn^{4+}, respectively. Therefore, for these samples the beam line apertures were almost fully closed up to 0.1×0.2, 0.1×0.0. Our XAS experimental spectra look similar with those reported in the literature[5,6].

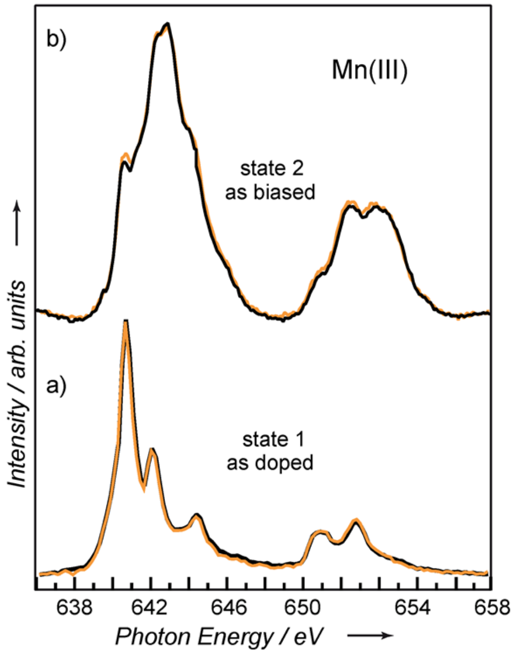

Figure S1. Radiation damage study of Mn(III) in the a) as doped (state1); and b) as biased (state 2). Yellow: fresh spot, Black: subsequent measurement on the same spot. The spectra show no changes in intensity when measured on a fresh spot or two times consecutively on the same spot with fixed beam line settings. In both cases the opening of beam line apertures was 0.8×0.8, 0.8×0.8 and the beamline slit was 20μm.

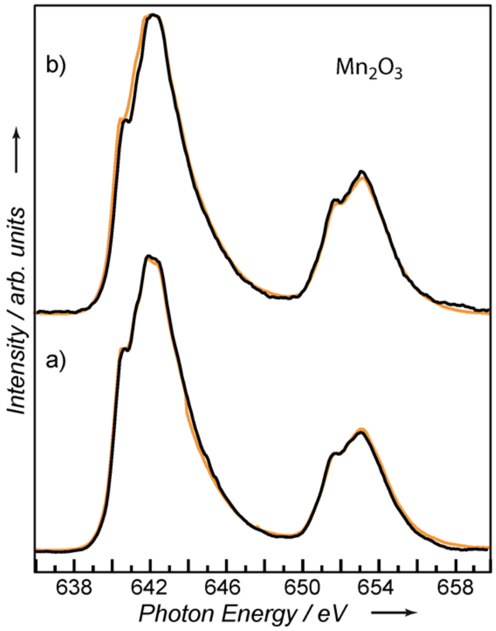

Figure S2. Radiation damage study of Mn_2O_3 oxide powder; yellow: fresh sample spot, black: subsequent measurement on the same spot. The spectra were recorded with beam line slit width of 20µm. a) Apertures of 0.8×0.8, 1.0×1.0. b) Apertures of 0.2×0.2, 02×0.2. The spectra apparently look similar for the two different aperture openings (different synchrotron beam flux). This indicates the Mn_2O_3 is quite stable with no specific radiation damage when exposed to soft x-rays.

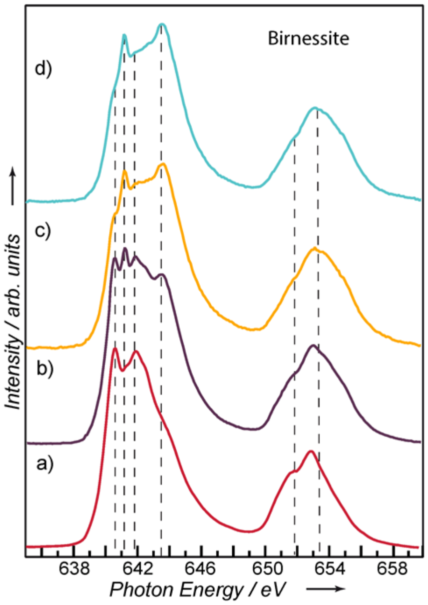

Figure S3. Radiation damage study of synthetic birnessite. It showed clear changes of the spectral features intensity, upon reduction of the photon flux. The damages were minimized by reducing the beam line apertures stepwise to the lowest possible values that allowed us to record the XAS spectrum. a) Apertures of 0.8×0.8, 0.8×0.8. b) Apertures of 0.2×0.2, 02×0.2. c) Apertures of 0.1×0.1, 0.1×0.1. d) Apertures of 0.1×0.1, 0.1×0.0.

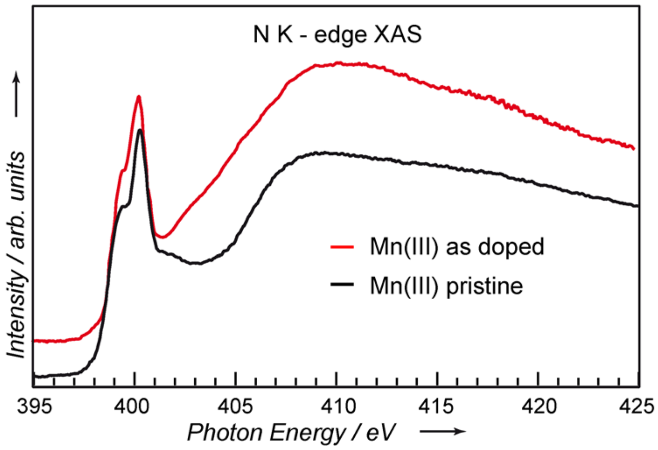

Figure S4. Nitrogen K-edge XAS spectra of Mn(III) complex. Black: the pristine complex dissolved in dichloromethane; red: the complex as doped into Nafion, State 1. The exact energetic location and resemblance of the near-edge double peak indicates that some of the Mn-N bonds are not broken, i.e., some TACN ligands remain coordinated to Mn inside the Nafion. The small intensity changes at Rydberg and shape resonance area (located at higher energies) manifest a change in the chemical local environment, most probably induced by the anionic sulfonate group of the Nafion matrix.

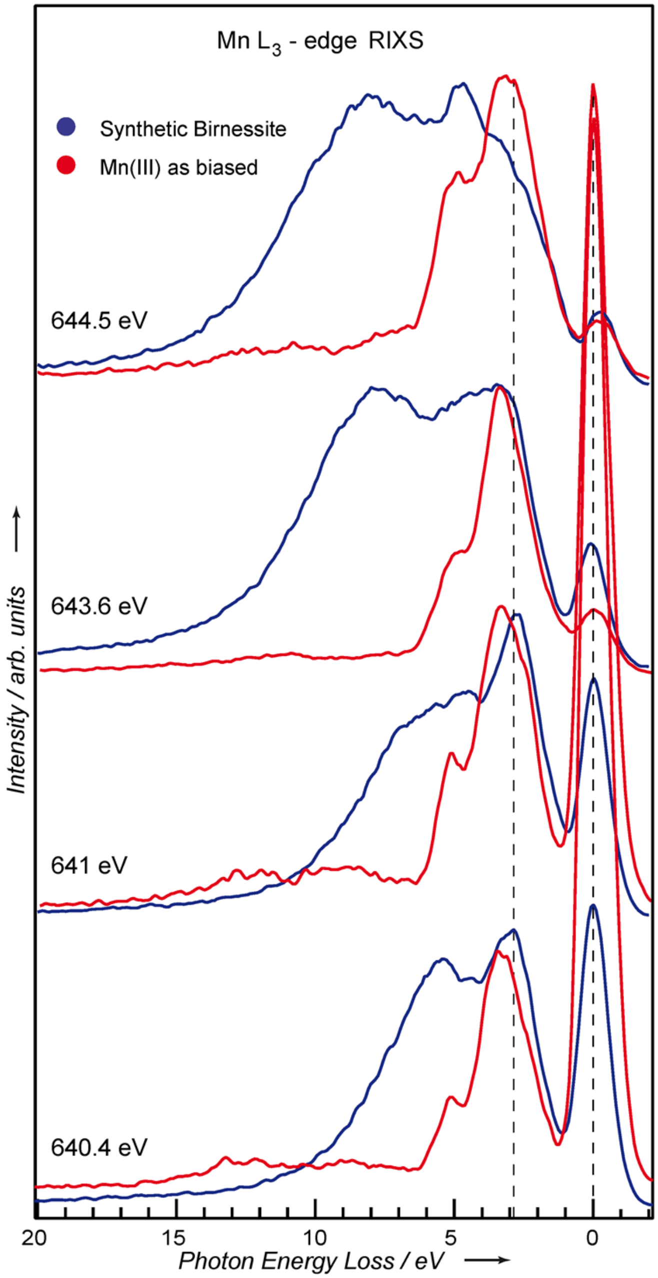

Figure S5. Experimental RIXS spectra measured at the Mn L$_{2,3}$-edge of Mn(III) catalysts and synthetic birnessite. Excitation energies for each RIXS spectrum are given in the Figure. Energy loss features of birnessite are expanded at higher energies than in Mn(III) State 2. According to the previous study reported by Ghiringhelli et al this result shows that the average oxidation state of the electro-oxidized Mn(III) cluster is lower than the synthetic birnessite[7].

Linear Fitting of XAS Spectra

The coefficients of linear fitting of Mn(III) in as biased and illuminated states along with Mn(II), and Mn(IV) in as biased state are shown in table S1. Previous investigations showed that MnOx catalysts adopt a distorted birnessite structure, which is indeed a mixture of Mn^{3+} and Mn^{4+} oxidation states. To estimate the amount of birrnesite, Mn^{2+}, Mn^{3+} and Mn^{4+} present in as biased state of all three complexes, the spectra are being fitted by two different linear combinations of: Experimental spectra of Mn(II) in as doped state (Mn^{2+}) + Mn$_2$O$_3$ (Mn^{3+}) + birnessite (Mn^{3+}, Mn^{4+}) samples; Experimental spectra of Mn(II) in as doped state (Mn^{2+}) + Mn$_2$O$_3$ (Mn^{3+}) +M$_3$O$_4$ (Mn^{4+}) samples. All spectra were first normalized with mirror current to avoid any intensity change of photon flux during the sequential measurements, followed by a linear background subtraction. The spectra were than normalized to maximum peak intensity before making different linear combinations to find the best fit.

Table 1. Fitting of XAS experimental spectra of MnO$_x$ catalysts with a linear combination of oxide powders experimental spectra accounting for Mn^{2+}, Mn^{3+}, Mn^{4+}, and birnessite state-like contributions.

Catalyst[a]	Fitting coefficients with: Mn^{2+} +Mn^{3+} + Birnessite	Fitting coefficient with: Mn^{2+} +Mn^{3+} + Mn^{4+}
Mn(III) as biased	60% Mn^{3+} + 40% Birnessite	5% Mn^{2+} + 70% Mn^{3+} + 25% Mn^{4+}
Mn(III) light shined	45% Mn^{2+} + 15% Mn^{3+} + 40% Birnessite	50% Mn^{2+} + 10% Mn^{3+} + 40% Mn^{4+}
Mn(II) as biased	60% Mn^{2+} + 10% Mn^{3+} + 30% Birnessite	60% Mn^{2+} + 10% Mn^{3+} + 30% Mn^{4+}
Mn(IV) as biased	10% Mn^{2+} + 60% Mn^{3+} + 30% Birnessite	10% Mn^{2+} + 60% Mn^{3+} + 30% Mn^{4+}

[a] Experimental Mn L-edge XAS spectrum of the catalyst.

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