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**Supporting information for article:**

# A Soft XAS Transmission Cell for Operando Studies

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## S1. Experimental Section

### S1.1. Chemicals

$MnCl_2 . 4H_2O$ (>99.0%), methylphosphonic acid (99.0-101.0%), NaOH (>98%) and $KNO_3$ (>99.0%) were purchased from Sigma-Aldrich. 0.05 mM Methyphosphate buffer ($MeP_i$, pH8.0) was prepared as in literature (Huynh *et al.*, 2014). $KNO_3$ was added to maintain ~2 M ionic strength of electrolyte. All electrolytes were prepared with DI water (18.6 MΩ.cm).

### S1.2. Electrodeposition of $MnO_x$

All electrochemical experiments for deposition and XAS tests were performed using CHI6016E working station (CHI Instruments) or EmStat3+ (PalmSens) in a three-electrode electrochemical system. All electrode potentials were converted to the NHE scale using E(NHE) = E(Ag/AgCl) + 0.199V. Electrodeposition was carried out at 0.85 V for 40 min without stirring and iR compensation in a freshly prepared nitrogen purged 0.5 mM $Mn^{2+}$ in 0.1 M $MeP_i$ buffer solution (Huynh *et al.*, 2014). A brown yellowish film was formed. After the catalyst deposition the coated $Si_3N_4$/Au membrane was rinsed with DI water.

### S1.3. In operando XAS measurements

In-operando electrochemical X-ray absorption measurements in transmission mode were performed with a new developed transmission electrochemical flowcell attached to the LiXEdrom 2.0 endstation at the U56-2 PGM2 beamline at Bessy II. XAS spectra were collected at several locations on the sample to ensure that the recorded spectra are representative of the sample. Energy calibration was performed with the 640.3 eV peak using the MnO powder spectra obtained by us and from literature (Khan *et al.*, 2015). Each Mn L-edge scan takes around 5 min. We averaged 4-9 scans to enhance the signal-to-noise ratio. The spectra were normalized by subtracting the background, integrating the area of both, $L_3$ and $L_2$ edge, and dividing the spectra by that area.

### S1.4. Spectra fitting

The experimental spectra were fitted with the linear combination fitting method by employing the Igor Pro program package. The percentage values were calculated as below:

Fitted spectrum = a*MnO + b* $Mn_2O_3$ + c* $MnO_2$

The percentage of each manganese oxide is obtained by MnO = a /(a + b + c), $Mn_2O_3$ = b /(a + b + c), etc. The Chi square value is used to evaluate the fitting quality, while the error bars in the figures are used to show the standard deviation.

### S1.5. Deposited dose

The dose D was calculated as reported by Leontowich et al.(Leontowich *et al.*, 2012):

$$D = \frac{F_{SA} \cdot E}{V\rho} \cdot t = Dr \cdot t$$

Where D is the dose in Grays (Gy = J $kg^{-1}$); Dr is the dose rate; $F_{SA}$ is the photon flux absorbed in the irradiated sample volume ($s^{-1}$), t is the irradiation time, E is the energy of a photon, V is the irradiated sample volume and ρ is the density of the sample.

We estimate the photon flux $F_{SA}$ before the sample, after the liquid layer, from the transmission current $I_T$ (Ampere) at the GaAsP photodiode:

$$I_T = e \cdot \xi \cdot F_S \cdot e^{-\mu d} \cdot e^{-\mu_{Au} d_{Au}} \cdot e^{-\mu_{SiN} d_{SiN}}$$

where e is the elementary charge, ξ is the quantum efficiency of the GaAsP photodiode and the three exponential factors account for absorption in the sample, the Au coating and the $Si_3N_4$ membrane with the respective thicknesses d, $d_{Au}$, $d_{SiN}$ and absorption coefficients μ, $\mu_{Au}$ and $\mu_{SiN}$. The photon flux absorbed in the sample is than given by

$$F_{SA} = F_S \cdot \ (1 - e^{-\mu d})$$

We find that if no liquid layer is present, a dose of 11.7 MGy is accumulated with each scan (5 minutes). For the liquid layer thickness employed during the measurements, a dose of 0.26 MGy was deposited during one scan.

**Table S1** Table S1. Details for the calculation of the dose deposited per scan in a $MnO_x$ film, with or without liquid layer present.

| | | With liquid | Without liquid | Unit | Remark |
|---|---|---|---|---|---|
| Transmission current | IT | 2 | 90 | nA | current at 635 eV (below Mn $L_3$-edge) |
| Typical attenuation length of MnOx | λ | 200 | 200 | nm | see (Ruosi *et al.*, 2014) |
| density | ρ | 3.3 | 3.3 | g / cm3 | density of $Mn(OH)_2$ |
| duration of exposure | t | 5 | 5 | min | duration of one scan |
| sample thickness | d | 200 | 200 | nm | determined by coulometry |
| illuminated area width | w | 900 | 900 | µm | beamline parameter |
| illuminated area height | h | 100 | 100 | µm | beamline parameter |
| photon energy | E | 640 | 640 | eV | below Mn $L_3$-edge |
| Au thickness | dAu | 20 | 20 | nm | working electrode contact |
| Au attenuation length (@640 eV) | λAu | 5.08E-02 | 5.08E-02 | µm | See http://www.cxro.lbl.gov/ |
| $Si_3N_4$ thickness | dSiN | 100 | 100 | nm | substrate |
| $Si_3N_4$ attenuation length (@640 eV) | λSiN | 0.38 | 0.38 | µm | See http://www.cxro.lbl.gov/ |
| | | | | | |
| GaAsP Quantum Efficiency (@640 eV) | ξ | 100 | 100 | | see (Krumrey & Tegeler, 1992) |
| photon flux at diode | FT | 1.25E+08 | 5.62E+09 | 1/s | =IT/ [e*ξ] |
| photon flux before sample | FS | 7.95E+08 | 3.58E+10 | 1/s | =IT/ [e*ξ*exp(-dAu/λAu)*exp(-dSiN/λSiN)*exp(-d/λ)] |
| photon flux absorbed in sample | FSA | 5.03E+08 | 2.26E+10 | 1/s | =FS* [1-exp(-d/λ)] |
| photon flux per area before sample | GS | 6.94E+09 | 3.12E+11 | 1/(s*mm2) | =FS/(w*h*π/4) |
| illuminated mass | m | 4.67E-11 | 4.67E-11 | kg | =w*h*π/4*d*ρ |
| dose rate | Dr | 0.0009 | 0.039 | MGy/s | =FSA*E/(w*h*π/4*d*ρ) |
| dose | D | 0.260 | 11.7 | MGy | =FSA*E/(w*h*π/4*d*ρ)*t |

**Figure S1** Schematic illustration (3D-model) of translational and angular part for positioning of the cell. X-ray photons enter from the lower left side through the translational part, through the angular part and then enter the transmission cell. The translational part allows precise positioning of the cell with a first bellow and a x-y stage. The angular part is attached to this and consists of a second bellow and three micrometer screws that control the rotation of the cell. The first flange of the bellow of the translational part and several components of the cell are not shown.

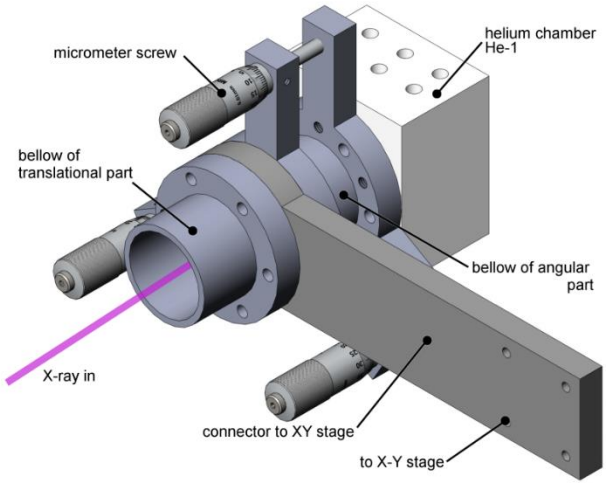



**Figure S2** Schematic illustration of cap which holds the pair of membranes for fast replacement of membranes. The part which prevents rotation of the membranes is shown in red.

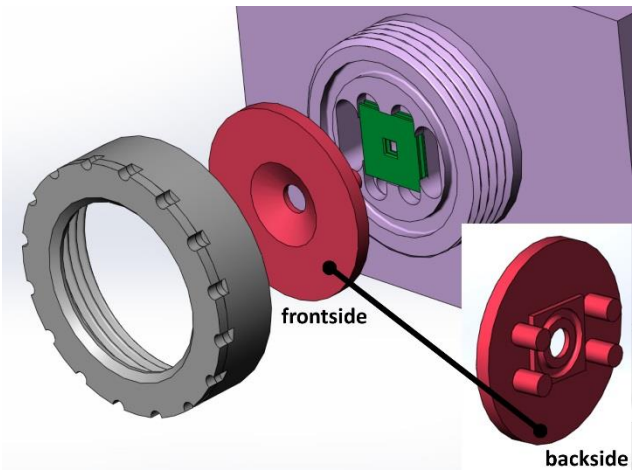
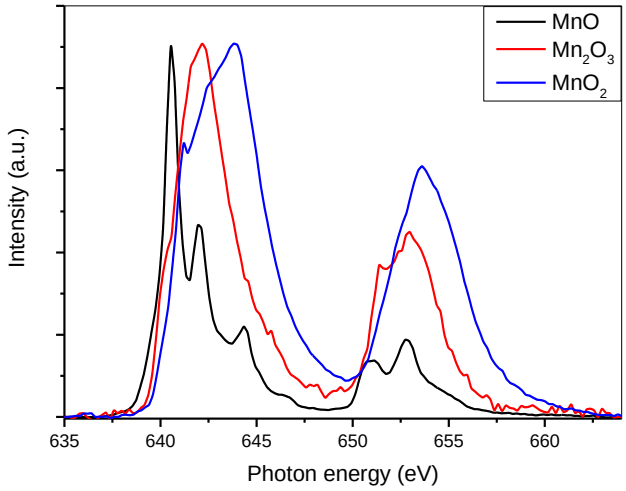


**Figure S3** Mn L-edge XA spectra of the reference manganese oxide powders (Huynh *et al.*, 2014). All spectra are normalized to their respective background. The spectra were recorded in total electron yield (TEY) mode.




### Supporting References

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