

Supporting Information for

Evaporated manganese films as a starting point for the preparation of thin-layer MnO_x water-oxidation anodes

Carolin E. Frey,^{a,§} Frances Kwok,^{b,§} Diego Gonzáles Flores,^c Jonas
Ohms,^a Kayla A. Cooley,^b Holger Dau,^c Ivelina Zaharieva,^{c,*} Timothy N.
Walter,^b Hamed Simchi,^b Suzanne E. Mohney^{b,*} and Philipp Kurz^{a,*}

^a *Institut für Anorganische und Analytische Chemie and
Freiburger Materialforschungszentrum (FMF), Albert-Ludwigs-Universität Freiburg,
Albertstraße 21, 79104 Freiburg, Germany.
E-mail: philipp.kurz@ac.uni-freiburg.de*

^b *Materials Research Institute, The Pennsylvania State University,
N209 Millennium Science Complex, University Park, PA 16802, USA.
E-mail: mohney@ems.psu.edu*

^c *Fachbereich Physik, Freie Universität Berlin,
Arnimallee 14, 14195 Berlin, Germany.
E-mail: ivelina.zaharieva@physik.fu-berlin.de*

Experimental details and analytical procedures

XRD of In-Sn Solid Solution

Indium forms a solid solution with Sn, where the amount of Sn varies from 0–10 at%. Although In maintains its tetragonal crystal structure, the lattice constants a and c shift based on the amount of Sn present. While a decreases from 0.3253 nm to 0.3234 nm, c increases from 0.495 nm to 0.503 nm over this composition range.¹ The effect of dissolved Sn within the tetragonal crystal structure of In was observed by XRD as shifts from peak positions expected for pure In. Using Bragg's law (Eq. S1) and the equation for interplanar spacings in a tetragonal crystal (Eq. S2), the 2θ peak positions for the In-Sn solid solution with approximately 5% Sn matches our pattern well. Table S1 lists the shifts of the first three peaks for In-Sn (5 at%).

$$n\lambda = 2d\sin(\theta) \text{ (Eq. S1)}$$

$$\frac{1}{d} = \left(\frac{h^2+k^2}{a^2}\right) + \frac{l^2}{c^2} \text{ (Eq. S2)}$$

Table S1.

Plane	In Diffraction Angle (2θ)	In-Sn (Sn: 5 at%) Diffraction Angle (2θ)	Experimental 2θ
(101)	32.95°	32.93°	32.9°
(002)	36.30°	35.92°	35.9°
(110)	39.16°	39.33°	39.4°

Electrochemical measurements: experiment sequence and conversion of electrode potentials.

The electrochemical measurements were carried out in the following sequence for each electrode:

- 1) recording of a *cyclic voltammogram* for the range of 0.83 V to 1.86 V at a scan rate of 20 mV·s⁻¹.
- 2) determination of *Tafel plots* by a staircase-type *chronoamperometry* program in which the potential of the working electrode was increased stepwise in 100mV steps from 1.12 V to 1.92 V and then back again to 1.12 V in the same way. At each step, the potential was kept constant for 5 min (300 s). The values used for i to calculate Tafel plots are the ones measured at the end of each step on the downward staircase. As these tend to be the lowest i values recorded for a specific electrode type and potential using our methodology, this seemed to us the fairest, though probably also “least optimistic” way of determining $\log(i)$ values for Tafel plots.
- 3) next, another *cyclic voltammogram* was recorded as described above (point 1) to monitor possible changes in electrochemical behaviour after the extensive “conditioning” of points 1) and especially 2).

- 4) at last, *long-term electrolyses* were carried out in the same way as described for the Tafel plot measurements, but here a “single-step” *chronoamperometry* trace was recorded keeping the potential constant at $E = 1.15\text{V vs. } E(\text{Ag}/\text{AgCl})$ ($E = 1.77\text{ V vs. RHE}$, $\eta \approx 540\text{ V}$) for the entire electrolysis time of 2 h.

The conversion between the electrode potentials of the reference and the reversible hydrogen electrode was carried out using the equation:

$$E_{\text{RHE}} = E(\text{Ag}/\text{AgCl}) + 0.205\text{ V} + (0.059\text{ V}\cdot\text{pH})$$

All electrochemical measurements were recorded at least two times, in each case starting with a freshly prepared electrode.

Additional Figures

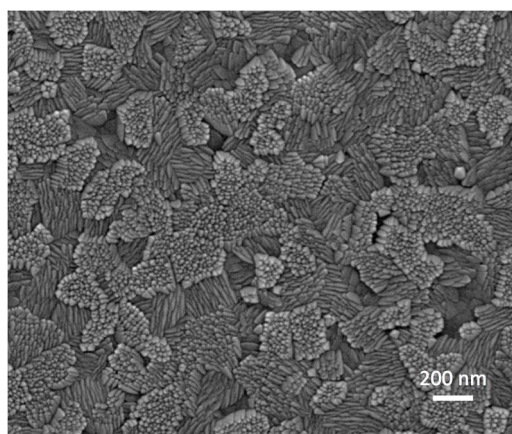


Figure S1. FESEM of the bare ITO/glass substrate, showing the surface morphology responsible for some of the features we see for Mn films deposited on top of this substrate (comp. Fig. 2).

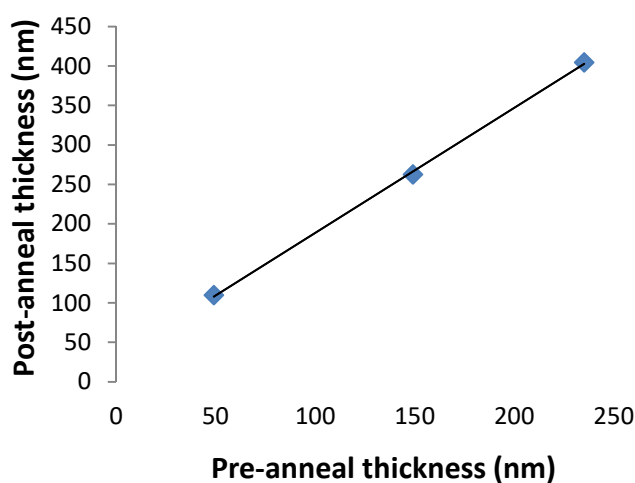


Figure S2. Thickness of the films before and after oxidation, as measured by profilometry.

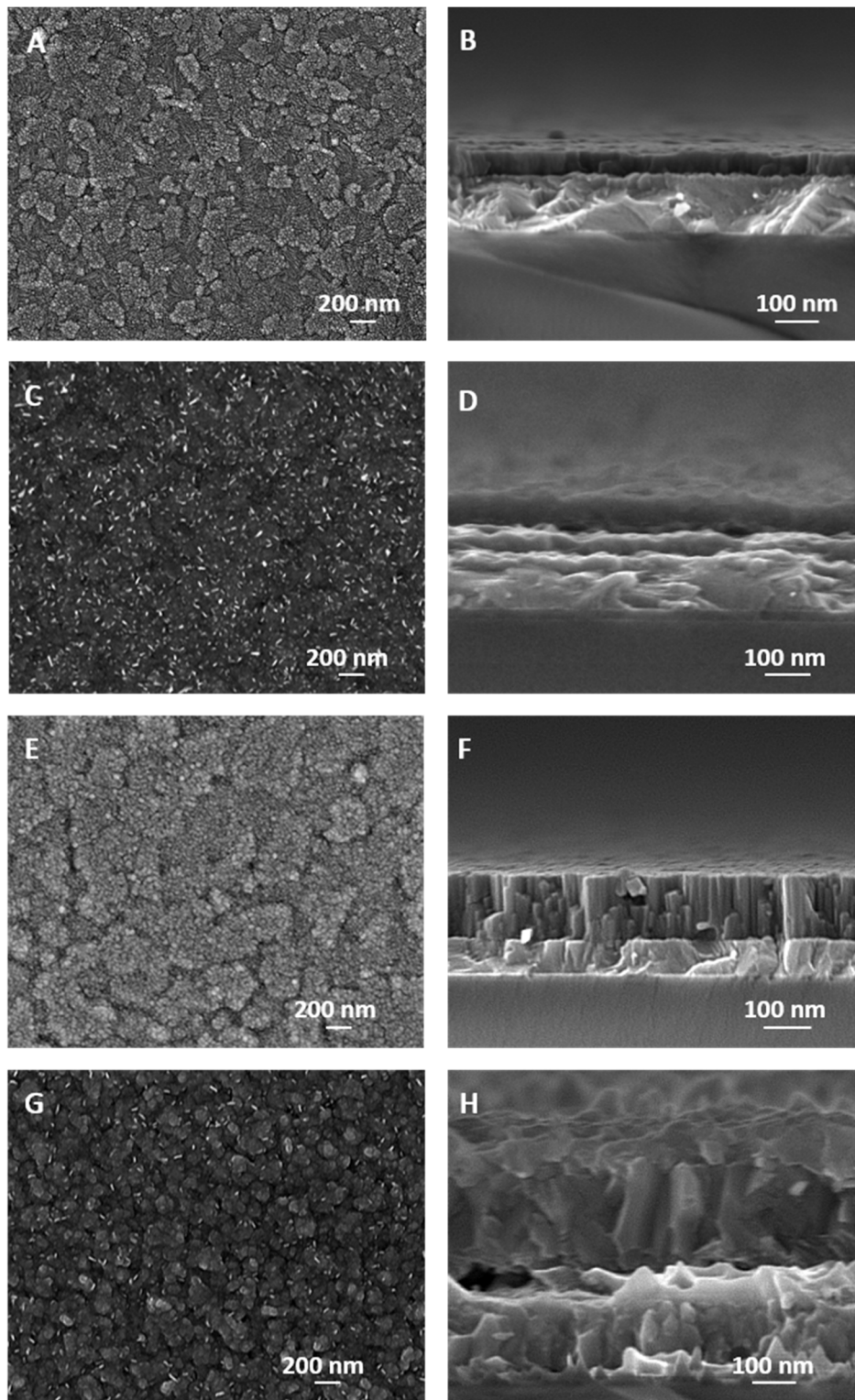


Figure S3. (A) Surface and (B) cross-sectional SEM images of 50 nm thick layers of metallic manganese films prepared by electron-beam evaporation on an ITO-coated glass substrate. Images (C) and (D) show the related micrographs for the MnO_x coating formed from such 50 nm Mn films by annealing in air. Images (E) - (H) show the analogous series starting from 235 nm thick Mn layers.

Thermodynamic calculations concerning the systems In-Mn-O and Sn-Mn-O

Using HSC Chemistry 8,² thermodynamic equilibrium in the In-Mn-O (Sn-Mn-O) ternary systems were calculated for a closed system with starting reactants in a molar ratio of 2:1 In_2O_3 :Mn (SnO_2 :Mn). The solid oxides in the database for In, Mn, and Sn are In_2O_3 , MnO, MnO_2 , Mn_2O_3 , Mn_3O_4 , SnO, and SnO_2 ; and all of these phases were included in the calculations. An inert environment (N_2 gas at 1 atm) was selected to simulate conditions in which oxygen is scarce due to slow kinetics of oxidation. Consistent with our experimental findings, elemental Mn is favored to reduce In_2O_3 (SnO_2), converting Mn to MnO and producing In (Sn), as shown in Figures S4 A and B. In equilibrium with air or O_2 at 1 atm, MnO_2 is still favored to co-exist with In_2O_3 and SnO_2 at 300 °C.

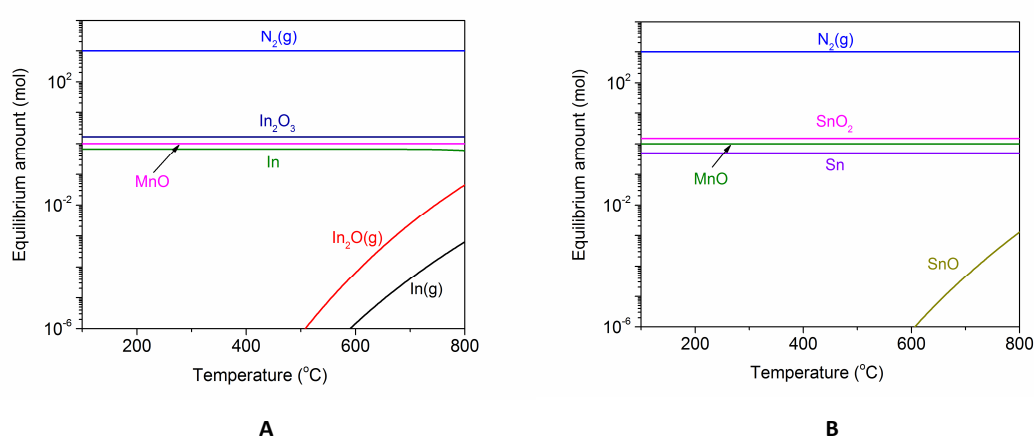


Figure S4. A: Moles of species in equilibrium under 1 atm of N_2 as a function of temperature with starting reactants In_2O_3 and Mn available in a molar ratio of 2:1. **B:** Moles of species in equilibrium under 1 atm of N_2 as a function of temperature with starting reactants SnO_2 and Mn available in a molar ratio of 2:1.

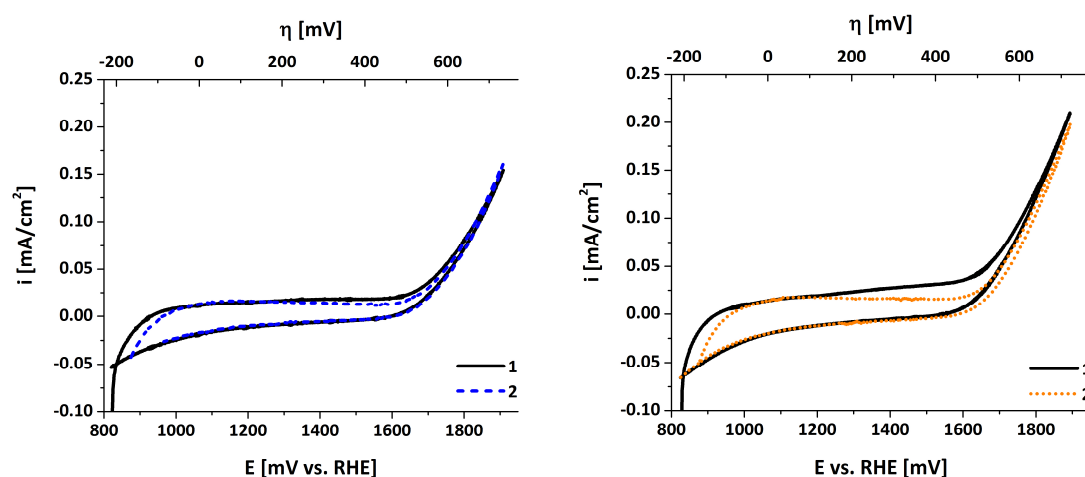


Figure S5. CV scans for annealed “150 nm-” (left) and “250nm-” (right) electrodes in aqueous phosphate buffer (pH 7, overpotential η for water-oxidation indicated at the top). The two curves show data for CVs recorded before (1) and after (2) a “Tafel plot sequence” involving about 30 min of operation at potentials >1.6 V (see ESI for details). Sweep rate: $20 \text{ mV}\cdot\text{s}^{-1}$.

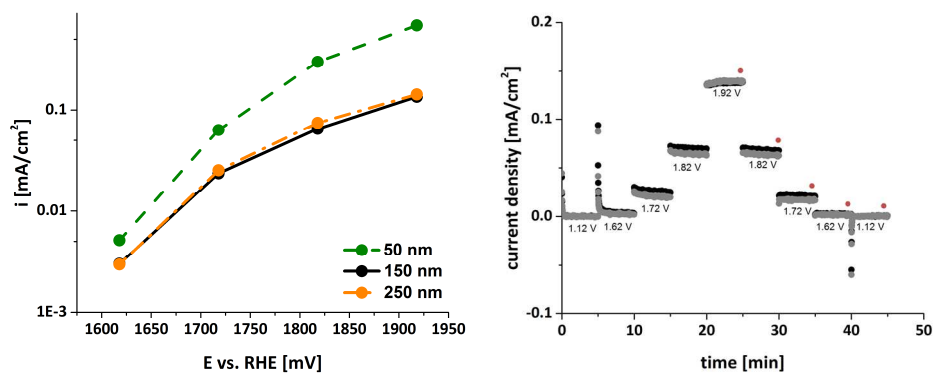


Figure S6. *left:* Tafel plots for air-annealed electrodes of different thickness of initially deposited metallic Mn layer. *right:* Example chronoamperometry trace for a “150 nm-electrode” subjected to the “staircase-program” to obtain data points for the Tafel analysis.

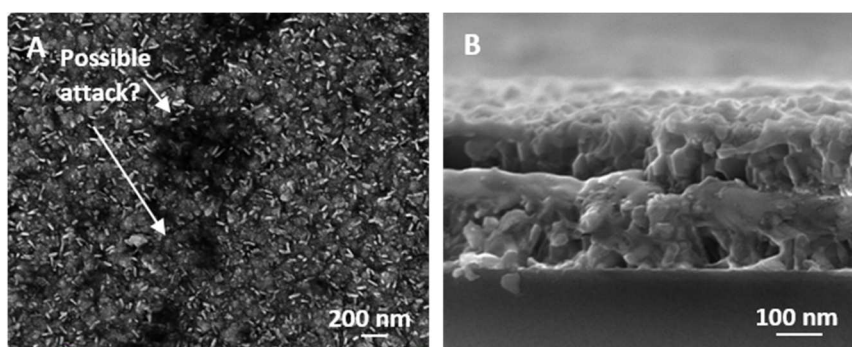


Figure S7. Scanning electron microscopy of the (A) surface and (B) cross-section of the oxidized 150 nm thick Mn film after electrochemical testing.

References

- 1 B. Predel, *Group IV Physical Chemistry 5G*, Landolt-Börnstein, Heidelberg, New York, 1997.
- 2 HSC Chemistry, Version 8, Outotec Oy, Finland, 2014.