Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Surfactant-Mediated Electrodeposition of a Water-Oxidizing Manganese Oxide

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1. Deposition Cyclic Voltammograms

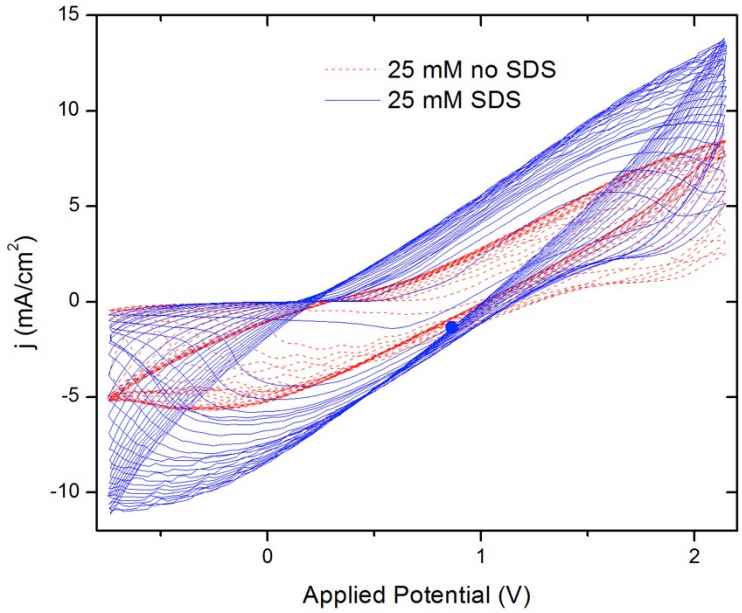

Figure S1. Deposition of 25 mM MnO_2 with and without SDS. Voltage is reported vs. NHE.

2. Control Experiment Without Mn^{2+}

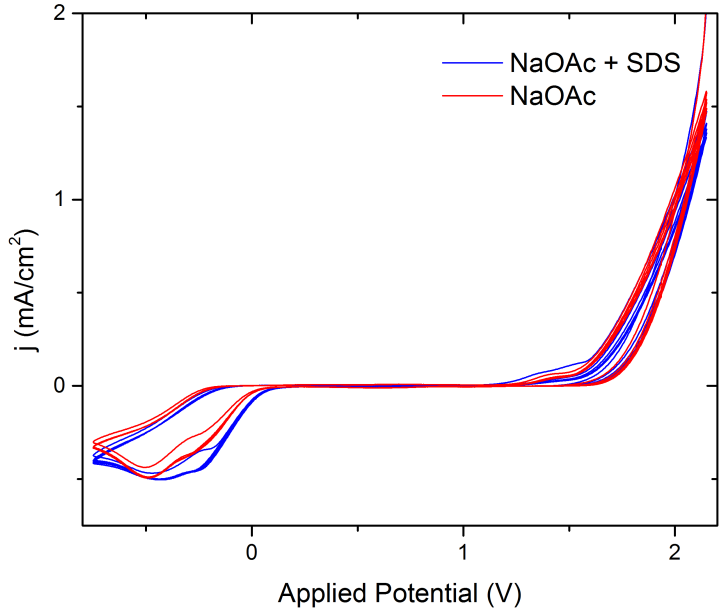

Figure S2. CVs of blank FTO in 25 mM sodium acetate (99.0%, Sigma Aldrich) with and without SDS. Voltage is reported vs. NHE.

3. Electrochemical Stability

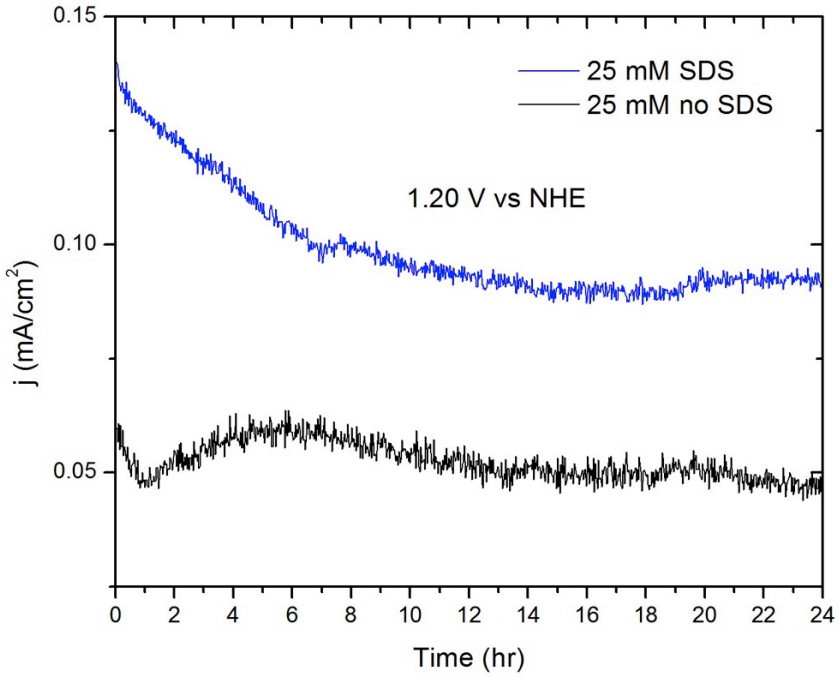

Figure S3. Stability of catalysts with and without SDS.

4. Photograph of Post-Electrolysis Slides With and Without SDS on FTO-coated Glass Electrodes

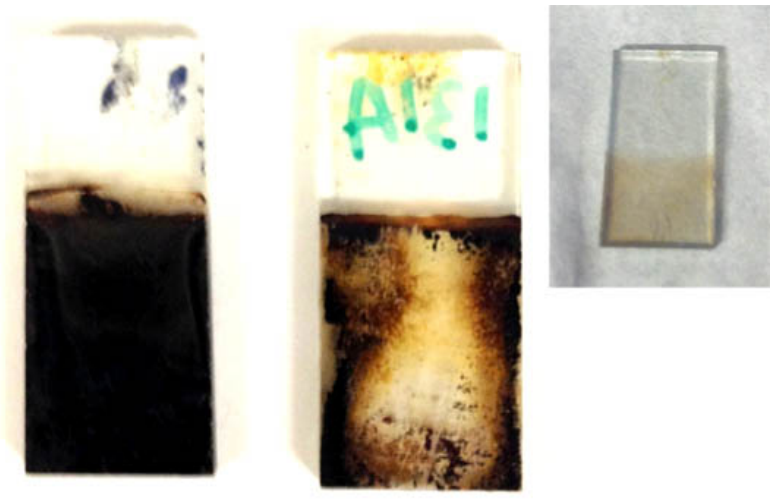

Figure S4. After 24 h of electrolysis, the slide with SDS (left) was visually not affected, while the slide with no SDS (middle) lost a significant amount of material. Right: for comparison, a slide containing a much more transparent film of a manganese oxide water-oxidation catalyst, that was prepared using protocol C from ref. 35 in the manuscript (deposited from 0.5 mM Mn acetate in deionized water), after 24 h of electrolysis.

5. Additional Stability Data

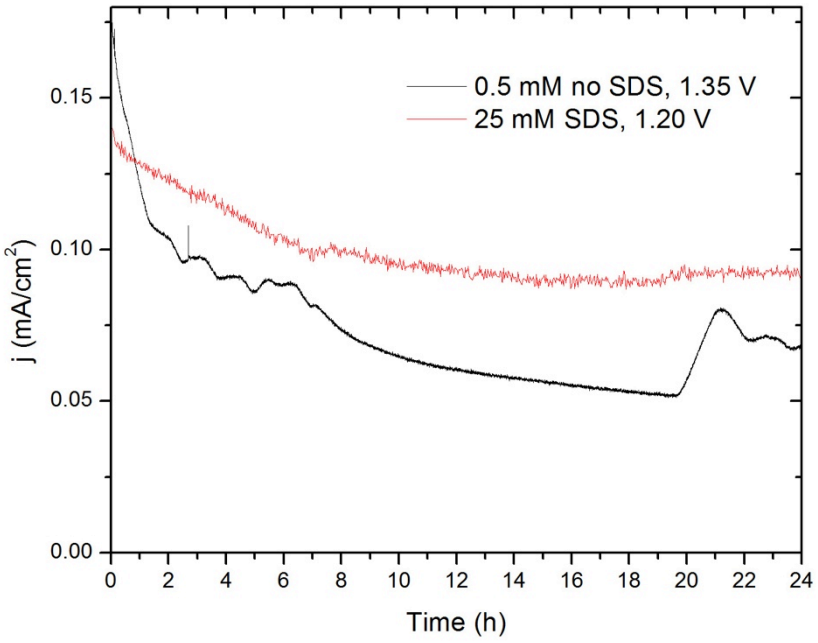

Figure S5. 24 h stability tests comparing the catalyst deposited using conditions from Protocol C in ref. 35 of the manuscript (0.5 mM Mn^{2+}, no SDS, black) at 1.35 V vs. NHE to a sample of 25 mM SDS (red) at 1.20 V vs. NHE.

6. X-ray photoelectron spectroscopy

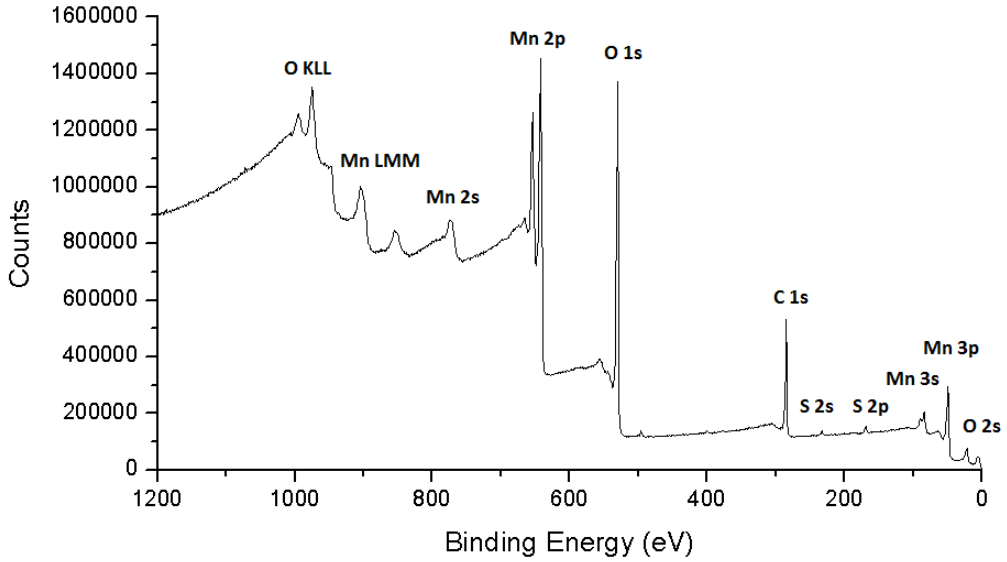

Figure S6. XPS spectrum of a sample with SDS before electrolysis.

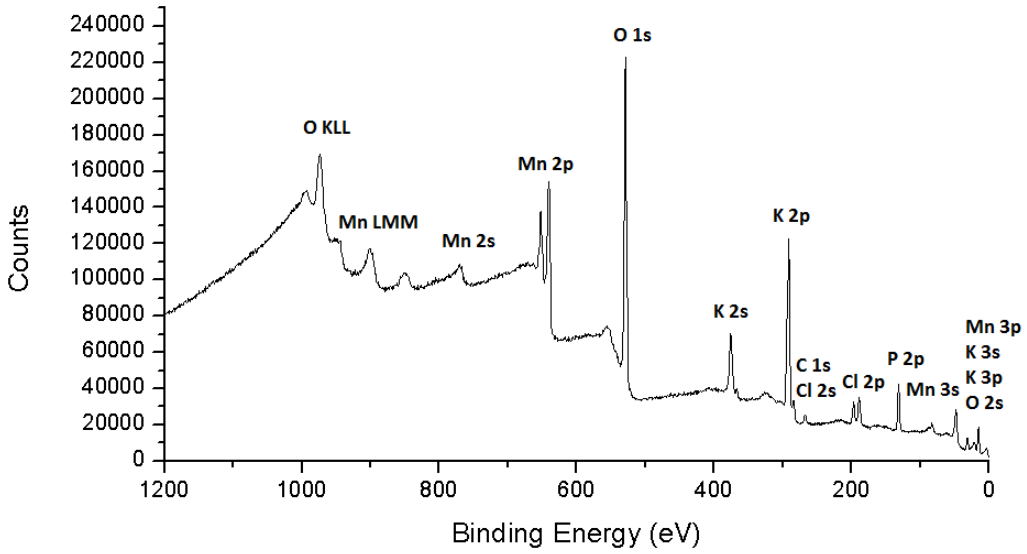

Figure S7. XPS spectrum of a sample with SDS after 24 hours of electrolysis. Phosphorus peak indicates the incorporation of the element from the phosphate buffer as shown in EDX (Figs. S10-S11).

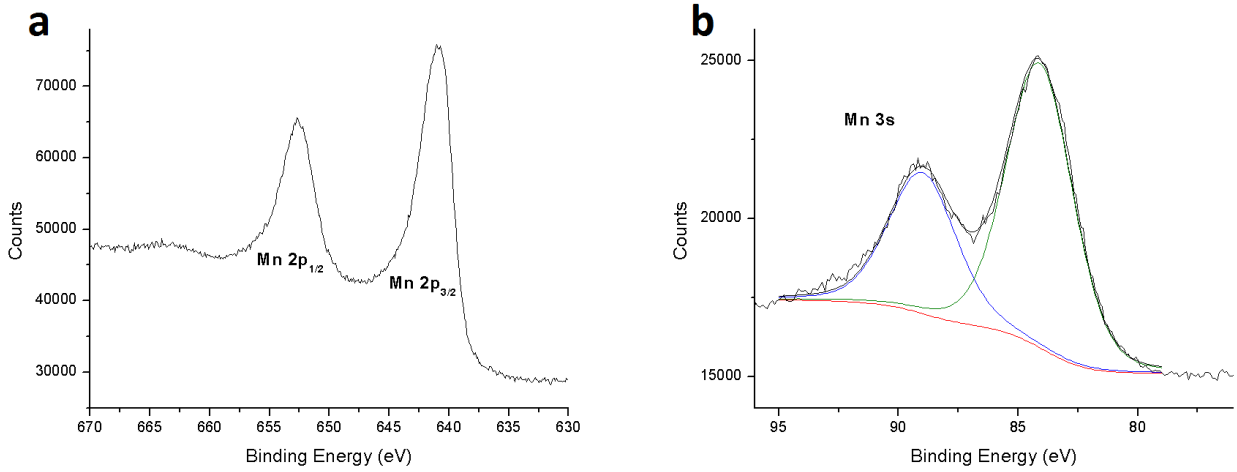

Figure S8. XPS spectra of a sample with SDS after 24 hours of electrolysis. (a) Mn 2p region showing the Mn $2p_{3/2,1/2}$ spin-orbit pair, with the Mn $2p_{3/2}$ multiplet centered near 641 eV. (b) Mn 3s region; the magnitude of peak splitting is a reliable indicator of Mn oxidation state. The energy difference between the multiplets (shown in green and blue, with Shirley background in red) is approximately 4.8 eV, diagnostic of an oxide containing predominantly Mn^{IV}.

7. Additional X-ray Diffraction Data and Fitting

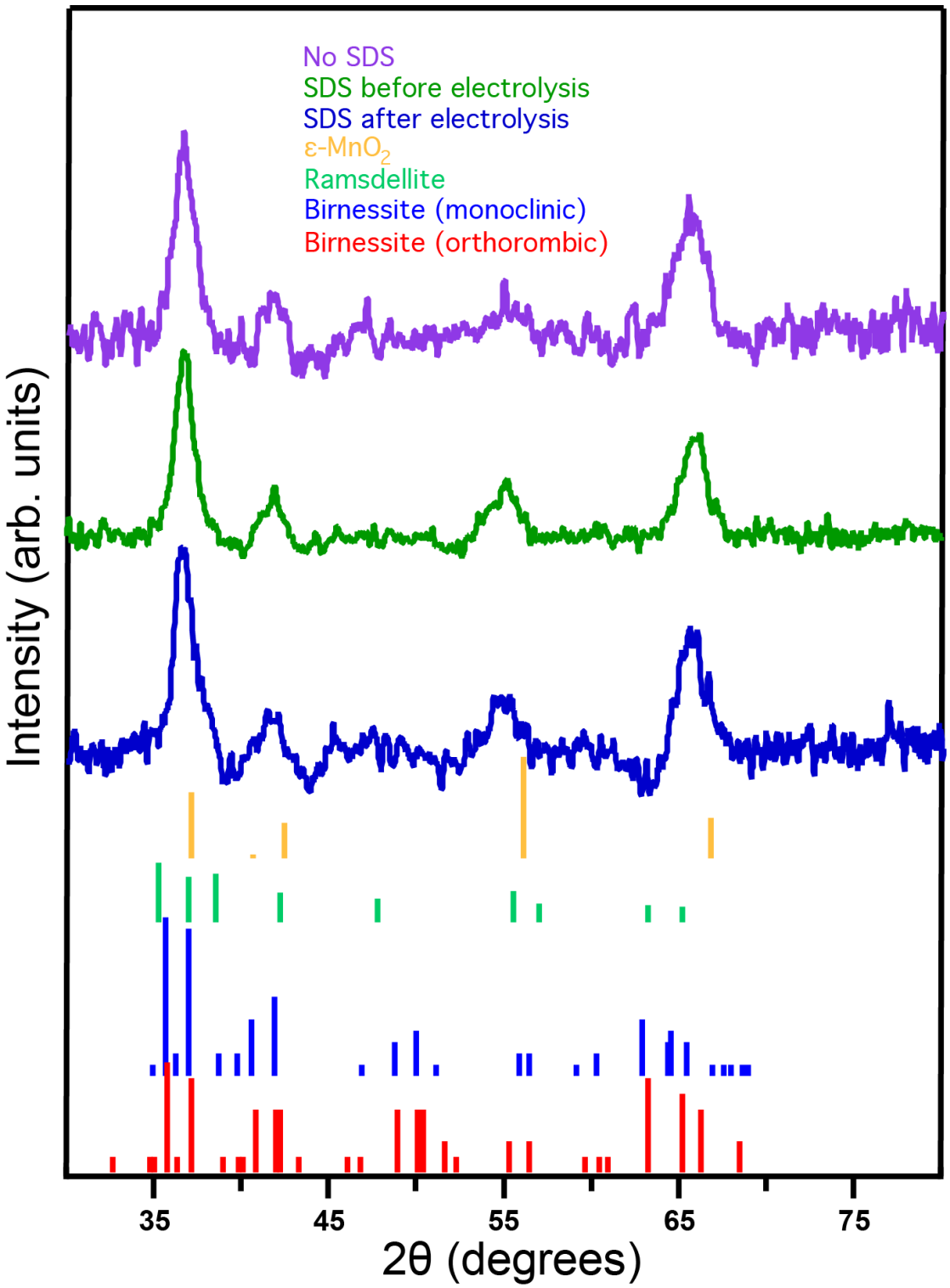

Figure S9. XRD data for 25 mM Mn^{2+} with and without SDS as well as before and after the electrolysis. Vertical bars present peaks of crystal structures from JCPDS database (ε-MnO_2: 30-0820; ramsdellite: 43-1455; monoclinic birnessite: 43-1456; orthorhombic birnessite: 23-1046).

8. Energy-dispersive X-ray Spectroscopy (EDX) Before Electrolysis

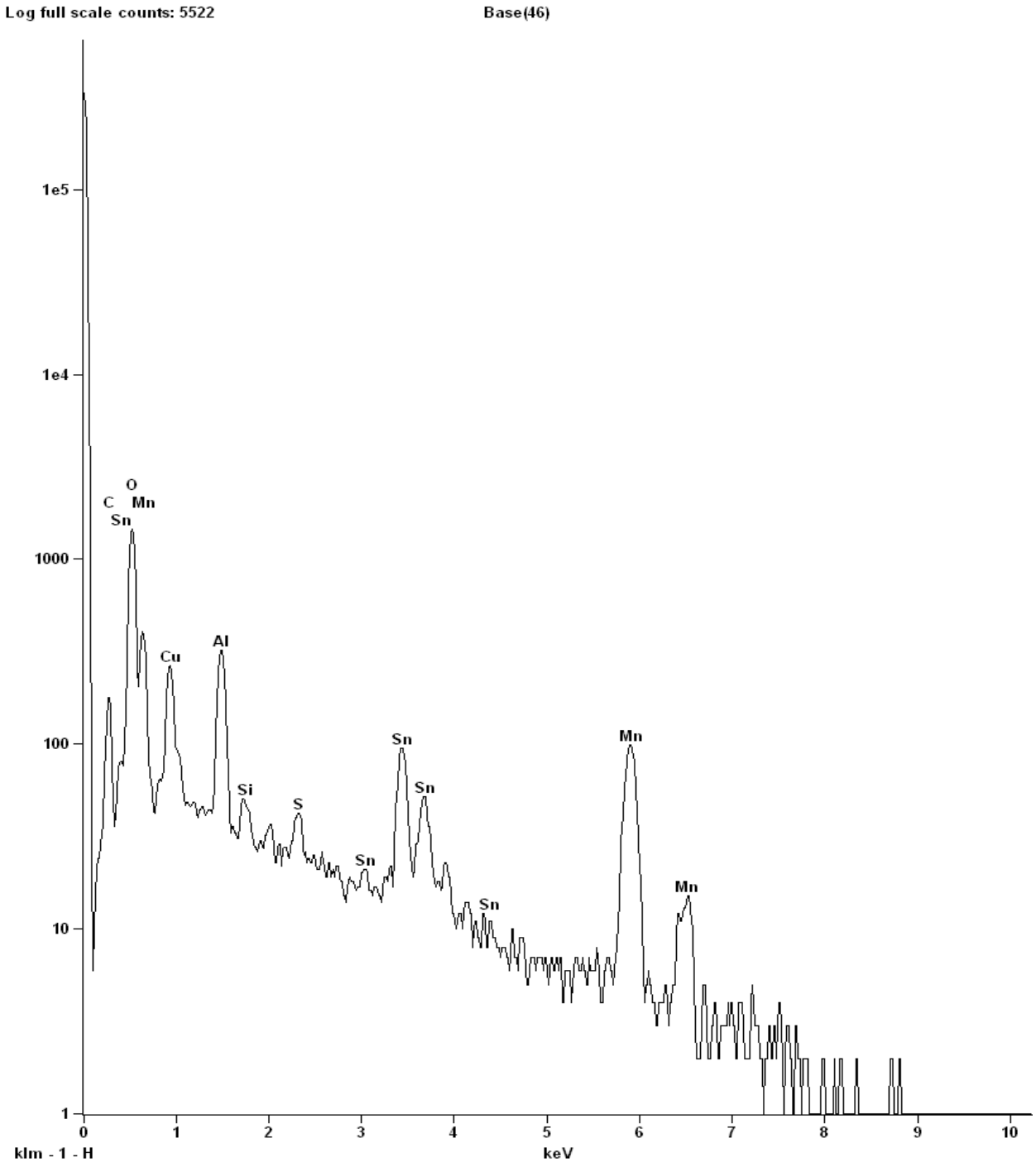

Figure S10. SEM-EDX spectrum of a sample of the Mn catalyst after deposition but prior to any water-oxidation catalysis. S is present due to SDS. Sn, Si, Cu, and Al signals arise from the FTO-coated glass substrate and sample holder.

9. EDX After Electrolysis

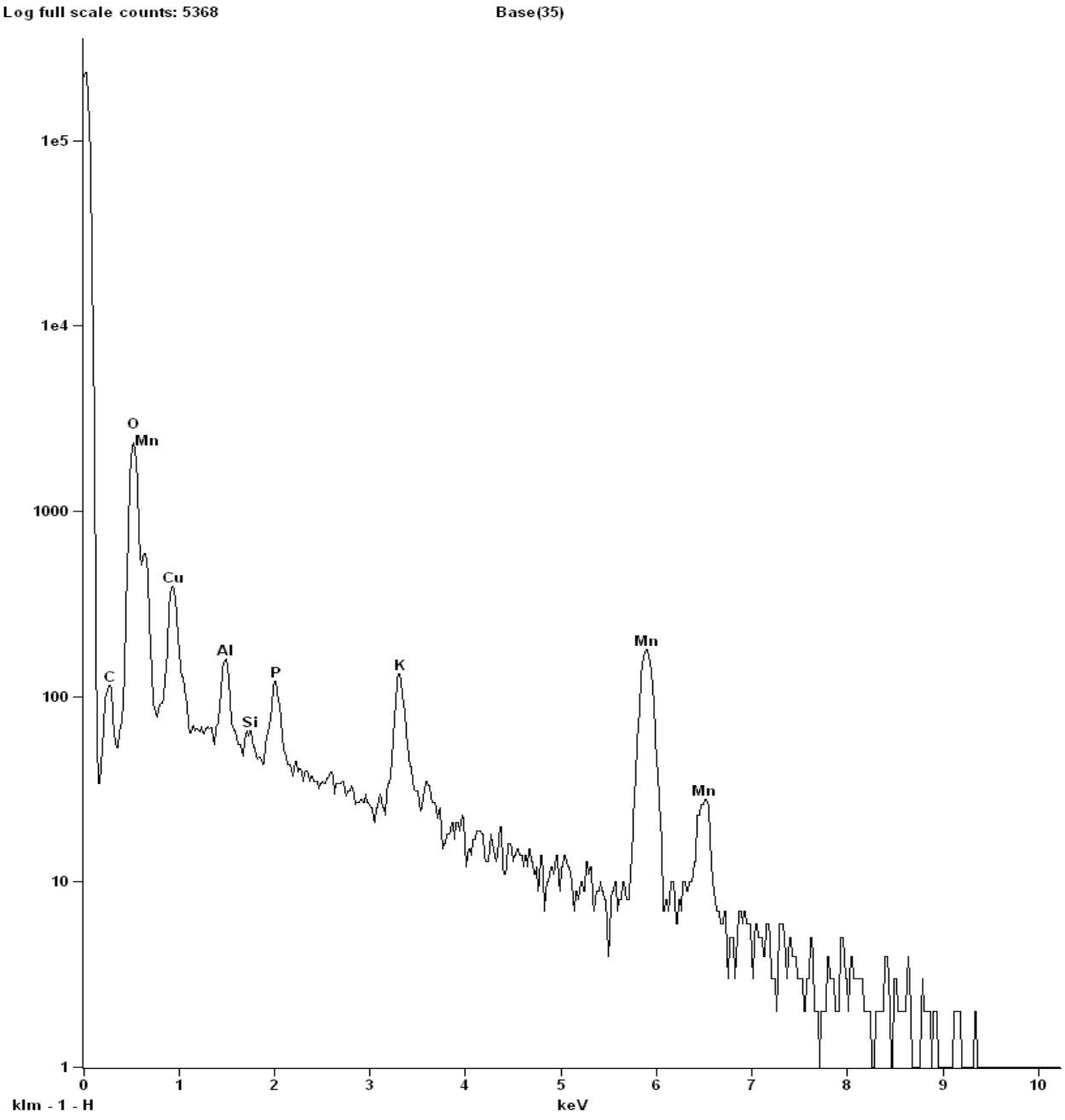

Figure S11. SEM-EDX spectrum of a sample after 24 h of electrolysis. S is no longer present, but K and P have been incorporated into the film. Si, Al, and Cu signals arise from the sample holder.

10. Additional Tafel Plots

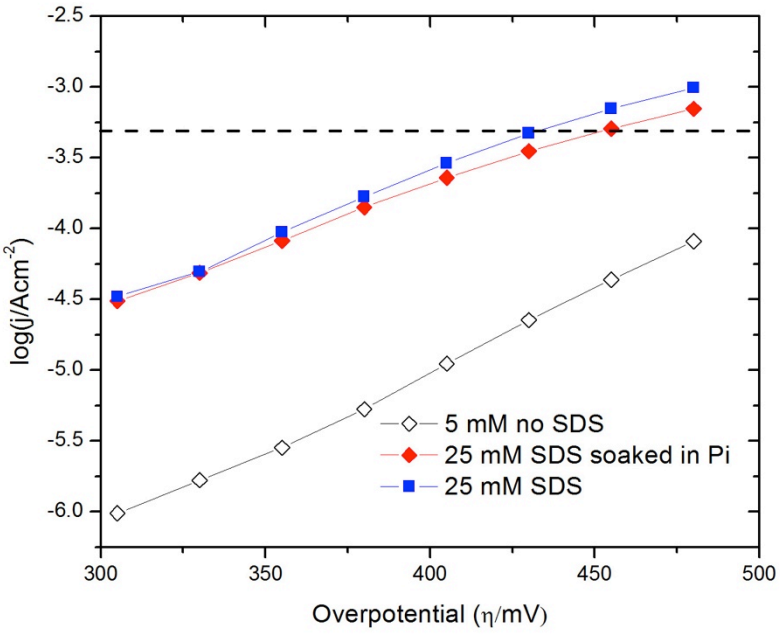

Figure S12. Tafel plots of catalyst deposited with and without SDS, at different concentrations, and with/without 36-hour-long pre-soaking in phosphate. Dashed line marks 0.5 mA/cm^2.