Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Origin of the heat-induced improvement of catalytic activity and stability of MnOx electrocatalysts for water oxidation

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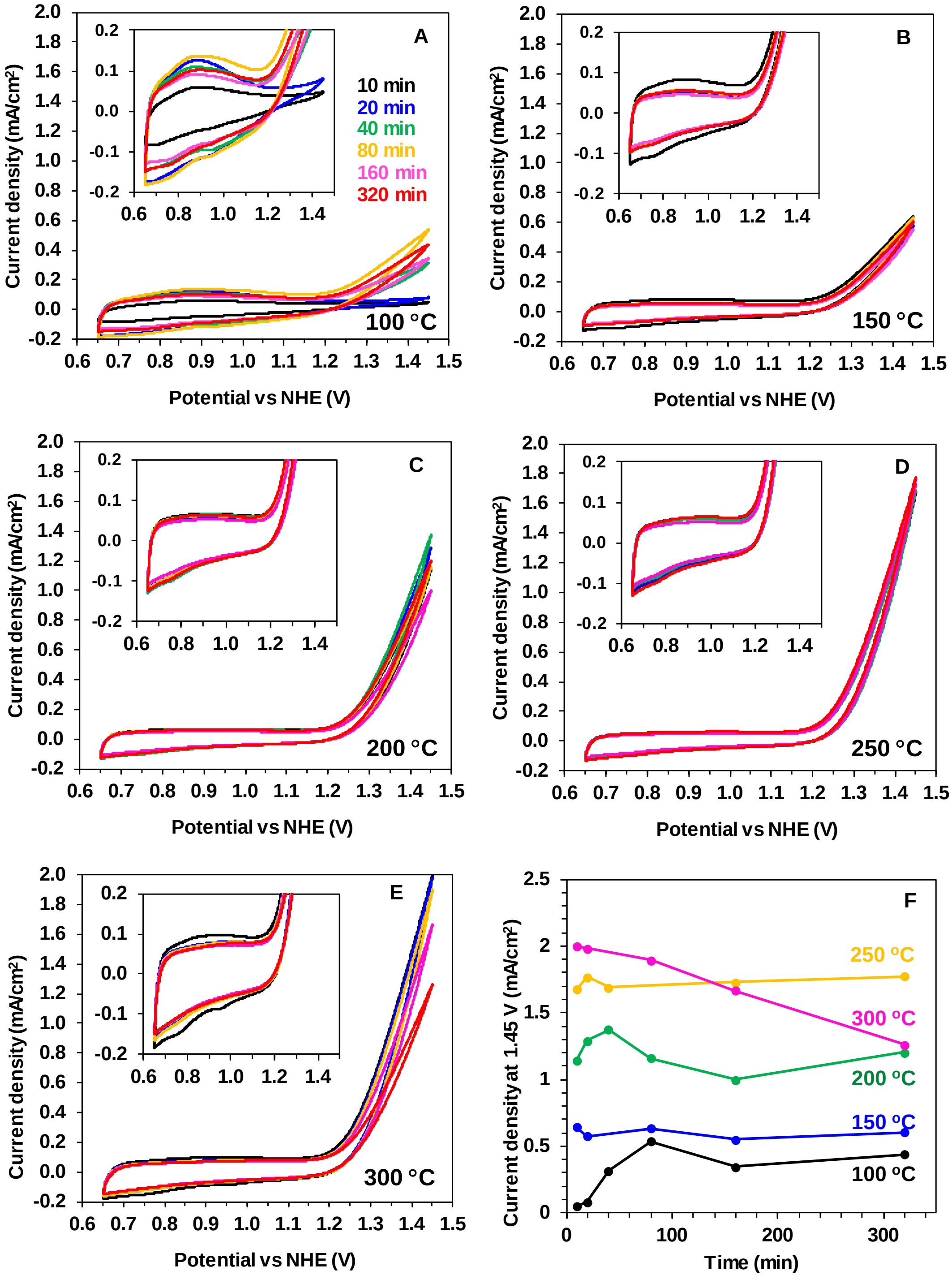

Figure S1. Effect of the heating duration on the catalytic activity of the Oxide **1** deposited at constant potential. **A-E**: CVs with 20 mV/s in 0.1 M KPi, pH 7. **F**: Current density reached at 1.45 V.

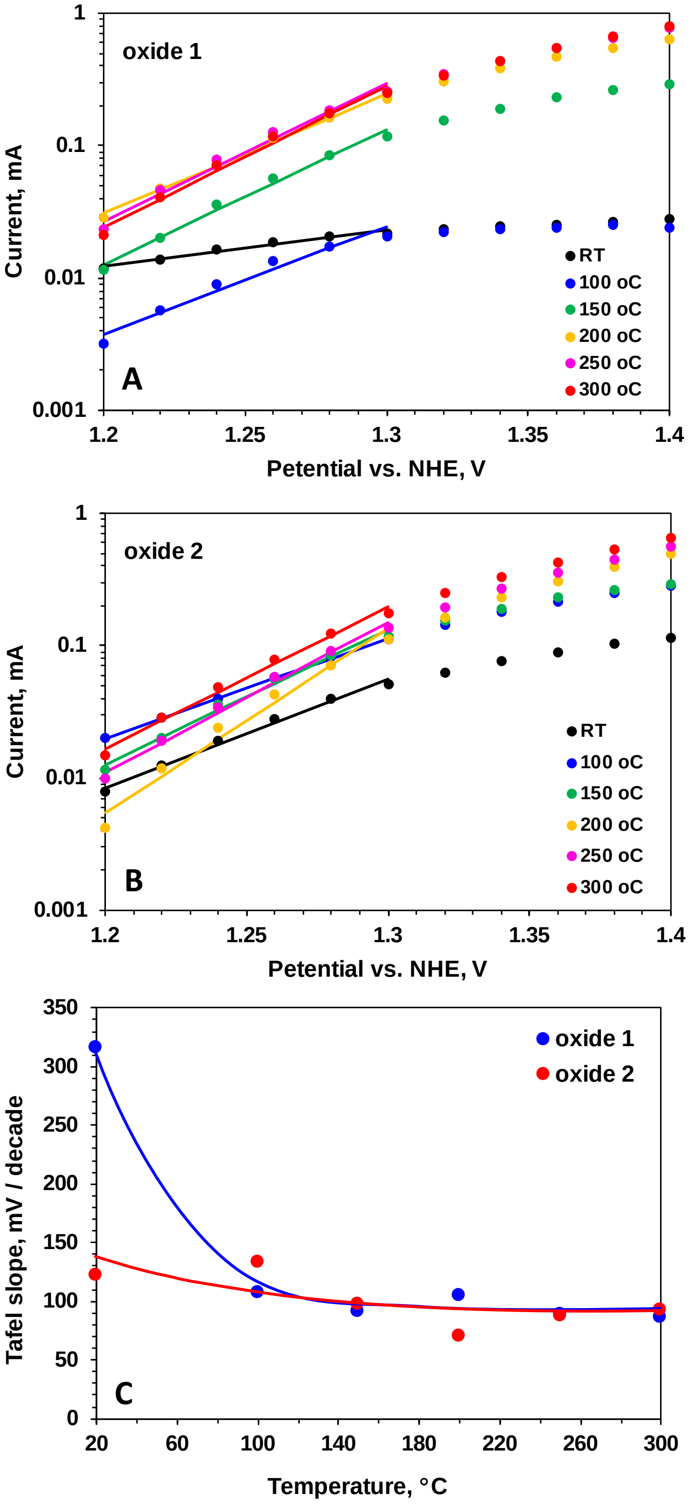

Figure S2. Tafel plots for the Mn oxide deposited at constant potential, Oxide **1** (**A**) and the MnCat, Oxide **2** (**B**) after 20 min heating at different temperatures. The current is measured after 90 s equilibration at the indicated potential. In panel **C** the Tafel slopes calculated for the potential range between 1.2 and 1.3 V are shown. At higher potentials (currents exceeding 100 μA) the diffusion limitations in the non-stirred electrolyte affect the catalytic behaviour.

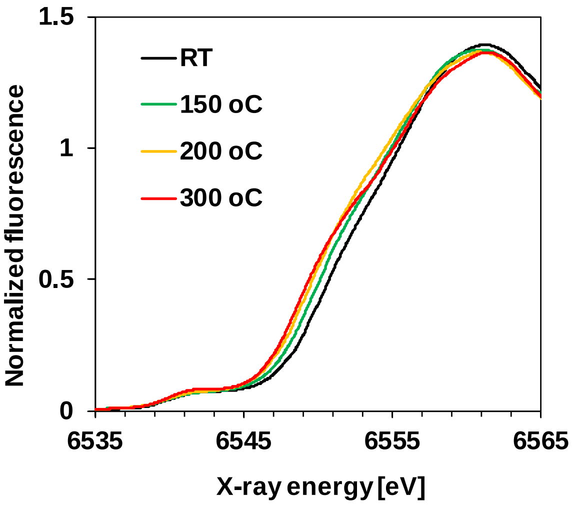

Figure S3. XANES spectra of the Oxide **2**, MnCat, heated to different temperatures. At 300 °C also a change in the edge shape is observed.

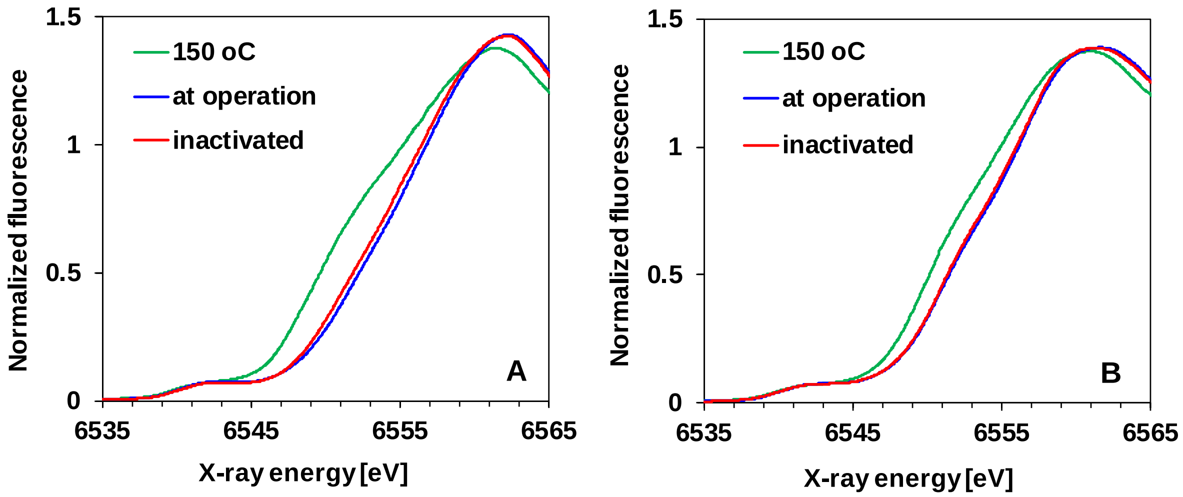

Figure S4. XANES spectra of the Oxide **1** (**A**) and MnCat, Oxide **2** (**B**) after heating to 150 °C (green line), exposure to 1.35 V for 3 min (blue line), or after inactivation via long chronopotentometry with current density 5 mA/cm^2 (red line). The chronopotentiometry curves were similar to those shown in Fig. 2, but the inactivation was faster (10 min for the Oxide **1** and about 3.5 h for the Oxide **2**, and the overpotentials were higher (about 3 V for the Oxide **1** and about 1.5 V for the Oxide **2**).

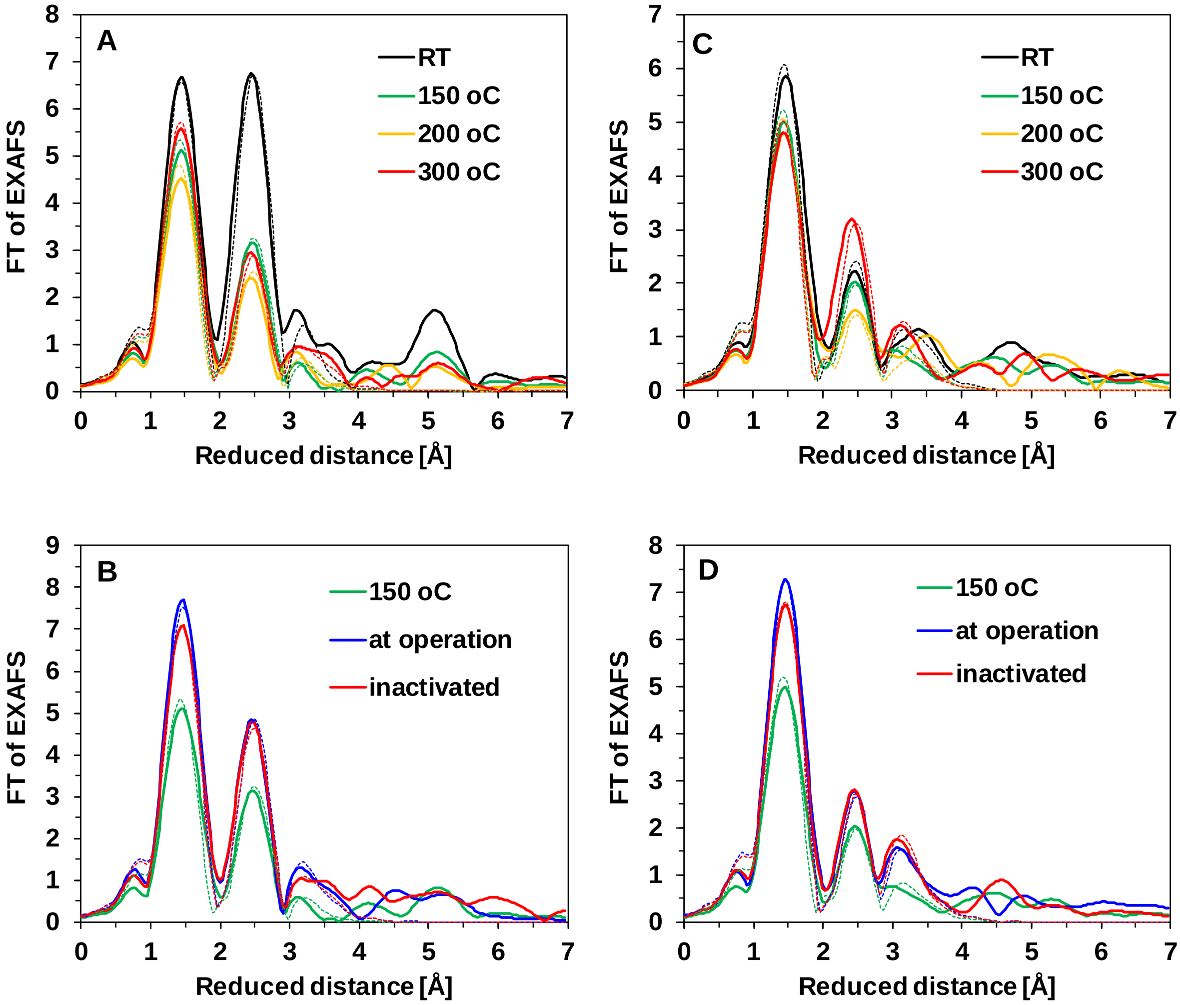

Figure S5. Fourier transformed EXAFS spectra of the Oxide **1** (**A, B**) and MnCat, Oxide **2** (**C, D**) after heating, after exposure to 1.35 V for 3 min (at operation) or after inactivation via long chronopotentometry with current density 5 mA/cm^2 (inactivated). Solid lines represent the experimental data, the dashed lines – simulations. The simulation parameters are shown in Fig. 4 in the main text and in Fig. S6.

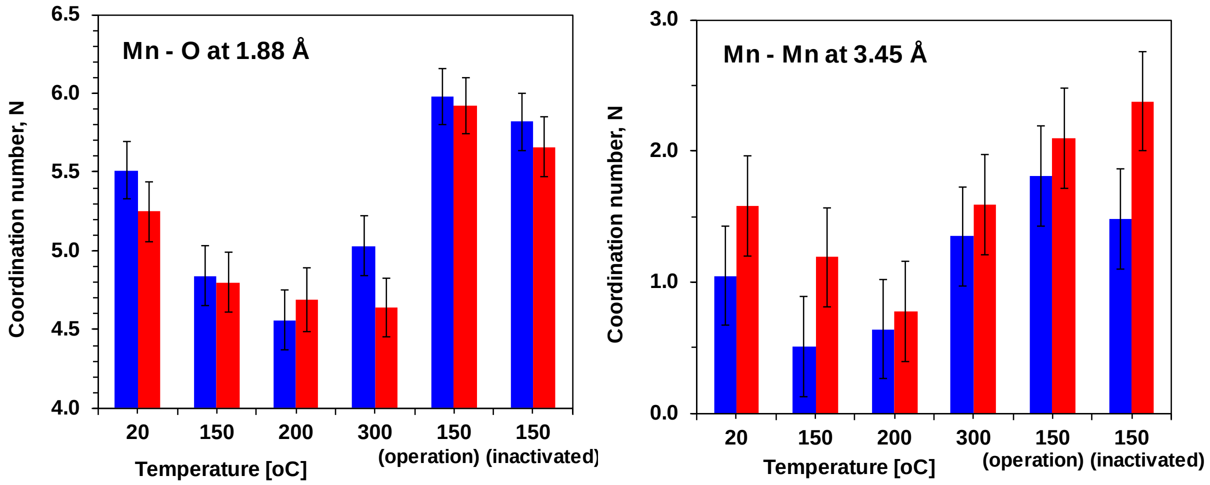

Figure S6. Simulation parameters for the EXAFS spectra of the Oxide **1** (blue bars) and MnCat, Oxide **2** (red bars) after heating, after exposure to 1.35 V for 3 min (operation) or after inactivation via long chronopotentometry with current density 5 mA/cm^2 (inactivated). The Debye-Waller factors for all shells were fixed to 0.063 Å in order to decrease the degrees of freedom and to increase the significance of the obtained fit parameters. The error bars for the coordination numbers shown in the plots correspond to 68% confidence interval. The 68% confidence interval for the interatomic distances is 0.01 Å.

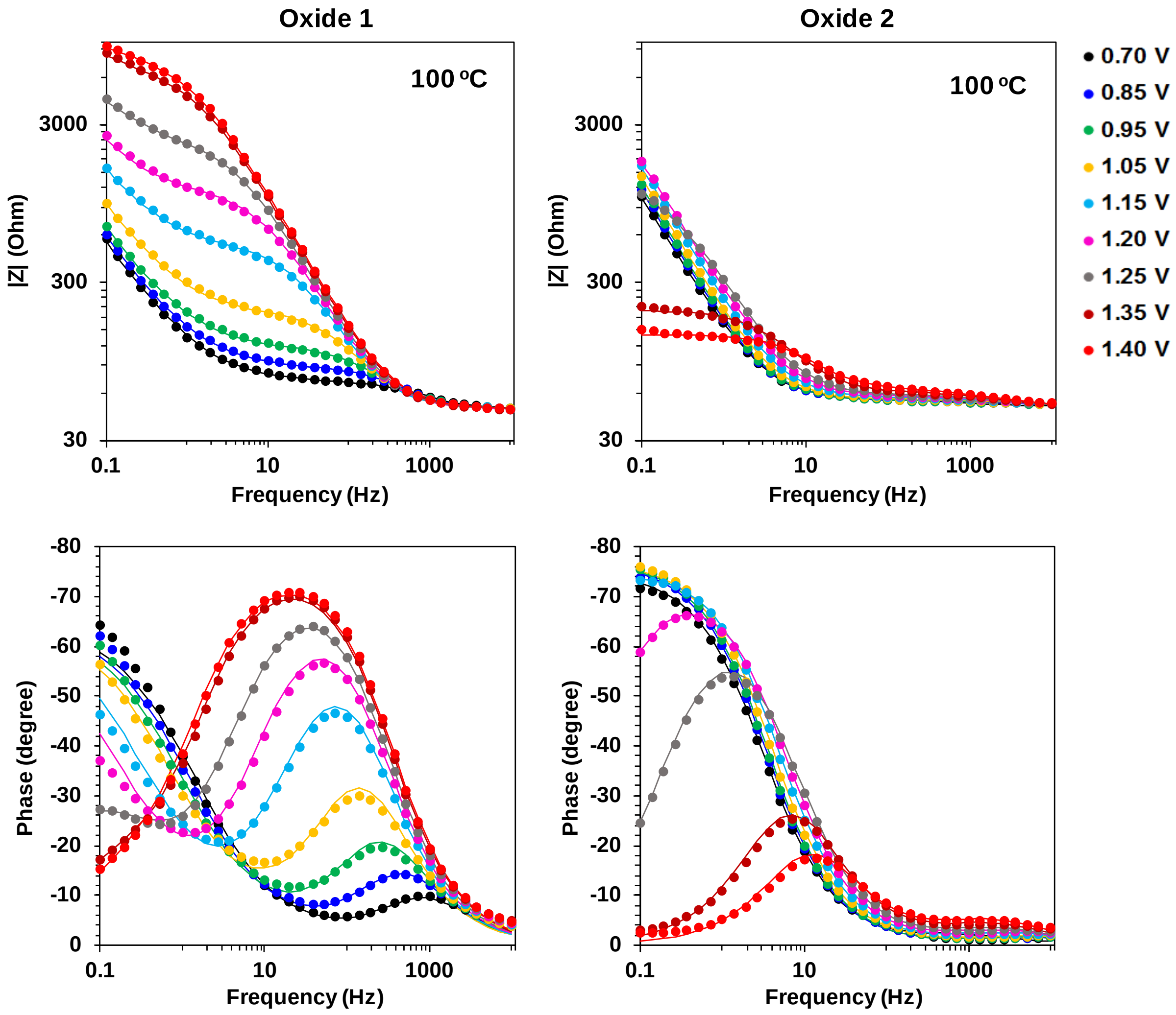

Figure S7. Impedance spectra measured at different potentials after heating of Oxide **1** (left) and Oxide **2** (right) at 100 °C for 20 min. Before the impedance measurements the film was conditioned at the corresponding potential for 60 s. Symbols – experimental data; lines – simulations according to the equivalent circuit shown in Fig. 6B in the main text.

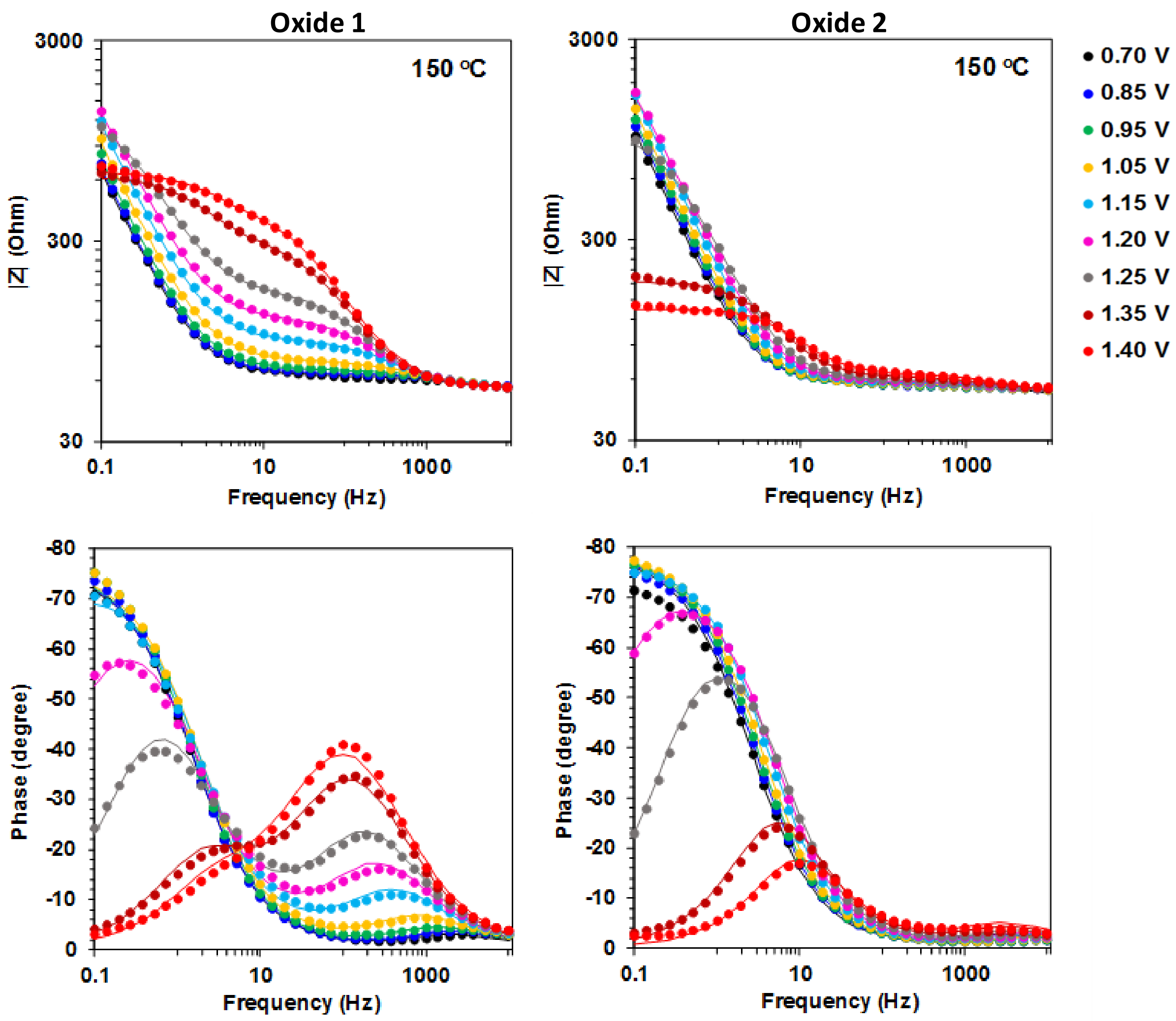

Figure S8. Impedance spectra measured at different potentials after heating of Oxide **1** (left) and Oxide **2** (right) at 150 °C for 20 min. Before the impedance measurements the film was conditioned at the corresponding potential for 60 s. Symbols – experimental data; lines – simulations according to the equivalent circuit shown in Fig. 6B in the main text.

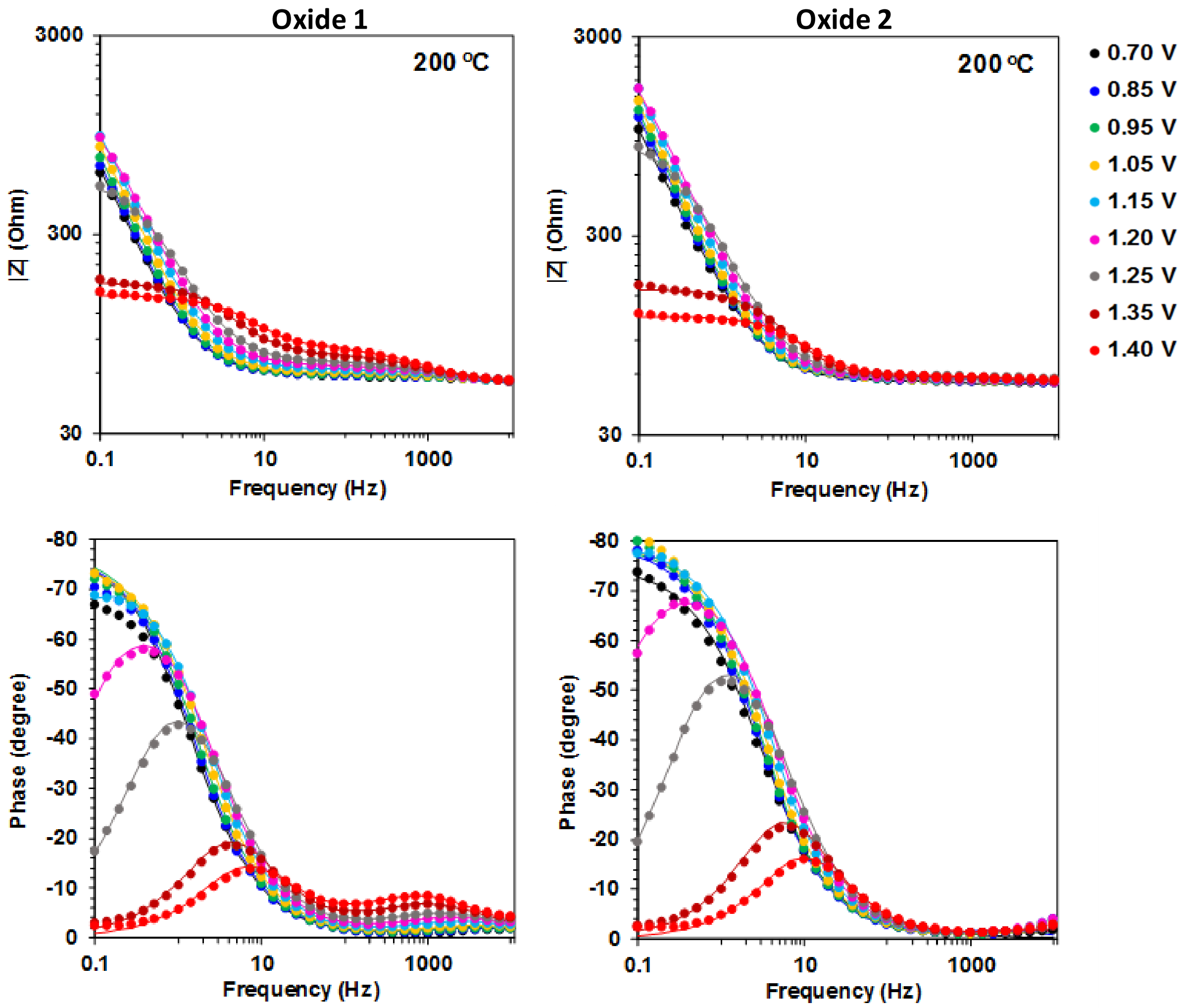

Figure S9. Impedance spectra measured at different potentials after heating of Oxide **1** (left) and Oxide **2** (right) at 200 °C for 20 min. Before the impedance measurements the film was conditioned at the corresponding potential for 60 s. Symbols – experimental data; lines – simulations according to the equivalent circuit shown in Fig. 6B in the main text.

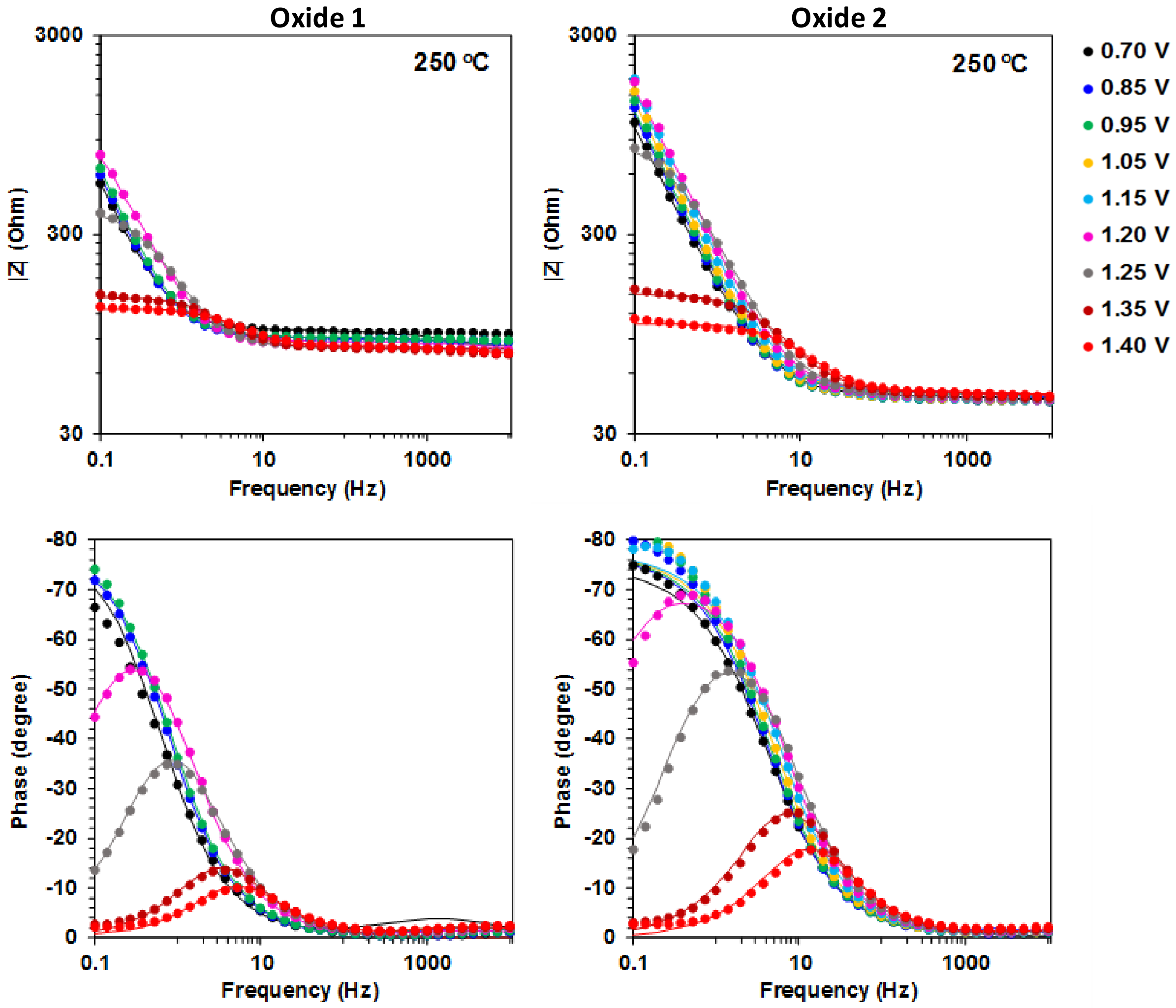

Figure S10. Impedance spectra measured at different potentials after heating of Oxide **1** (left) and Oxide **2** (right) at 250 °C for 20 min. Before the impedance measurements the film was conditioned at the corresponding potential for 60 s. Symbols – experimental data; lines – simulations according to the equivalent circuit shown in Fig. 6B in the main text.

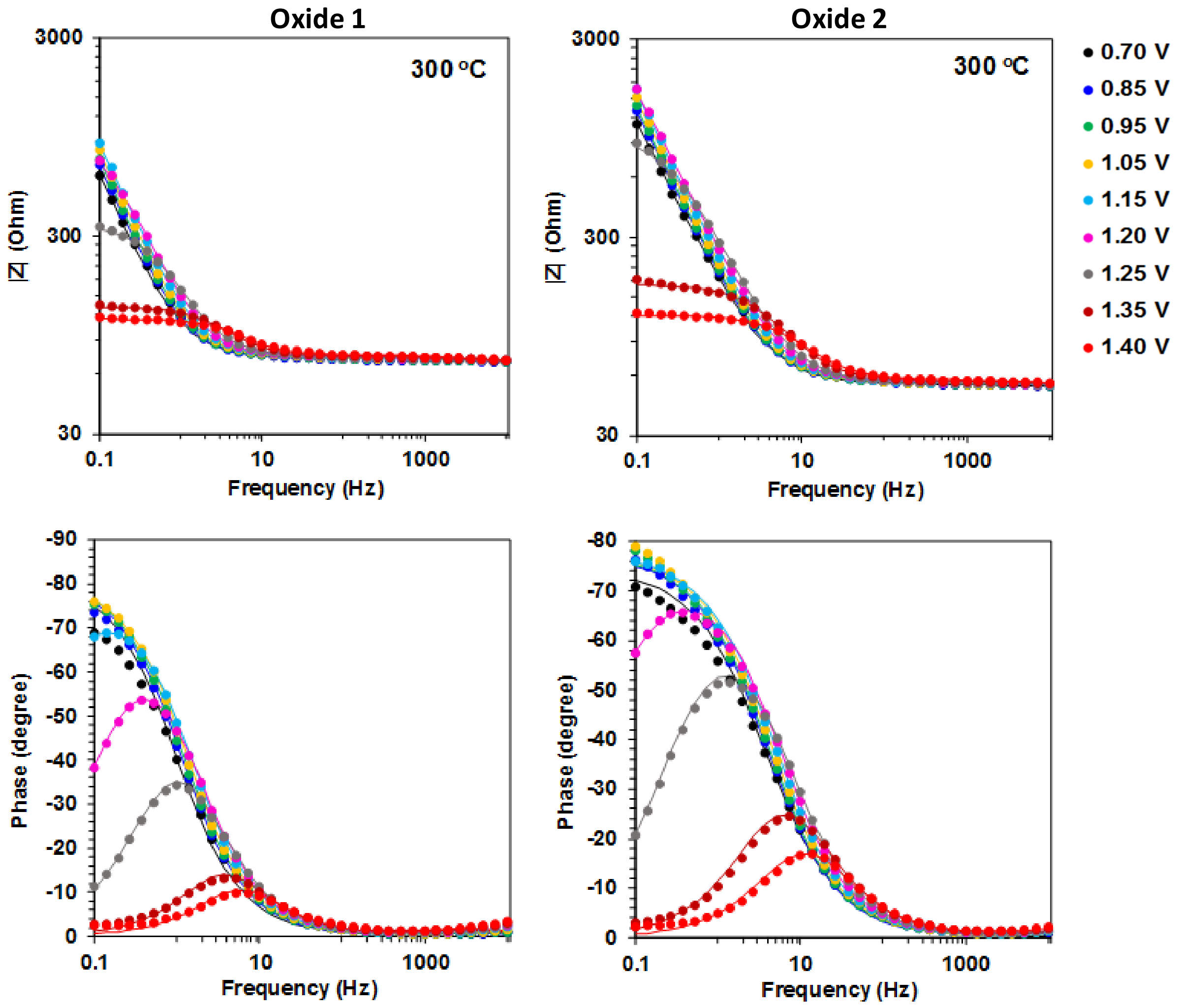

Figure S11. Impedance spectra measured at different potentials after heating of Oxide **1** (left) and Oxide **2** (right) at 300 °C for 20 min. Before the impedance measurements the film was conditioned at the corresponding potential for 60 s. Symbols – experimental data; lines – simulations according to the equivalent circuit shown in Fig. 6B in the main text.

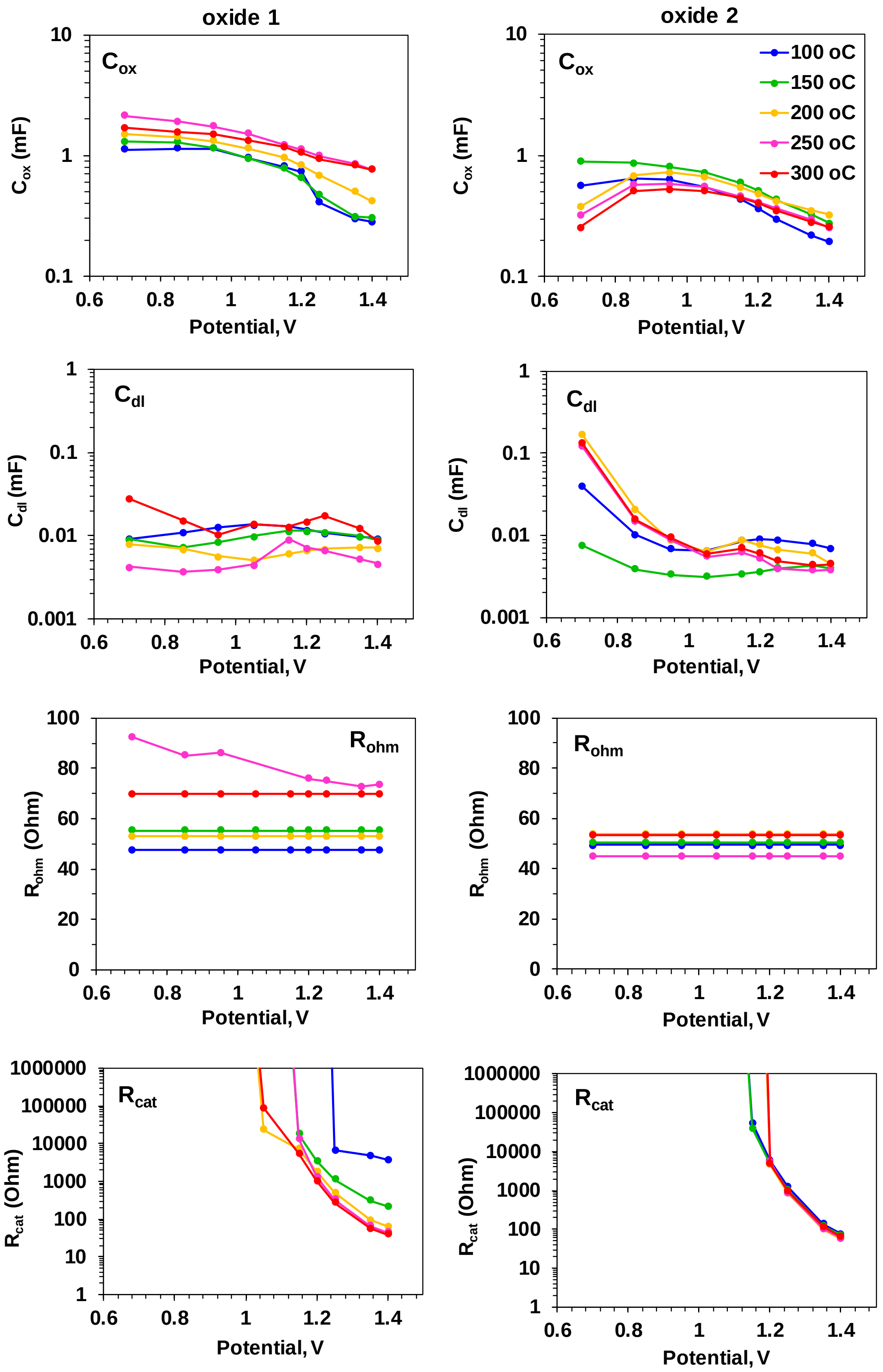

Figure S12. Parameters for the simulation of the impedance spectra according to the equivalent circuit shown in the inset of Fig. 6B in the main text. Left: Oxide **1**; right: Oxide **2** (MnCat). C_{ox} – capacitance describing oxidation state changes of the catalyst film (in other contexts also denoted as pseudo-capacitance), modelled as a constant phase element; C_{dl} – double-layer capacitance, modelled as a constant-phase element; R_{Ohm} – summed Ohmic resistance of electrolyte and ITO electrode; R_{cat} – catalytic resistance of the oxide (charge-transfer resistance).

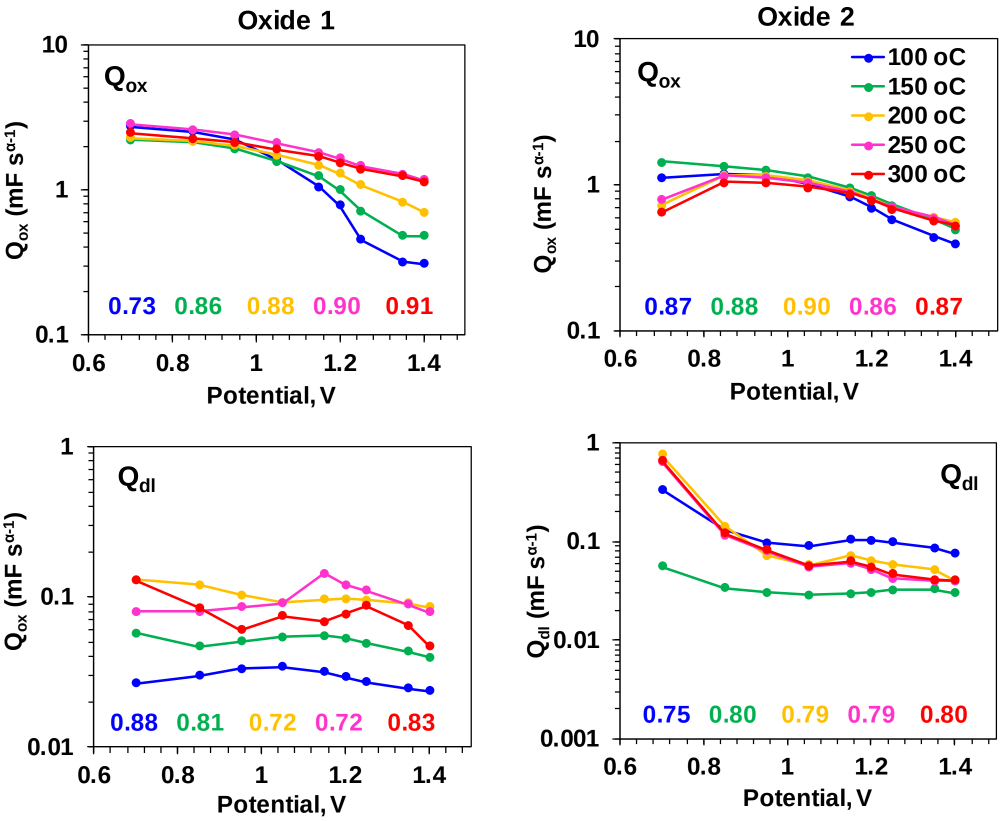

Figure S13. Parameters for the simulation of the constant phase elements according to the equivalent circuit shown in the inset of Fig. 6B in the main text. Left: Oxide 1; right: Oxide 2 (MnCat). The double layer capacitance (C_{dl}) and the oxidation capacitance (C_{ox}) were calculated following the Brug conversion rules (G. J. Brug, A. L. G. van den Eeden, M. Sluyters-Rehbach and J. H. Sluyters, J. Elelectroanal. Chem., 1984, 176, 275-295) according to the equations:

$$C_{ox} = \left[Q_{ox} \left(\frac{1}{R_{ohm} + R_{ox}} + \frac{1}{R_{cat}} \right)^{\alpha - 1} \right]^{1/\alpha}$$

$$C_{dl} = \left[Q_{dl} \left(\frac{1}{R_{ohm}} + \frac{1}{R_{ox}} \right)^{\alpha - 1} \right]^{1/\alpha}$$

where Q is the capacitance parameter of the constant phase element in units of $Fs^{(\alpha-1)}$ and α is the phase parameter of the constant phase element. The values for α were kept constant for each sample for the entire set of 9 different potentials. The results are given in the corresponding panel following the color code of the legend (increasing temperature from left to right).

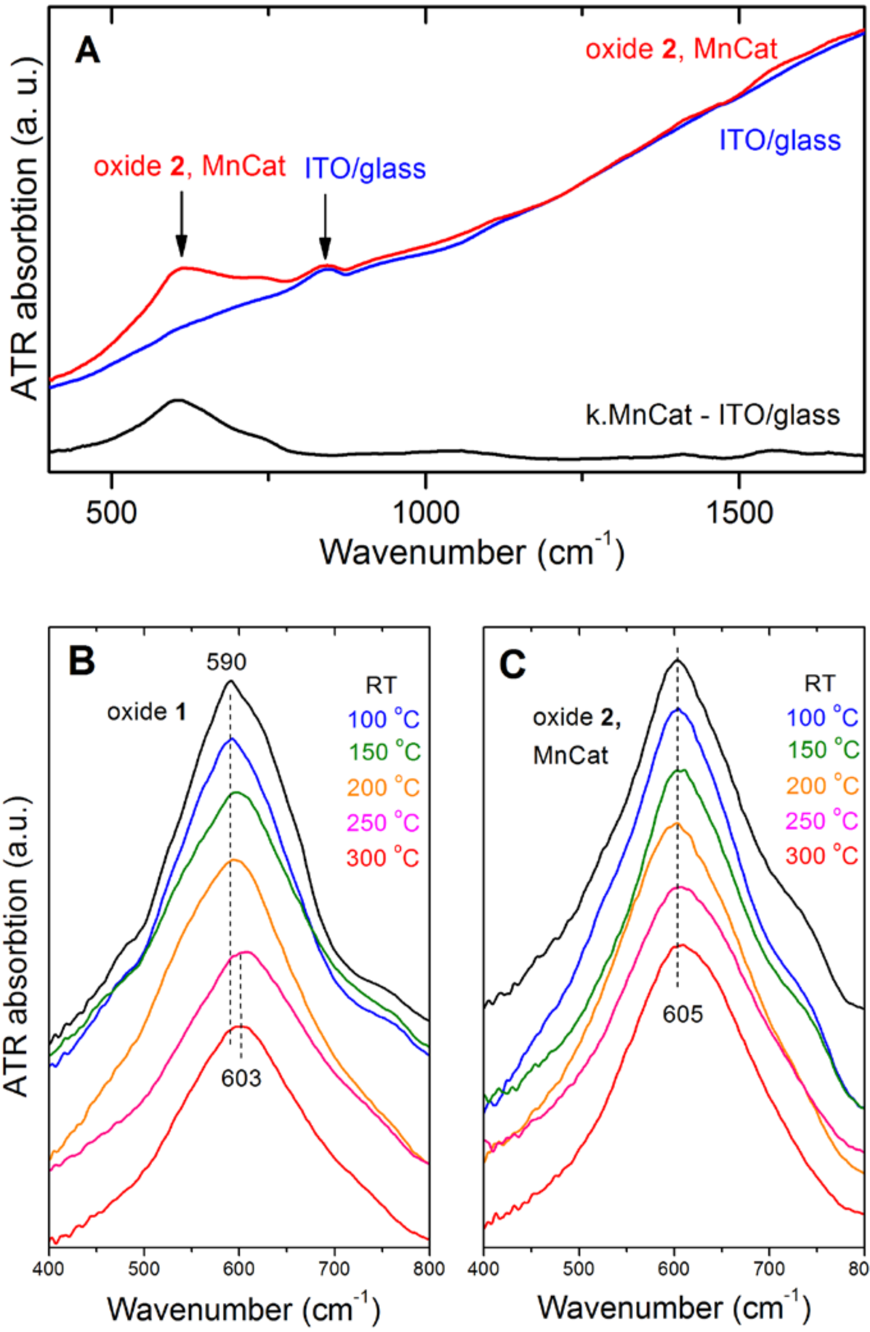

Figure S14. ATR detected FTIR spectra. (A) Comparison of the ATR spectrum of ITO/glass substrate, the one of deposited Oxide **2**, MnCat film, and the corrected one of Oxide **2**, MnCat film. The spectrum of ITO/glass has a strong background with a band near 850 cm^{-1}. To obtain the “pure” spectrum of MnCat film (shown in black), the substrate spectrum was subtracted from the MnCat oxide spectrum after multiplication of the MnCat spectrum by the coefficient k (about 1). (B) Corrected ATR FTIR spectra of Oxide **1** films, heated for 20 min at different temperatures, and (C) corrected Oxide **2**, MnCat, films. For better view the spectra are vertically shifted.

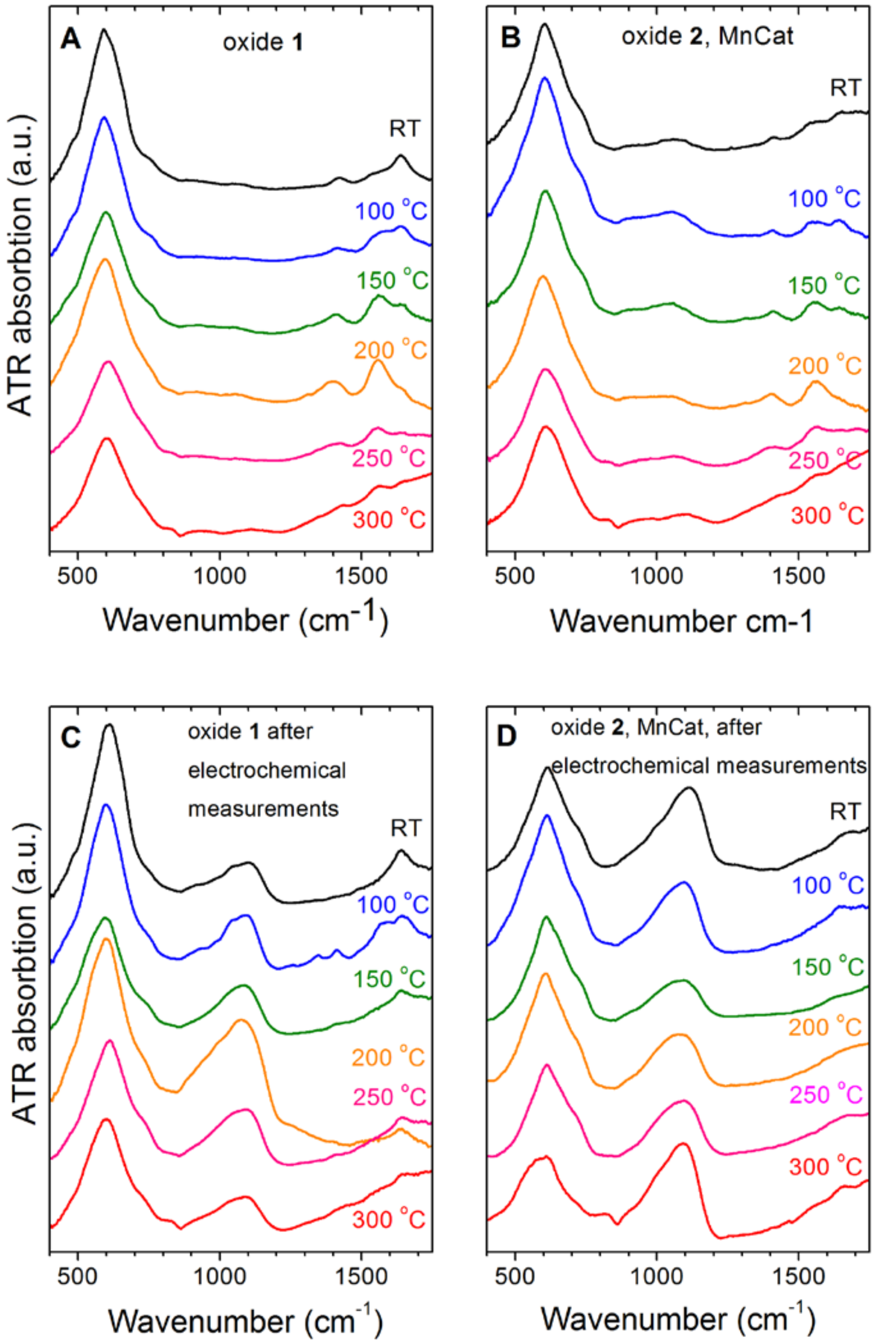

Figure S15. ATR detected FTIR spectra of (**A**) Oxide **1** films and (**B**) Oxide 2, MnCat films, heated for 20 min at different temperatures; (**C**) and (**D**) – the same samples after the measurements of their electrocatalitic properties.

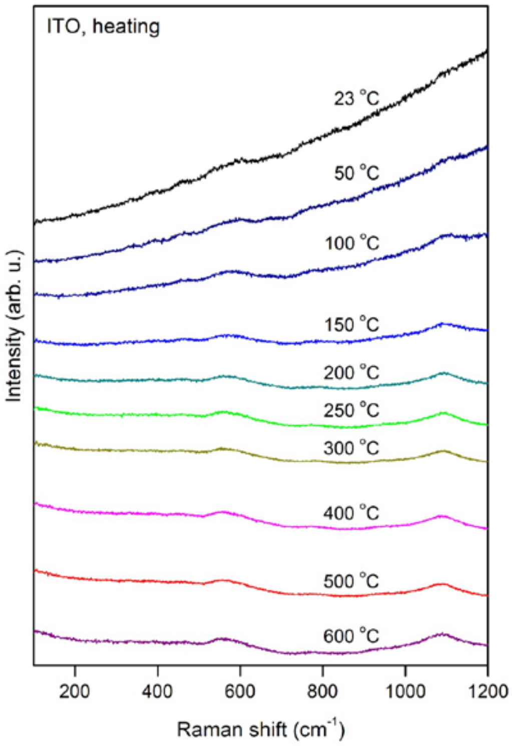

Figure S16. Raman spectra measured at the indicated temperatures during heating of bare ITO substrate. The disappearance of the background at high temperatures indicates that it is related to the conduction properties of the ITO layer at room temperature. We note that as opposite to these measurements, the spectra presented in Fig. 8 in the main text are all recorded at room temperature (after annealing) when the properties of the ITO are restored.

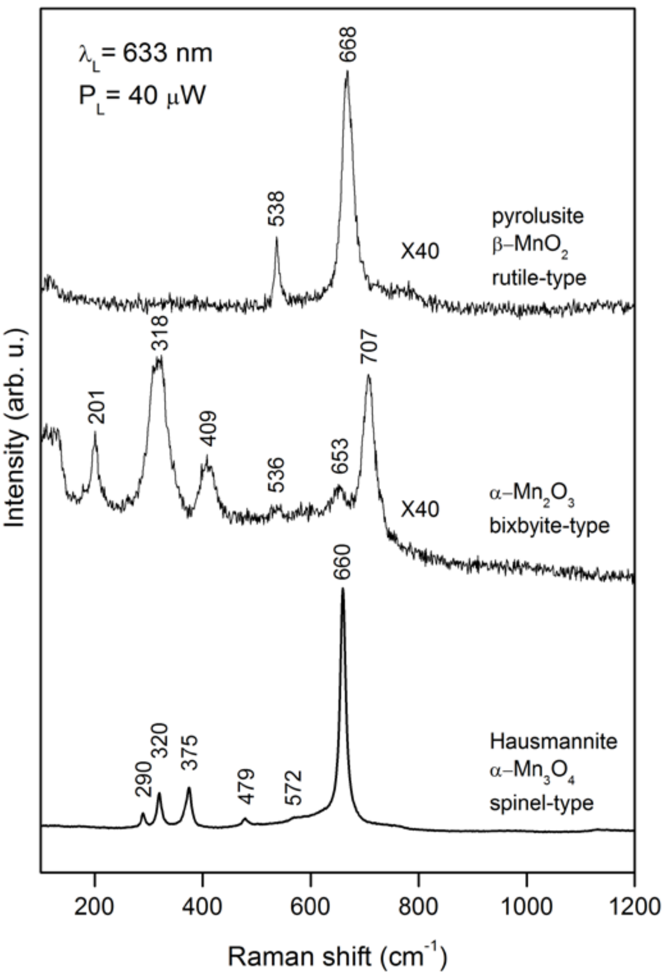

Figure S17. Raman spectra of M_xO_y oxides with simple crystal structure. For better viewing the upper two spectra are multiplied by a factor of 40 and shifted vertically. The type of the structure and measurement conditions are indicated in the figure.

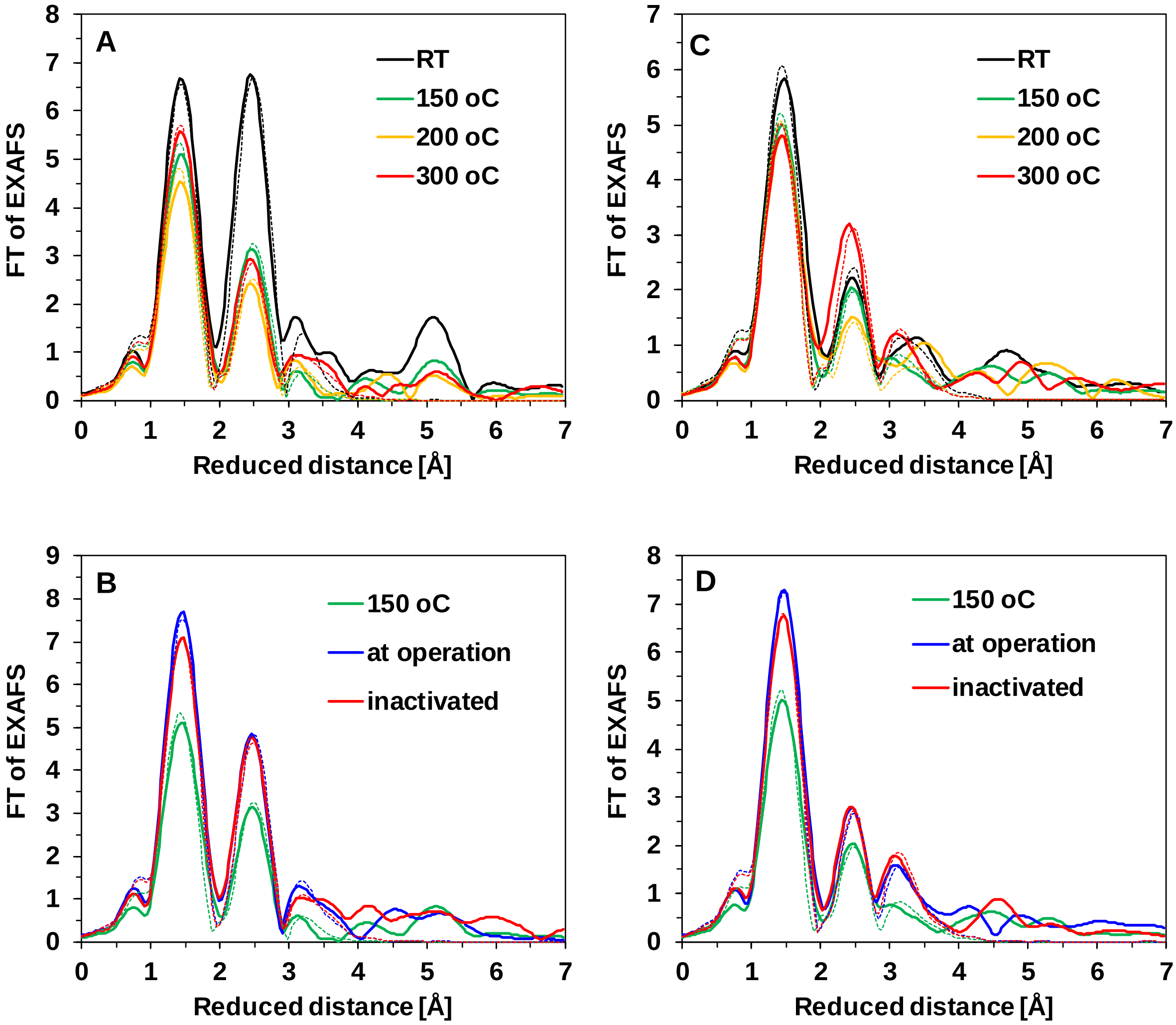

Figure S18. Fourier transformed EXAFS spectra of the Oxide **1** (**A, B**) and Oxide **2**, MnCat (**C, D**) after heating, after exposure to 1.35 V for 3 min (at operation) or after inactivation via long chronopotentiometry with current density 5 mA/cm^2 (inactive). Solid lines represent the experimental data, the dashed lines – simulations, where additional Mn-Mn shell with 3.04 ± 0.01 Å interatomic distance was added as compared with the simulation shown in Fig. S5. The simulation parameters are shown in Fig. S19.

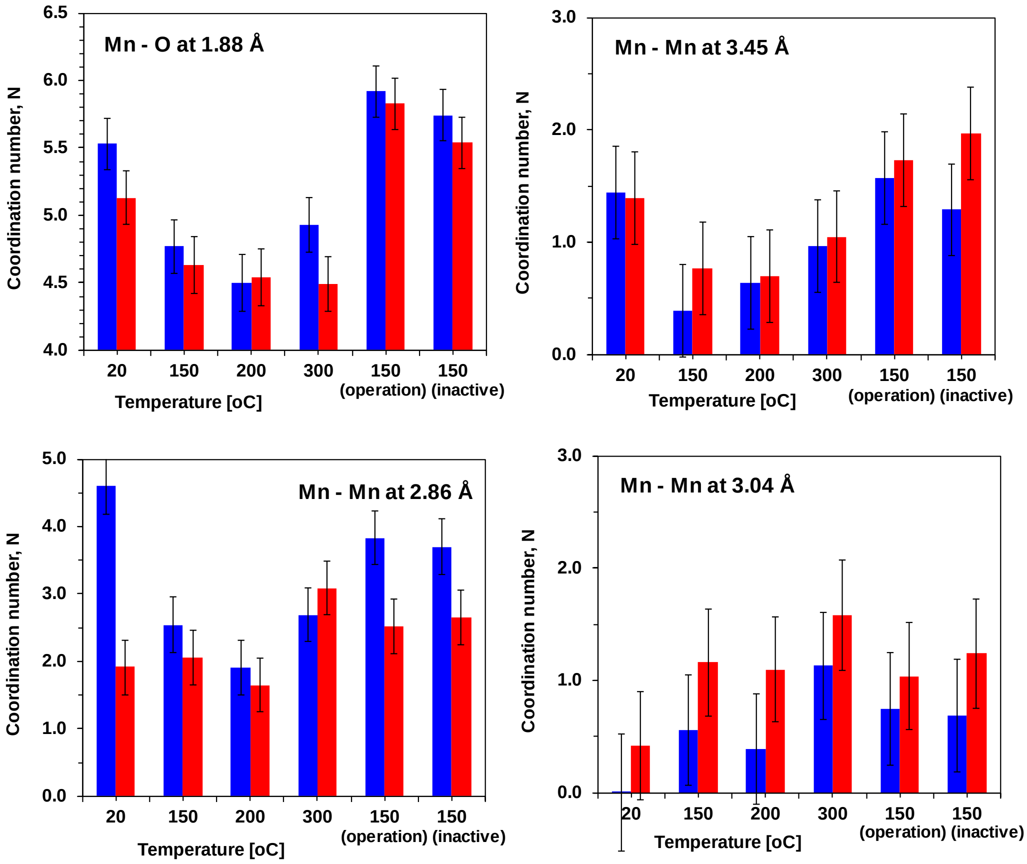

Figure S19. Simulation parameters for the EXAFS spectra of Oxide **1** (blue bars) and Oxide **2**, MnCat (red bars) after heating, after exposure to 1.35 V for 3 min (operation) or after inactivation via long chronopotentometry with current density 5 mA/cm^2 (inactive). As compared to the results presented in Fig. 4 and Fig. S6, in this simulation approach an additional Mn-Mn distance at 3.04 Å was added to simulation to account for the presence of ζ-Mn_2O_3. The Debye-Waller factors for all shells were fixed to 0.063 Å in order decrease the degrees of freedom and increase the significance of the obtained fit parameters. The error bars for the coordination numbers shown in the plots correspond to 68% confidence interval. The 68% confidence interval for the interatomic distances is 0.01 Å.

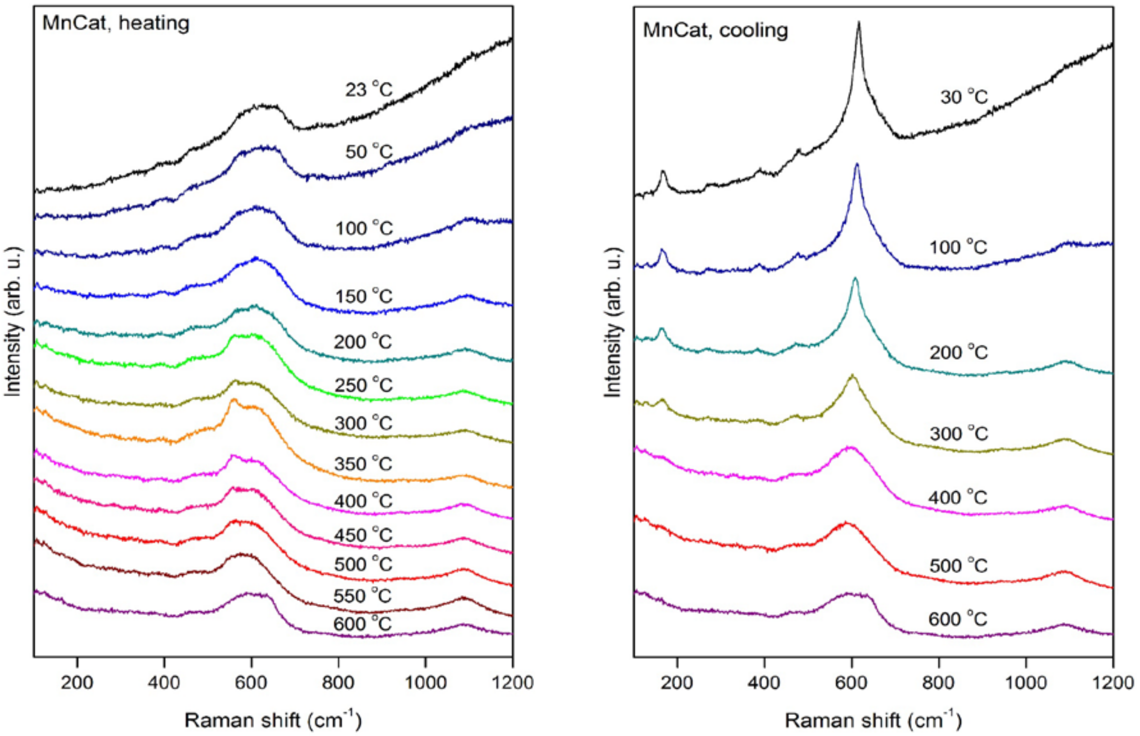

Figure S20. Raman spectra measured at the indicated temperatures during heating and cooling of the MnCat (Oxide **2**). The film was gradually heated with a rate 10 degrees/min. 3 min after the desired temperature was reached, 3 Raman spectra were collected using 0.8 mW laser power and total time for one spectrum data collection 180 s. For each scan a new spot was used. The total time of the heating/cooling cycle was about 6 hours.

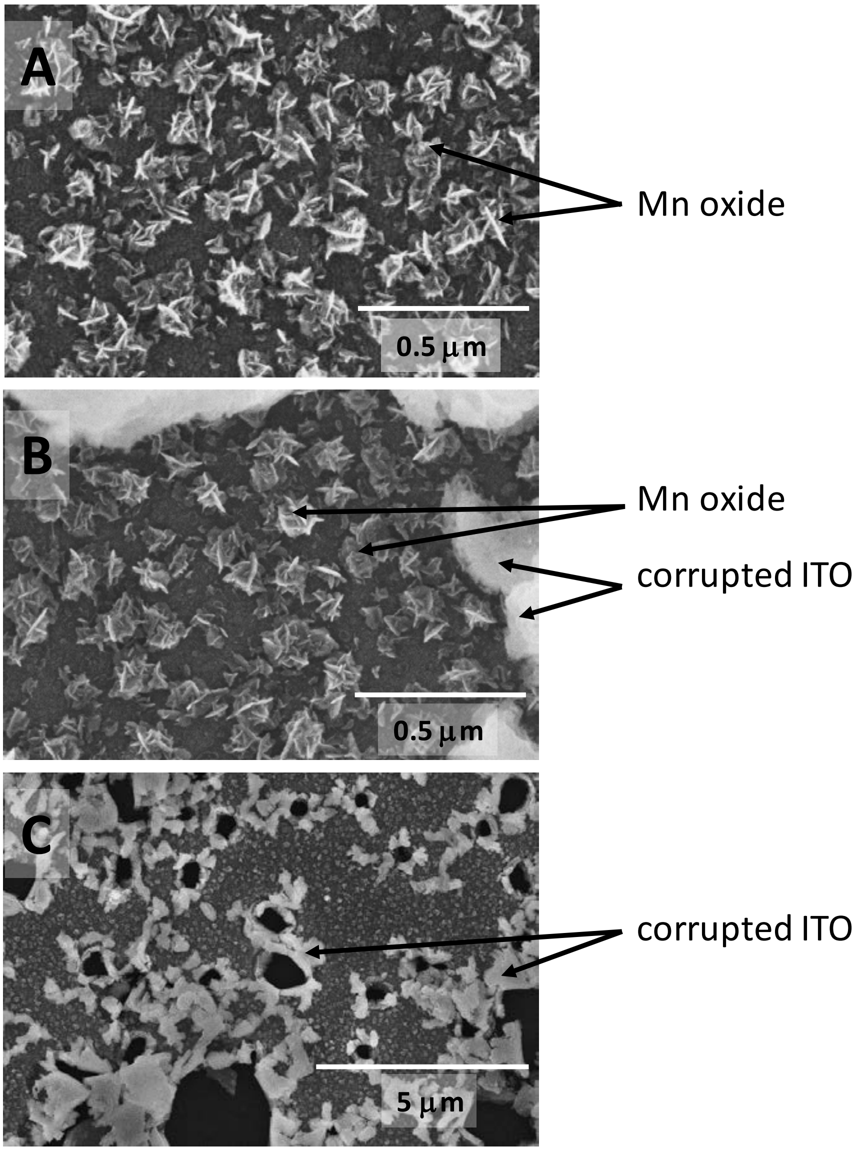

Figure S21. SEM images of the, Oxide **2**, MnCat, heated to 150 °C for 20 min. A – before electrochemical operation. B and C – after operation at 1 mA/cm^2 until the overpotential exceeded 3 V. Different magnifications are used to illustrate the corruption of the ITO layer while the Mn oxide particles remain unchanged.

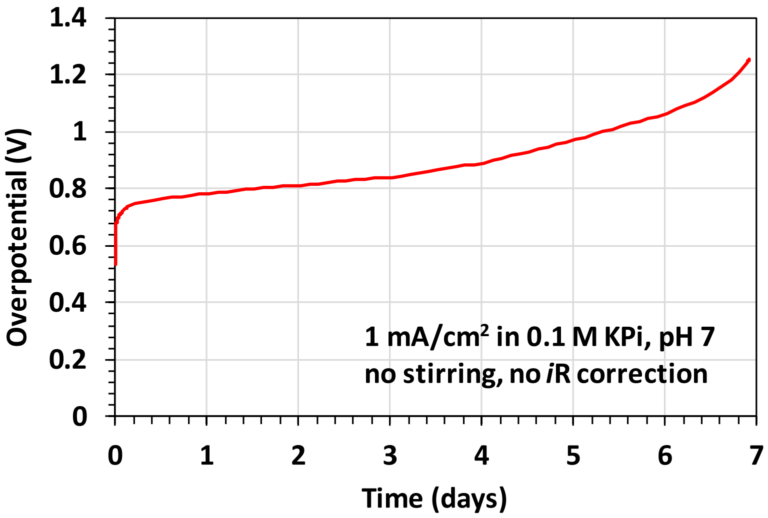

Figure S22. Chronopotentiometric measurements at 1 mA/cm^2 in 0.1 M KPi (pH 7) for the Oxide **2**, MnCat, heated for 20 min at 150 °C. The solution was not stirred or de-aerated during the experiment. No *i*R correction was applied.

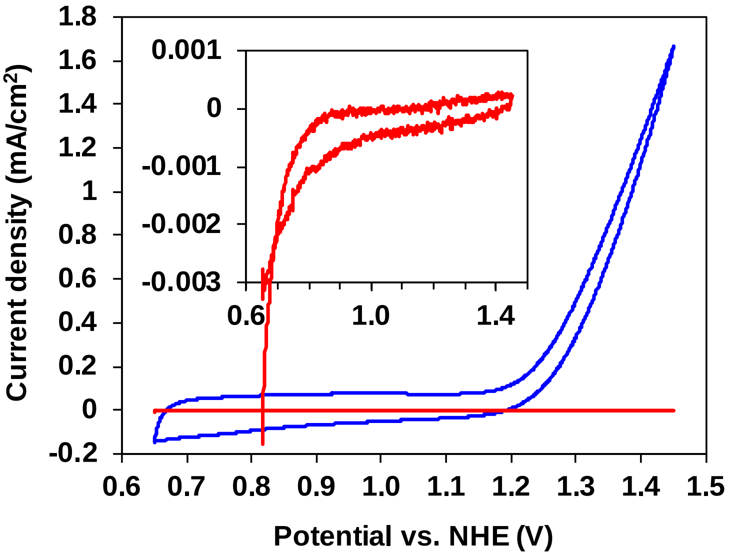

Figure S23. CVs recorded with 20 mV/s in 0.1 M KPi (pH 7) of the Oxide **1** heated for 20 min at 250 °C. Blue: CV before chronopotentiometry measurement (1 mA/cm^2, data shown in Fig. 2A in the main text). Red: CV after the potential-induced inactivation of the film. Inset shows the CV after inactivation on an expanded vertical scale.

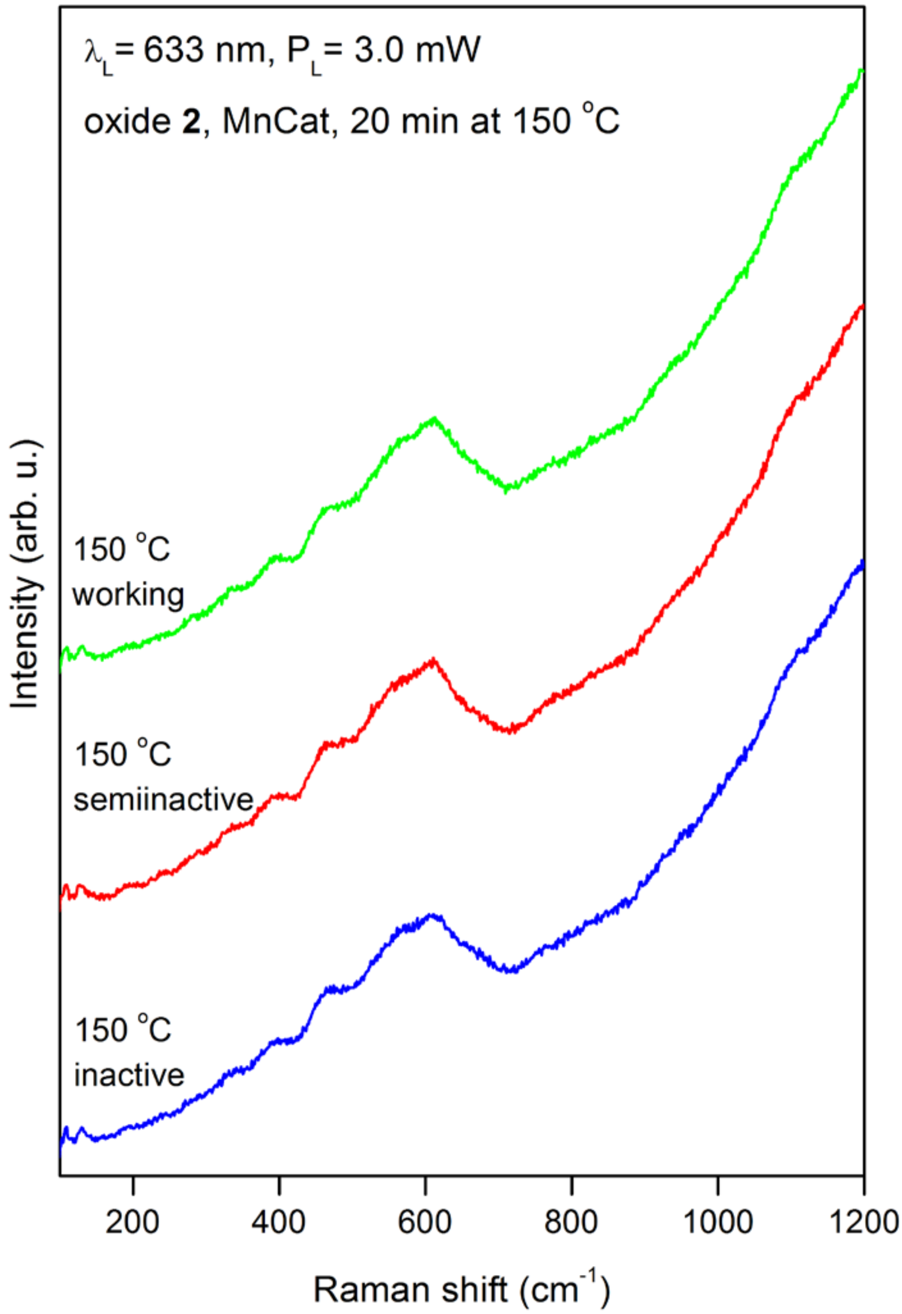

Figure S24. Raman spectra measured at room temperature of MnCat (Oxide **2**) heated at 150 °C at different stages of inactivation. For this experiment a chronopotentiometric experiment in 0.1 KPi (pH 7) was started, keeping constant current density of 5 mA/cm2. Green line: The experiment was stopped after 3 min operation, the electrode was rinsed with water and air dried before the Raman spectrum was measured. Red line: experiment was interrupted when the overpotential increased to a plateau level (approx. after 2 h). Blue line: the electrode was rinsed with distilled water, dried in air and measured after complete inactivation. Different electrodes were used for the three measurements. Raman spectra are vertically shifted.

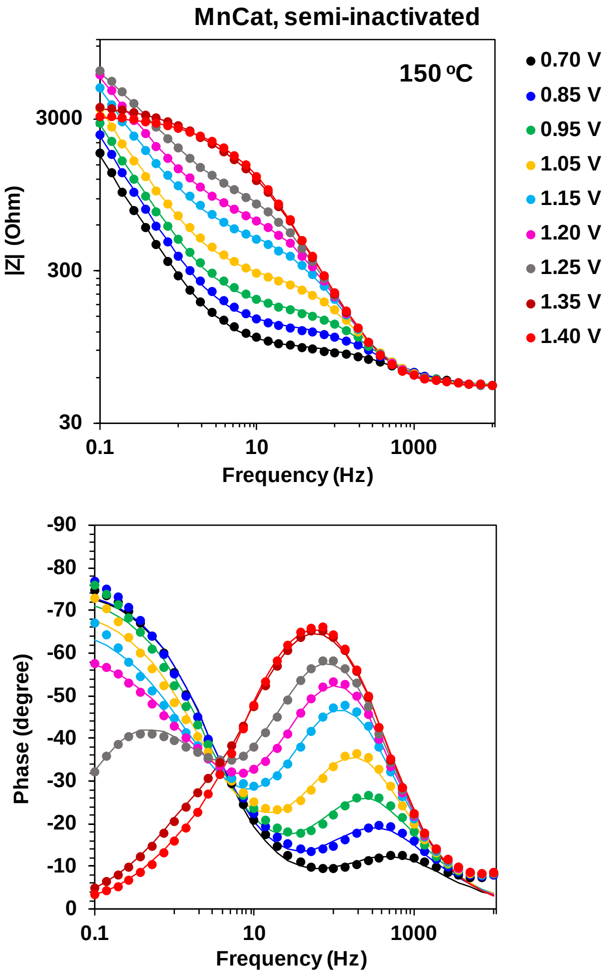

Figure S25. Impedance spectra measured at different potentials after potential-induced semi-inactivation (operation for 7 days at 1 mA/cm^2, data shown in Fig. S22) of the MnCat (Oxide **2**), heated at 150 °C for 20 min. Before the impedance measurements the film was conditioned at the corresponding potential for 60 s. Symbols – experimental data; lines – simulations according to the equivalent circuit shown in Fig. 6B in the main text.

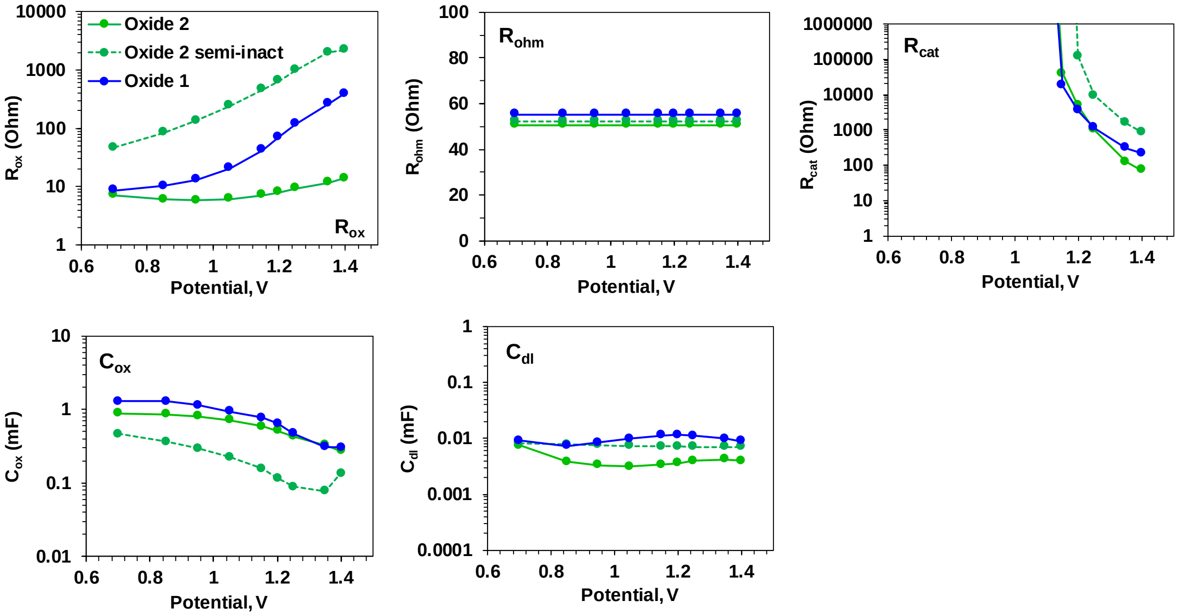

Figure S26. Parameters for the simulation of the impedance spectra according to the equivalent circuit shown in the inset of Fig. 6B in the main text. Compared are oxides heated to 150 °C for 20 min: Oxide **1** (inactive, solid blue line), Oxide **2** (MnCat, solid green line) and Oxide **2** after 7 days exposure to oxidizing potential (semi-inactive MnCat, dashed green line, chronopotentiometric data shown in Fig. S22). R_{ox} - resistance describing the oxidation state changes; R_{Ohm} – summed Ohmic resistance of electrolyte and ITO electrode; R_{cat} – catalytic resistance of the oxide (charge-transfer resistance); 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.

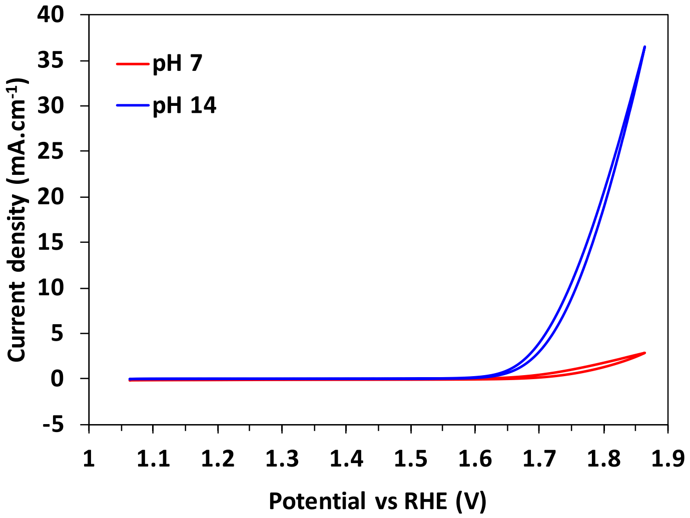

Figure S27. Comparison of the current densities in 0.1 M KPi buffer (pH 7) and in 1 M KOH. To allow for direct comparison of the overpotentials applied, the potentials are given vs reversible hydrogen electrode (RHE). For this experiment Pt electrodes were used as substrate. The curves were not corrected for the non-compensated *iR* drop.