Electronic Supplementary Material (ESI) for Energy & Environmental Science
This journal is © The Royal Society of Chemistry 2013

Electronic Supplementary Information

Electrochemical Water Splitting by Layered and 3D Cross-linked Manganese Oxides: Correlating Structural Motifs and Catalytic Activity

Arno Bergmann,*[a] Ivelina Zaharieva,*[b] Holger Dau[b] and Peter Strasser[a]

[a] Department of Chemistry, Chemical and Materials Engineering Division, The Electrochemical Energy, Catalysis and Materials Science Laboratory, Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany.
E-Mail: bergmann@chem.tu-berlin.de; pstrasser@tu-berlin.de
Fax: +49 30-314 22261; Tel: +49 30-314 29542;
[b] Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany.
E-Mail: ivelina.zaharieva@fu-berlin.de; holger.dau@fu-berlin.de;
Fax: +49 30 838 56299; Tel: +49 30 838 3581

Experimental

S-1. Details of experimental procedures

Syntheses

Carbon-supported manganese oxide has been synthesized via two different preparation methods – symproportionation deposition-precipitation (s-MnO_x) and incipient wetness impregnation (i-MnO_x). In both cases multi-walled carbon nanotubes (MWNT, Bayer MaterialScience AG, 95 % C) has been pre-treated with concentrated HNO_3 at 100°C for 16 h to remove the residual growth catalyst and amorphous carbon impurities and to functionalize their inner and outer surfaces by oxidation.

s-MnO_x has been prepared via impregnation of the carbon support with Mn^{2+} from 0.015 M manganese(II) nitrate tetrahydrate/ 0.09 M ammonium chloride solution *($Mn(NO_3)_2 \cdot 4H_2O$, Merck)* and drop wise addition of an 0.01 M aqueous potassium permanganate solution *($KMnO_4$, Roth)* under vigorous stirring. A constant pH of 8 was ensured via titration with ammonia. Afterwards, the compound was thoroughly washed, filtered and dried in air at 110 °C for 16 h.

i-MnO_x has been prepared via incipient wetness impregnation of the carbon support with a nominal loading of 10 wt.% of Mn^{2+} ions in an aqueous $Mn(NO_3)_2$ solution. The compound was consecutively dried in air for 6 h and 24 h at 60 °C and 110 °C, respectively.

Determination of the manganese loading of the carbon nanotubes was performed using a 715-ES-inductively coupled plasma (ICP) analysis system (Varian). Therefore, the powder samples were dissolved in aqua regia over night, the remaining carbon filtrated and the solution diluted with MilliQ water to the desired Mn concentration.

Calculation of overpotential η

The overpotential η in Fig. 8 has been calculated via

$$\eta = E_{NHE} + {}^{59\,\mathrm{mV}}\!/_{\mathrm{pH\ unit}} \cdot \mathrm{pH} - 1.23\ \mathrm{V}$$

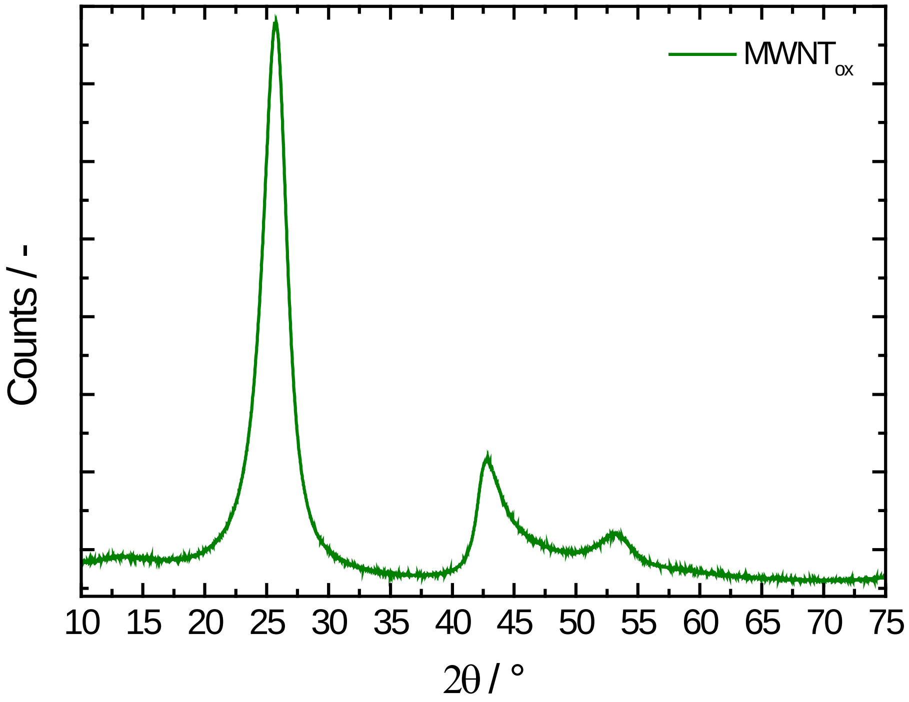

Fig. S1. Powder x-ray diffraction pattern of MWNT$_{ox}$ between 10° and 75° at Cu K_α radiation.

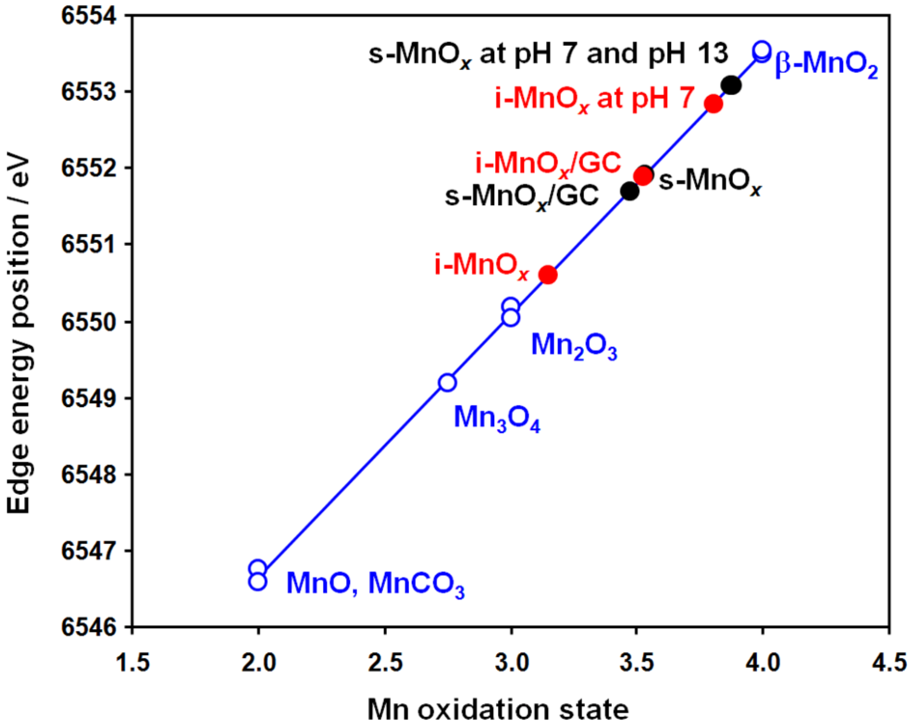

Fig. S2. Calibration line based on Mn compounds with known structure and oxidation state (in blue). Black symbols and labels indicate the edge position and estimated mean Mn oxidation state for s-MnO$_x$ powder before (s-MnO$_x$) and after (s-MnO$_x$/GC) deposition on the electrode, and after electrocatalytic operation at 1.763 V vs. RHE for 3 min at pH 7 (0.1 M KPi) or pH 13 (0.1 M KOH). Red symbols and label represent the corresponding values for the i-MnOx.

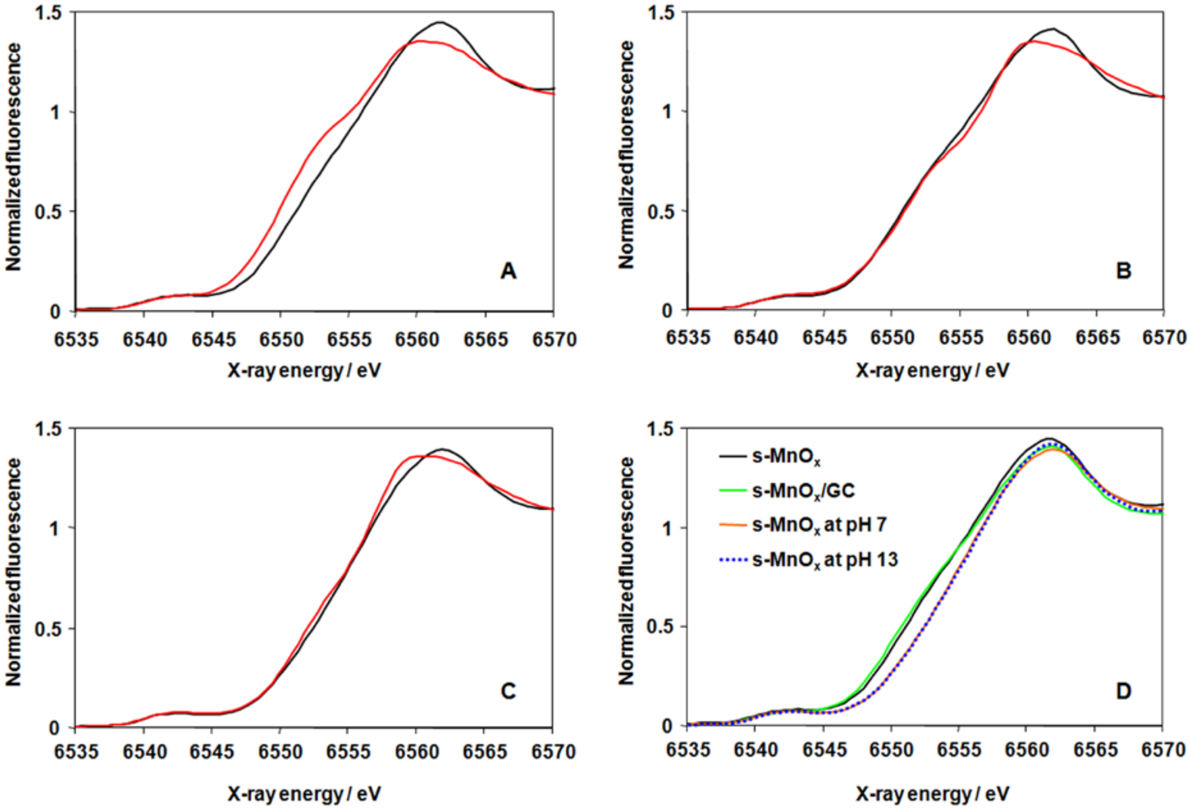

Fig. S3. XANES spectra of s-MnO$_x$ (in black) and i-MnO$_x$ (in red) after synthesis (A), after deposition on GC electrode (B), and after operating for 3 min at 1.763 V vs. RHE in 0.1 M KPi, pH 7 (C). In (D) is shown a comparison of the XANES spectra recorded from s-MnO$_x$ at different stages of catalyst preparation.

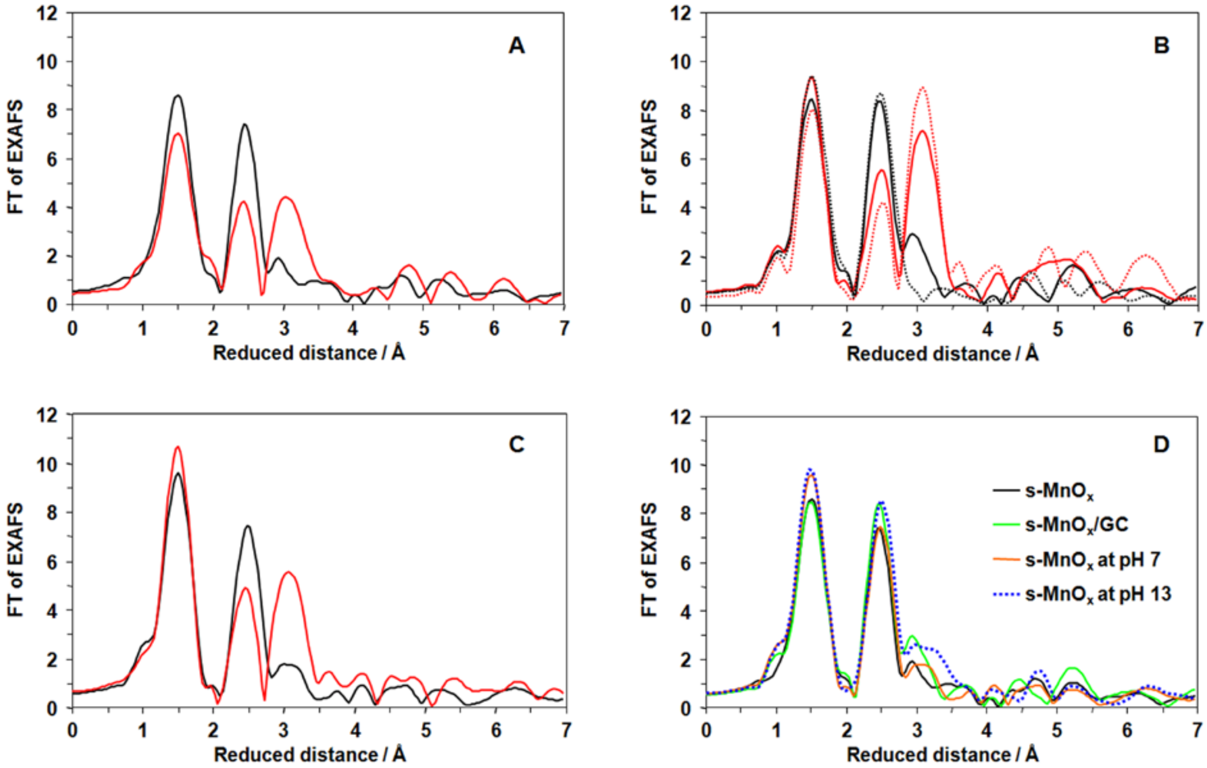

Fig. S4. Fourier-transformed EXAFS spectra of s-MnO$_x$ (black solid lines) and i-MnO$_x$ (red solid lines) after synthesis (A), after deposition on GC electrode (B), and after operating for 3 min at 1.763 V vs. RHE in 0.1 M phosphate buffer, pH 7 (C). In (B) the spectra from δ-MnO$_2$ and β-MnO$_2$ reference compounds are shown using black and red dotted lines, respectively. In (D) a comparison of the Fourier-transformed EXAFS spectra recorded from s-MnO$_x$ at different stages of catalyst preparation is shown.

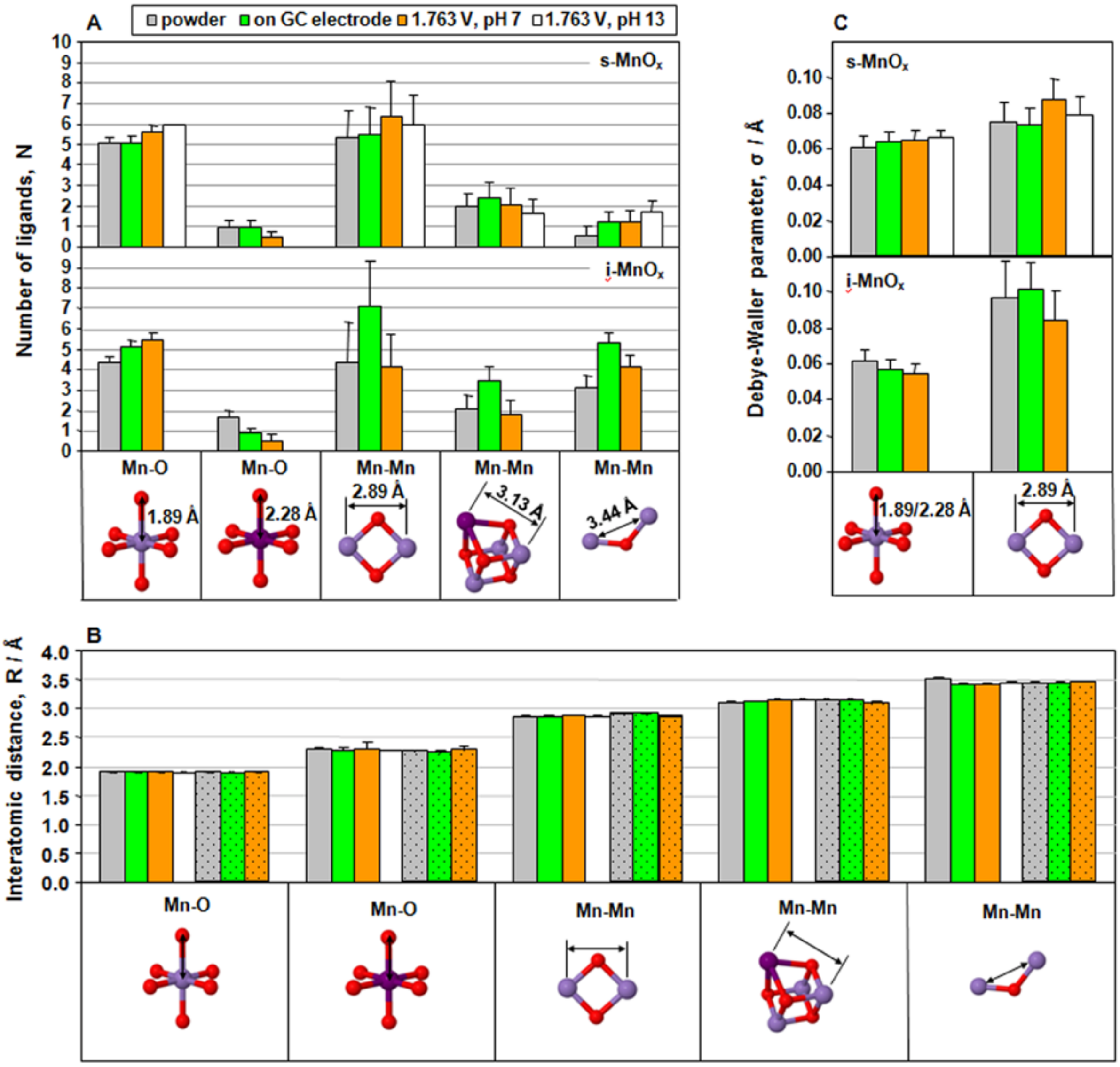

Fig. S5. Simulation results for the independent fits of the k^3-weighted EXAFS spectra from s-MnO_x and i-MnO_x before and after operation as water oxidation catalysts in 0.1 M KPi (pH 7) or 0.1 M KOH (pH 13). (A) – EXAFS coordination numbers, (B) – interatomic distances, (C) – Debye-Waller parameters. During the simulation, the sum of the coordination numbers for the two oxygen shells was kept equal to 6 and the same Debye-Waller parameter was used for each of the two oxygen shells. The Debye-Waller parameters for the last two Mn-Mn shells were fixed to 0.063 Å. The errors represent a 68% confidence interval.

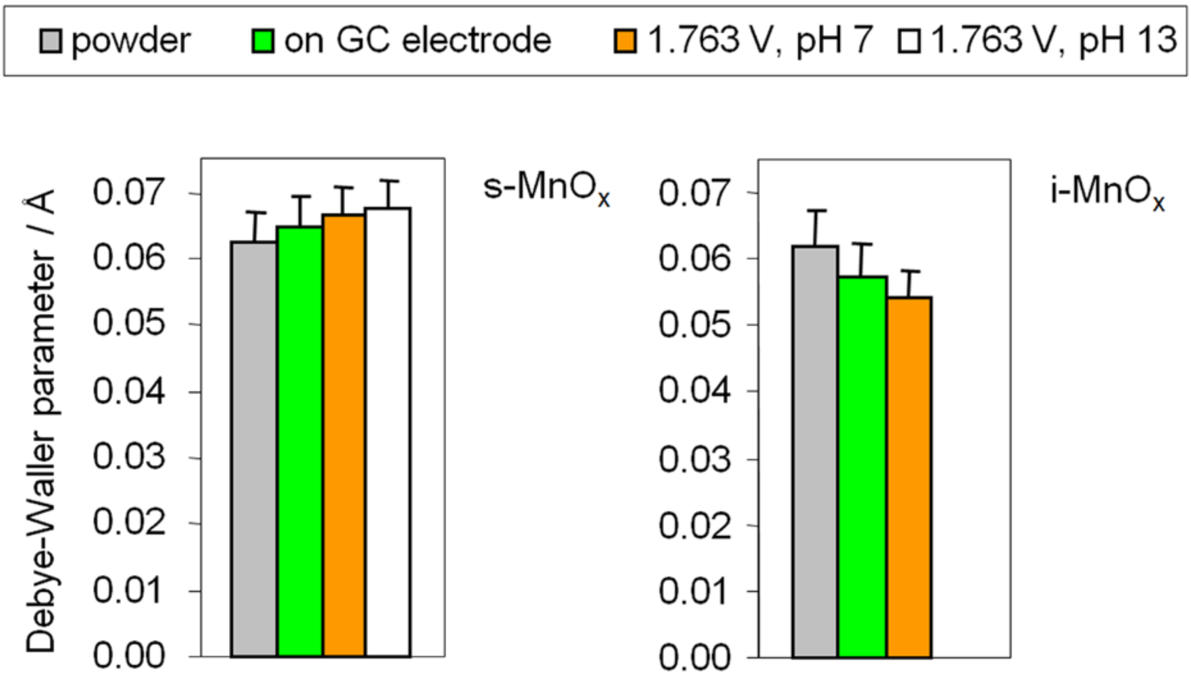

Fig. S6. Debye-Waller parameters for the oxygen shell of backscattering atoms. The other fit parameters are presented in Fig. 3 in the main text.

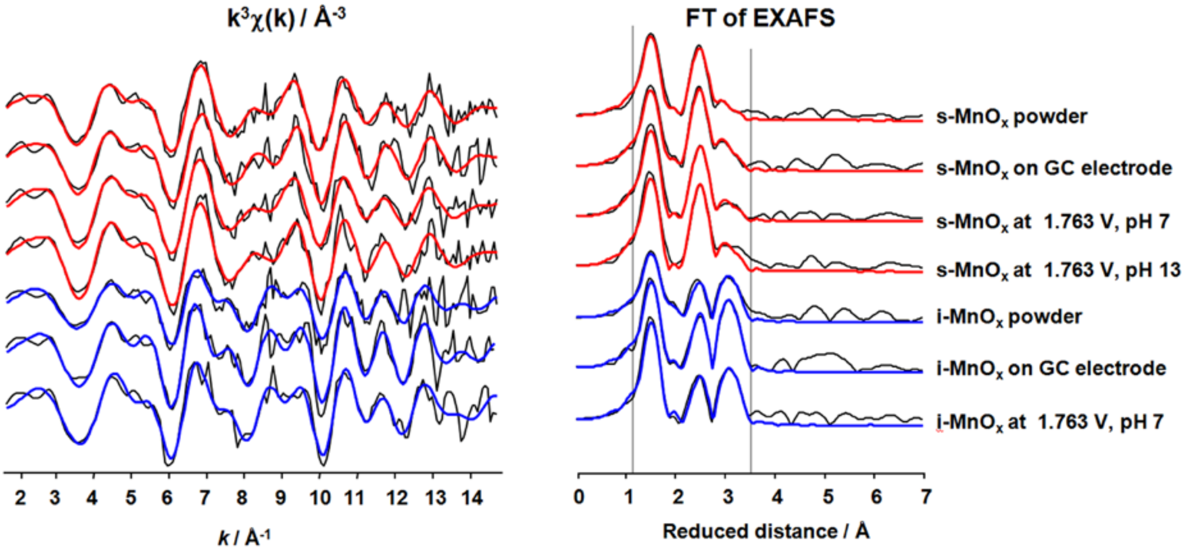

Fig. S7. k^3-weighted experimental EXAFS spectra of the studied Mn oxides (thin black lines) and the joint-fit simulation result (red lines for s-MnO$_x$, blue for the i-MnO$_x$). The fit parameters are given in Fig. 3 of the main manuscript. The grey vertical lines indicate the range used to calculate the RF error factor. The averaged RF-values equalled 15.1% for the joint-fit simulation approach and 13.6% for simulations with independently variable interatomic distances.

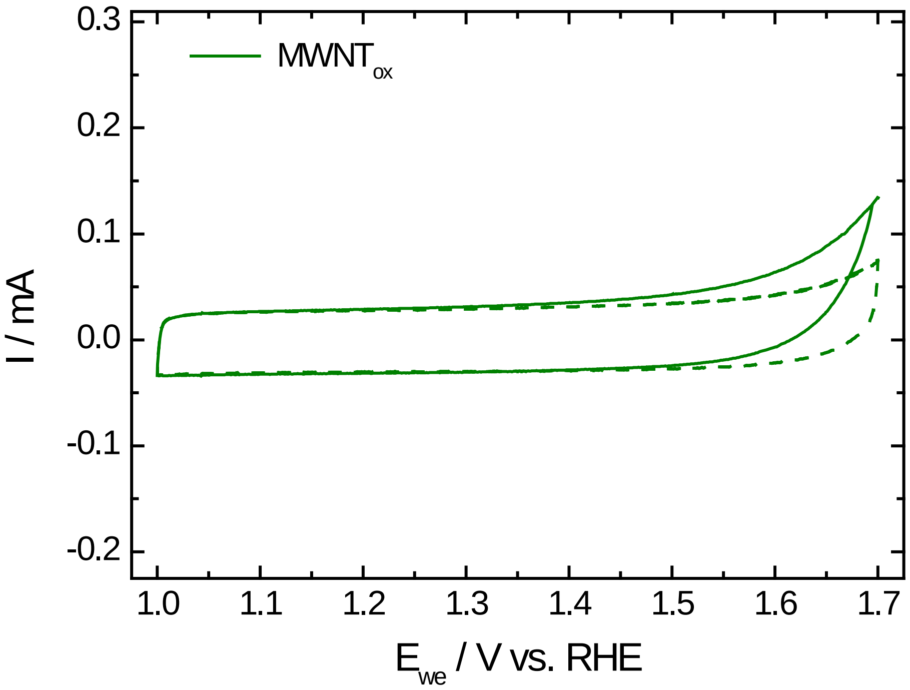

Fig. S8. First (solid) and 11th (dashed) voltammogram of MWNT$_{ox}$ (without catalyst) recorded in 0.1 M KPi at pH 7 with a scan rate of 100 mV s^{-1}.

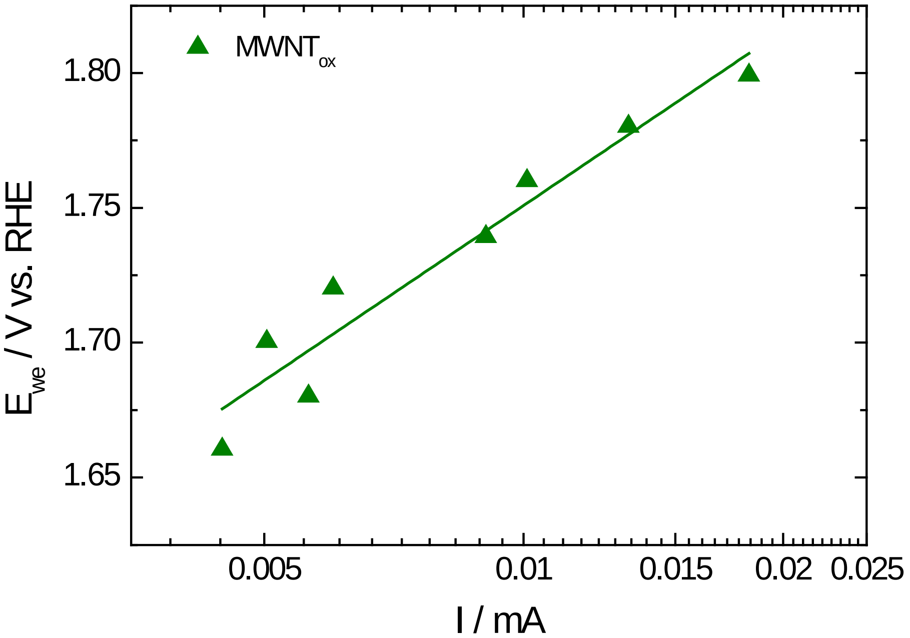

Fig. S9 Background current of MWNT$_{ox}$ without deposited catalysts. The Tafel plot of MWNT$_{ox}$ in 0.1 M KPi at pH 7 was extracted from quasi-stationary potential-step RDE experiments at a rotation speed of 1600 rpm. All electrode potentials have been *iR*-corrected. We note that the current values are significantly lower than the corresponding figures in the presence of the investigated Mn oxide catalysts. The Tafel slope was determined to 216 mV dec^{-1} from linear regression between 1.675 and 1.8 V.

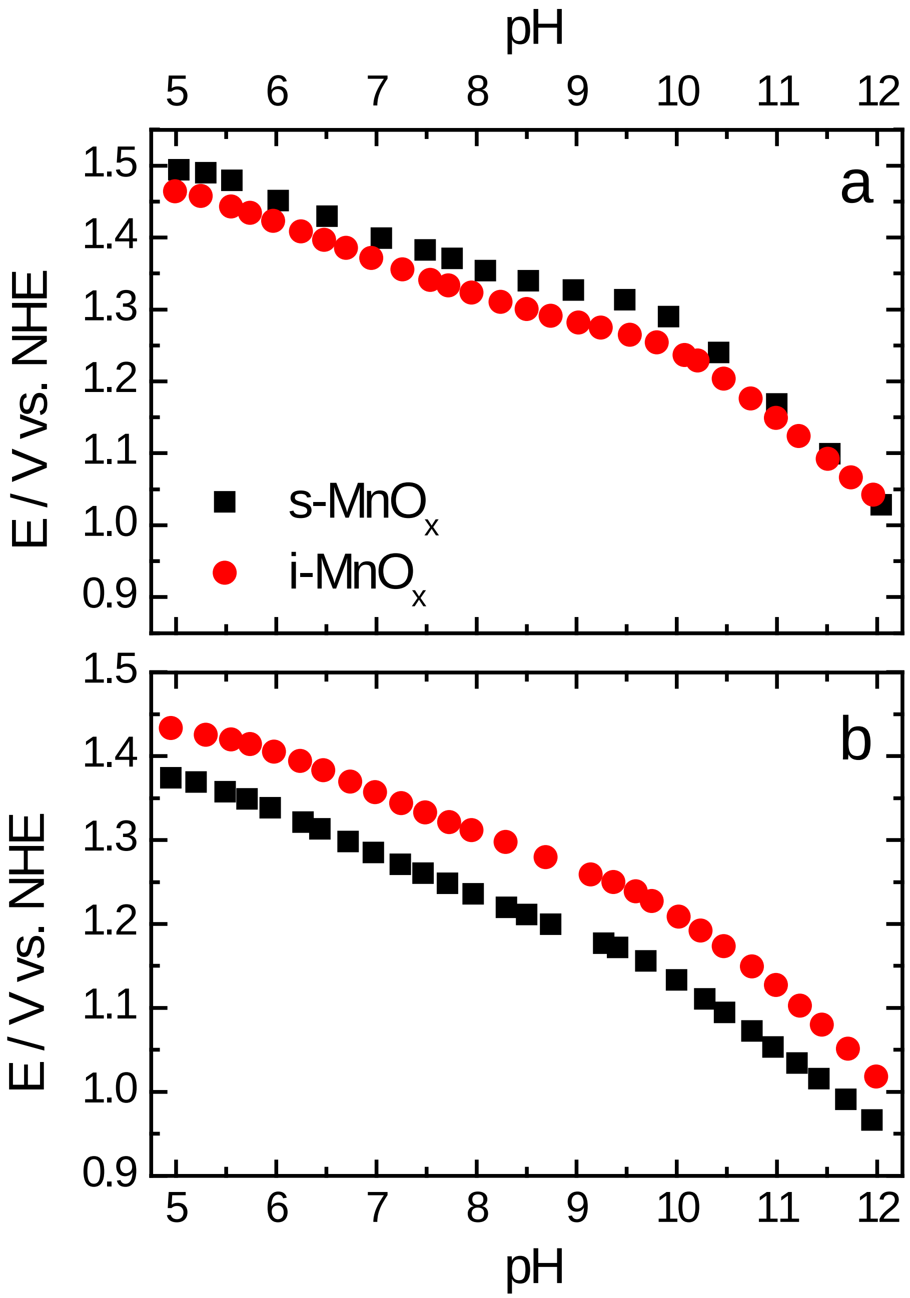

Fig. S10 pH dependence of the electrode potential vs. NHE at a constant current of (a) 50 µA and (b) 20 µA recorded during titration of aliquots of 40 wt.% KOH into 0.1 M KPi increasing the pH between 5 and 12. At each pH values the corresponding potential was detected after equilibration for 3 min.

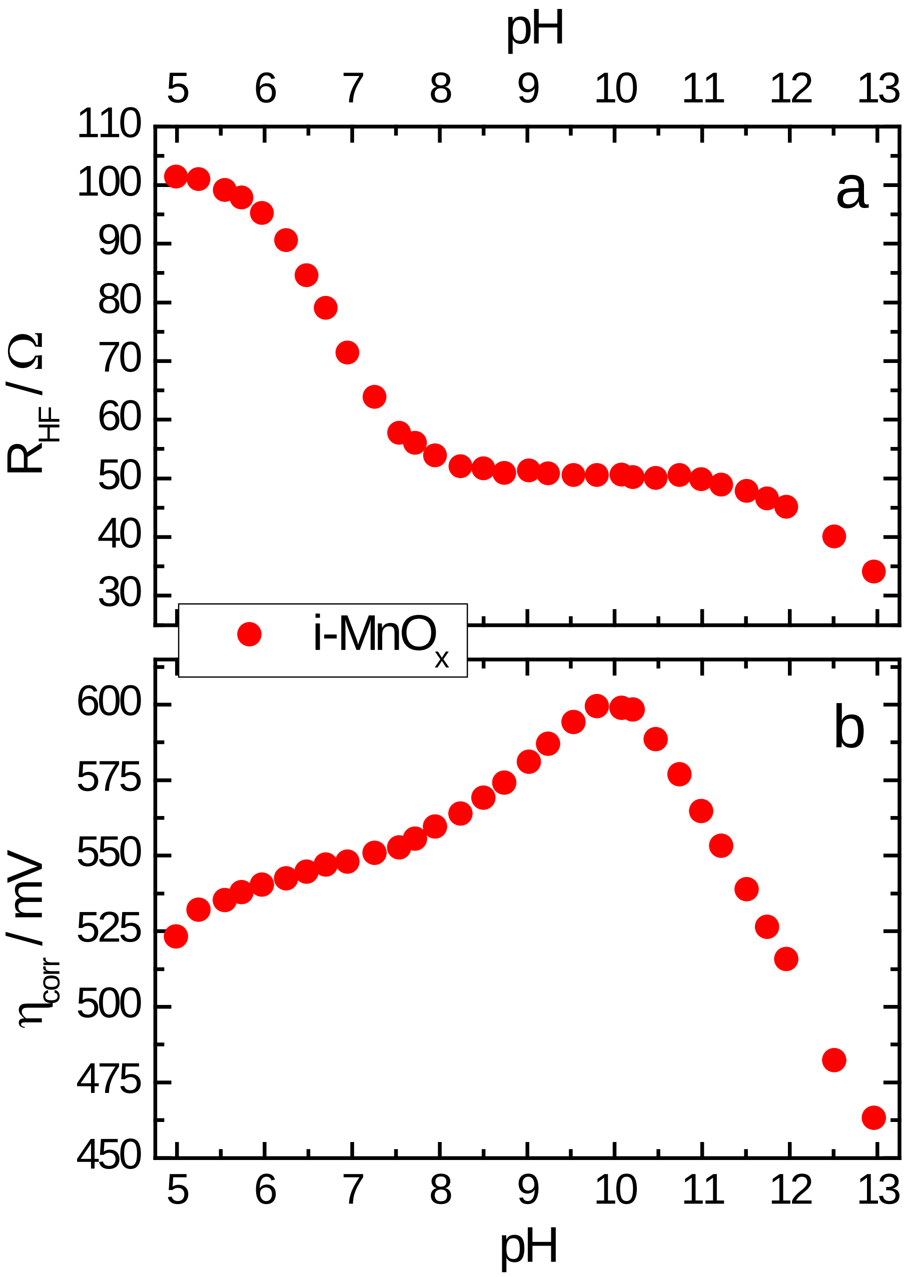

Fig. S11. pH dependence of electrolyte resistance (a) and η-pH profile after correction for ohmic losses (*iR* correction) (b). In (a), the high frequency resistance R_{HF} of the bulk electrolyte has been determined via electrochemical impedance spectroscopy at 1.35 V vs. NHE. The pH was adjusted via titration of aliquots of 40 wt.% KOH.

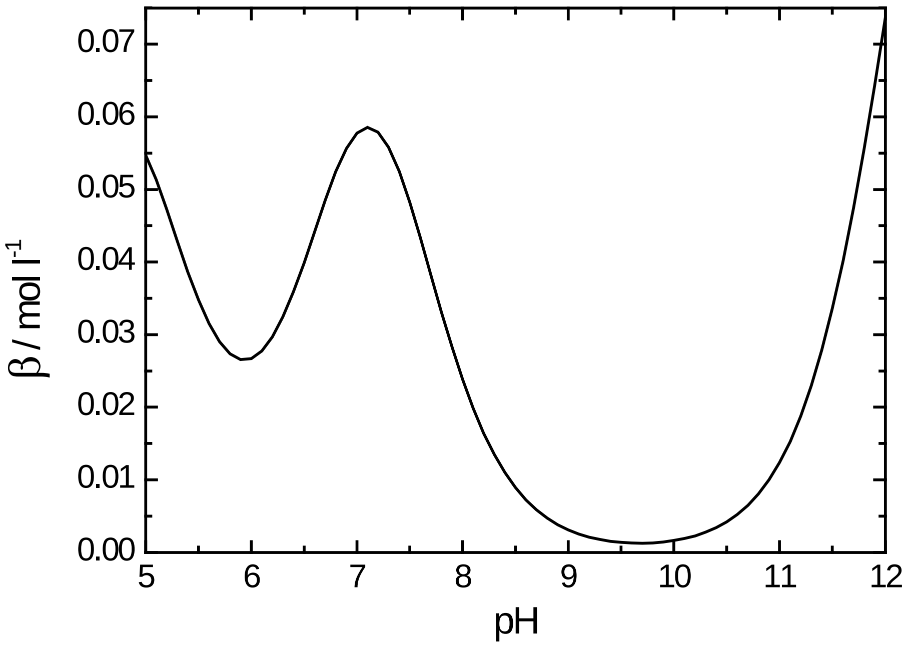

Fig. S12. pH dependence of the calculated buffer strength (β). For a concentration of the potassium phosphate buffer of 0.1 M, the buffer strength was calculated as described in ref.[1]

1. A. Hulanicki, Reactions of acids and bases in analytical chemistry, Ellis Horwood Ltd, 1987.