Supplementary information to 'Manganese oxide films with controlled oxidation state for water splitting devices through a combination of atomic layer deposition and post-deposition annealing'

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Experimental details on the linear sweep voltammetry

An electrochemical setup as represented in figure 1 was used. 3-electrode electrochemical voltammetric experiments were performed using manganese oxides on carbon fiber Toray substrate served as the working electrode (WE), a Pt mesh as counter electrode (CE) and an Ag/AgCl (3M KCl, sat. AgCl, Radiometer Analytical) reference electrode. 1M KOH was used as electrolyte. The solution was vigorously stirred with a magnetic stirrer while bubbling a high oxygen flow through the solution for 10 minutes before every experiment. Additionally, oxygen was purged through the headspace of the container. During the experiments the O_2 purge and stirring was maintained. Linear voltammetric sweeps were performed on the as-prepared samples with a sweep rate of $2\,\mathrm{mV\,s^{-1}}$. As a control experiment, the Ag/AgCl (3M KCl) was referenced against a Hg/HgO electrode in 1M KOH. From this measurement we could conclude that the potential of Ag/AgCl (3M KCl) in 1M KOH was +0.22V vs. RHE. This scale was used for analysis of voltammetric curves.
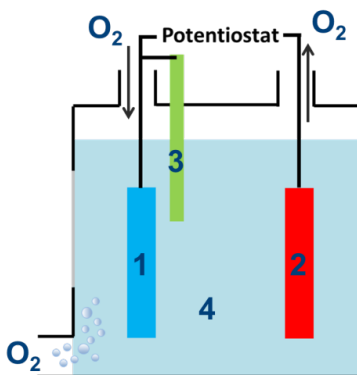

Figure 1: Schematic representation of electrochemical setup. 1 = working electrode (MnOx on Toray paper); 2 = counter electrode (Pt mesh); 3 = reference electrode (Ag/AgCl) and 4 = electrolyte (1M KOH).

Oxidation state confirmation by XPS

XPS on four selected films was performed to confirm the oxidations state obtained by XRD. As was done in our earlier work,[1] the linear relation between the Mn oxidation state and the energy difference between the Mn $2p^{3/2}$ maximum and the peak position of the lowest energy component of the O 1s spectrum (Mn-O-Mn bond) was used to estimate the oxidation state.[2–5] Figure 2 shows the results of this analysis, alongside with the recipe to obtain these films and the manganese oxide state found from XRD. Besides an offset to lower oxidation states, likely caused by the spread in literature data, the trend in oxidation states is clearly visible, confirming that the XRD analysis is sufficient to obtain the oxidation state for these manganese oxide thin films.
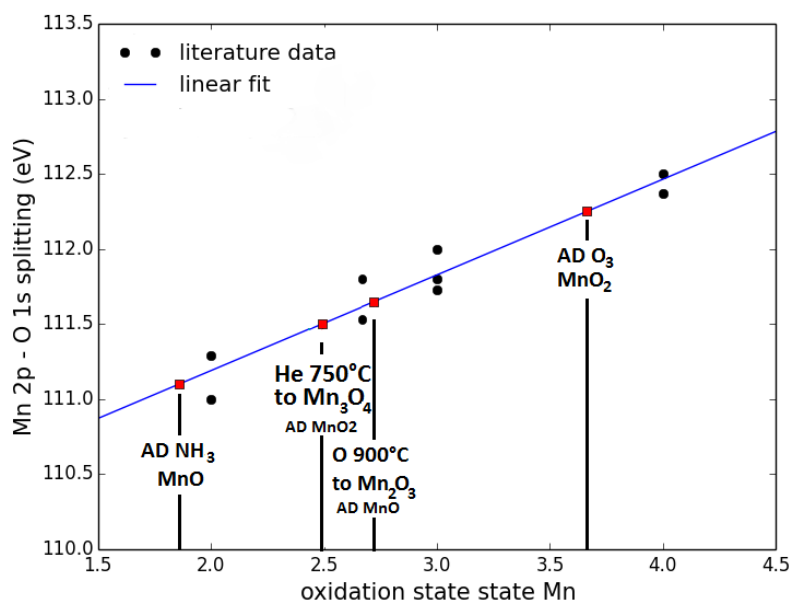

Figure 2: Relation between difference in binding energy of the Mn $2p^{3/2}$ maximum and the peak position of the lowest energy component of the O 1s spectrum (Mn-O-Mn bond) found from literature,[2–5] and the oxidation states of the reported films. The energy difference for selected ALD and annealed films are plotted on this graph to obtain the oxidation state, which matches to the oxidation state obtained from crystal phase analysis, save an offset to lower oxidations states.

AFM confirmation by SEM

Scanning electron microscopy was used to further study the surface topology. Similar surfaces were found to the surfaces obtained from AFM, confirming the validity of AFM even on the roughest films.
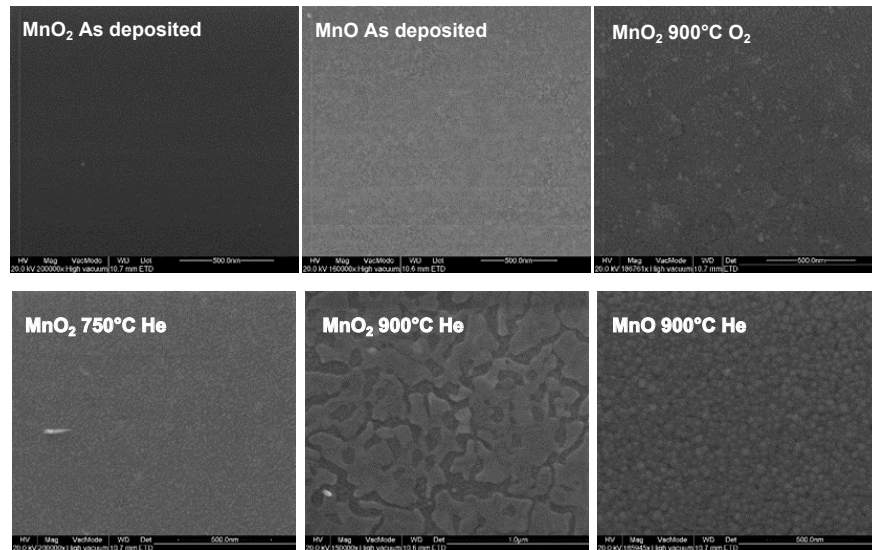

Figure 3: SEM imaging on selected samples to confirm the surface topology found from AFM.

Tafel plot

To illustrate the difference in activity between the MnO_2 and derived Mn_2O_3 OER catalysts, a Tafel plot resulting from the linear sweep voltammogram is shown in figure 4. It can be seen that MnO_2 and Mn_2O_3 show similar onset potentials. However, the overpotential at $10\,mA\,cm^{-2}$ of both catalysts is very different and since the electrodes are operating in diffusion limitation regime during the linear sweep, this difference is best explained by a difference in Tafel slopes in figure 4. The derived Tafel slopes are $68\,mV\,dec^{-1}$ and $96\,mV\,dec^{-1}$ for MnO_2 and Mn_2O_3, respectively. Extrapolation of these results would result in overpotentials of $529\,mV$ and $592\,mV$ for MnO_2 and Mn_2O_3, respectively, indicating a higher activity for the MnO_2 films.
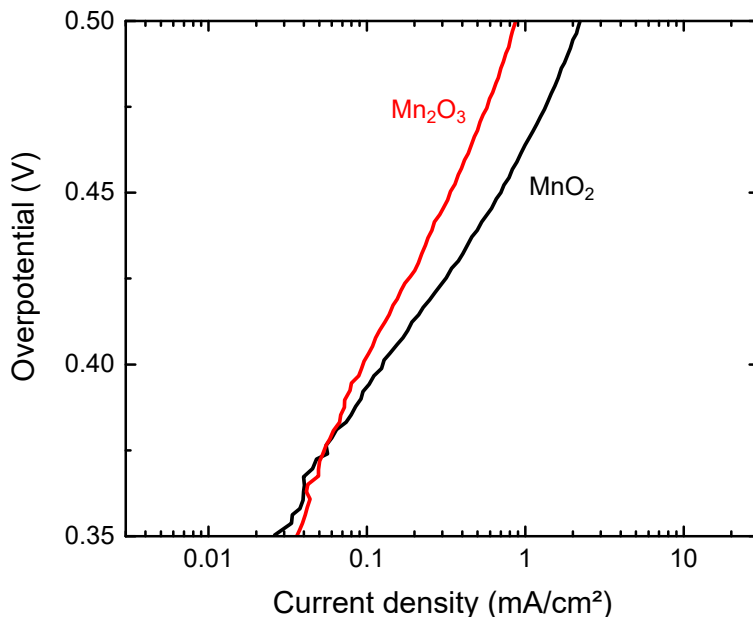

Figure 4: Tafel plot of the manganese oxides under investigation. Only the linear regime is shown to highlight the difference in activity.

References

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