

Electrochemical deposited Manganese- and Cobalt-Oxides as catalysts for water oxidation

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Solar radiation can be used as a nearly inexhaustible energy source to convert light into chemical energy. In this way fossil fuels can be replaced and a sustainable society established in the future. One promising concept is the production of hydrogen by light powered water electrolysis. In order to provide the required high photo-voltage suitable semiconducting materials or combinations of them are under development which should be stable under electrochemical conditions. However, none of them reveals sufficiently high catalytic activity towards electrochemical water splitting so that high overvoltages have to be overcome in addition.

Especially the slow kinetics of the anodic oxygen evolution reaction (OER) limits the overall efficiency of water electrolysis. Therefore, a challenging task is the development of low cost, but highly efficient oxygen evolving catalysts, which can be combined with semiconducting absorber materials.

In this contribution manganese oxides, such as α - Mn_2O_3 , Mn_3O_4 and $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ as well as cobalt oxide (Co_3O_4), were prepared as thin layers by anodic deposition onto F:SnO_2 -glass substrates from a manganese and cobalt containing solution, respectively. This preparation method allows the formation of highly active OER catalysts even at low temperatures, a precondition to avoid annealing damages of heat sensitive photovoltaic device structures which could be used as PV-hybrid electrolyzers.

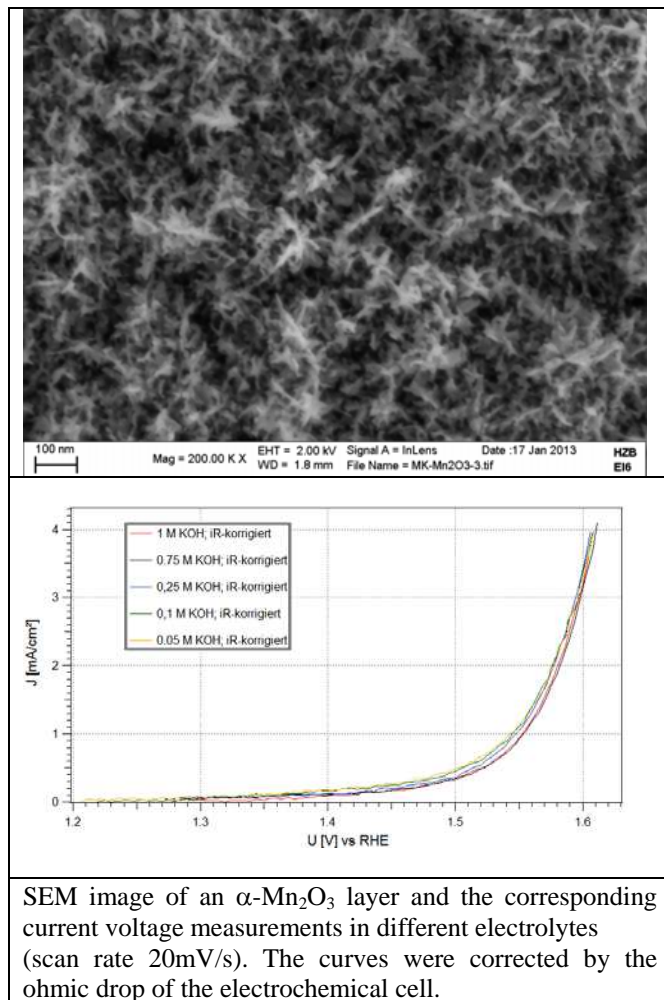
Furthermore, sputtered manganese oxide layers were produced varying substrates and process parameters and compared with electrodeposited layers in terms of crystallinity and morphology related to electrochemical activity towards OER.

X-ray Diffractometry (XRD), Raman spectroscopy and Scanning Electron Microscopy (SEM/EDX) as well as Transmission Electron Microscopy (TEM) confirmed the presence of pure phases in all pristine films as well as changes in the crystallinity after heat treatment steps of the deposited layers.

The electrochemical characterization was performed by CV-measurements and by differential electrochemical mass spectrometry (DEMS) in electrolytes at pH values ranging from 7 to 14. DEMS allows us to simultaneously detect oxygen during cycling and to distinguish between the OER reaction and other oxidation processes occurring at the electrode/electrolyte interface. By that in all cases oxidation currents are observed prior to the onset of the OER. In-line XPS and valence-band spectra were performed at the Berlin synchrotron radiation source, BESSY, in order to detect changes in the oxidation state and the chemical environment of manganese and cobalt atoms at the surface of the electrodes.

As a result, α - Mn_2O_3 and Co_3O_4 reveal the highest electrochemical activity towards OER at a low overvoltage of about 320mV at a current density of $1\text{mA}/\text{cm}^2$ and pH14. Furthermore the samples have a remarkable stability in alkaline electrolytes. Whereas cobalt oxide

shows a change in the valence band spectra as a function of the applied potential while manganese oxides mainly remained unchanged. Possible reasons and conclusions of the data are discussed in view of the question which oxidation states of manganese or cobalt could be responsible for the high electrochemical activity.



SEM image of an α - Mn_2O_3 layer and the corresponding current voltage measurements in different electrolytes (scan rate 20mV/s). The curves were corrected by the ohmic drop of the electrochemical cell.