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Evaluation of electrodeposited α -Mn₂O₃ as a catalyst for the oxygen evolution reaction

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ABSTRACT

α -Mn₂O₃ is of interest as a low-cost and environmentally benign electrocatalyst for the Oxygen Evolution Reaction (OER) in the process of water splitting. Mechanically stable α -Mn₂O₃ electrodes are prepared by annealing of galvanostatically deposited MnOOH_x layers on F:SnO₂-coated glass. The overpotential η to achieve a current density of $j = 10 \text{ mAcm}^{-2}$ decreases from 590 to 340 mV with increasing layer thickness. Differential capacitance measurements reveal that this high OER activity can be attributed to the large electrochemically active surface area (ECSA), which scales linearly with the thickness of these highly porous and electrolyte-permeable films. The oxide layers exhibit a reversible oxidation behavior from Mn(III) \leftrightarrow Mn(IV). Although the intrinsic activity is small compared to that of other OER catalysts, such as NiFeO_x, the combination of high ECSA and good electrical conductivity of these α -Mn₂O₃ films ensures that high OER activities can be obtained. The films are found to be stable for > 2 h in alkaline conditions, as long as the potential does not exceed the corrosion potential of 1.7 V vs. RHE. These findings show that α -Mn₂O₃ is a promising OER catalyst for water splitting devices.

1. Introduction

The generation of hydrogen by solar-driven electrochemical water splitting is a promising approach to store renewable energies as a non-fossil fuel in large quantities. To achieve this goal, earth-abundant and highly active catalysts for both half reactions, the Hydrogen Evolution Reaction (HER) and the kinetically more challenging Oxygen Evolution Reaction (OER), have to be identified and developed for a mass market. These catalysts can be used in advanced electrolyzers, for example photoelectrochemical water splitting devices, by being deposited as co-catalysts on the surface or at the back contact of suitable photoelectrodes.

In nature, OER active catalysts are found in photosystem II which is located in the thylakoid membrane of the chloroplasts in the cells of plants and green algae. The catalytic center in this system consists of CaMn₄O₅-clusters embedded in a complex protein environment. In attempts to mimic this OER catalyst, metal oxides based on low-cost, earth-abundant and environmentally benign manganese compounds and complexes are being intensely studied. This interest is caused by the wide gamut of different and stable oxidation states which manganese ions can adopt, ranging from Mn^{II} to Mn^{VII}, and in addition by its relatively fast redox kinetics. These properties also form the basis for the application of manganese oxides as anode material in rechargeable

lithium ion batteries [1,2] and in supercapacitors [3]. Besides approaches to mimic the O₂-evolving center in PS II in metal organic complexes [4,5], inorganic Ca-Mn-oxides and Mn-oxides have been successfully synthesized and tested with respect to their ability to act as efficient OER catalysts [6–16]. Among these manganese-based catalysts, α -Mn₂O₃ showed the most promising activity in alkaline solution. It is able to produce a current density of 10 mAcm⁻² at an overpotential of $\eta = 360 \text{ mV}$ in 1 M KOH [14]. α -Mn₂O₃ can be synthesized via a simple and low-cost galvanostatic deposition on conductive substrates following a recipe for the preparation of MnO₂ layers [3]. In our modified process, amorphous MnOOH_x is deposited from a solution containing Mn²⁺-cations in a first step and afterwards annealed in air at 773 K to form crystalline α -Mn₂O₃ [17]. α -Mn₂O₃ possesses an orthorhombic crystal structure (space group *Pcab*), in which Mn³⁺-cations are octahedrally coordinated by O²⁻-anions. These [MnO₆] octahedra are sharing corners and edges similar to the mineral bixbyite (Fe_xMn_{1-x})₂O₃ [18]. Due to the spin state 3d³ of Mn(III) in α -Mn₂O₃ highly distorted [MnO₆] octahedra are found in the lattice leading to a variety of different Mn–Mn and Mn–O distances which might beneficially influence the OER activity [18].

To prepare an OER active photoanode in a light-driven electrolysis device [19,20], the co-catalyst deposited on top of the light sensitive absorber has not only to be catalytically active, but also optically

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transparent in order to ensure that the incident light reaches the photoabsorber with negligible intensity losses. Since most catalysts are colored to some extent, the specific activity of the catalyst needs to be as high as possible. This demand is less stringent for catalysts used in electrolyzers, where optical transparency is not required.

In the literature, α -Mn₂O₃ and also other MnO_x phases were electrochemically deposited as porous films with different thicknesses [8,14,16]. McCrory et al. [21,22] described a benchmarking protocol to evaluate activity, stability, and Faradaic efficiency of electrodeposited OER catalysts. The primary figure of merit is the overpotential required to achieve a current density of 10 mAcm⁻². Moreover, turnover frequencies and specific activities can be calculated from the estimated electrochemical active surface area (ECSA) of the electrodes enabling a meaningful comparison of different catalysts. In ref. [21] and [22] binary (e.g. CoO_x, NiO_x, IrO_x) and ternary (e.g. CoFeO_x, Ni(Ce,Co,Cu,-Fe,La)O_x) electrocatalysts were investigated in acidic and alkaline electrolytes. The authors estimated the ECSA for each electrode material from the electrochemical double-layer capacitance C_d divided by the specific capacitance C_s of a smooth planar electrode surface of the same electrode material (see also eq. 1 below). Since the determination of C_s is difficult, a mean value of 40 μ F cm⁻² was used by them for all catalysts measured in 1 M NaOH. This value was derived from an extensive survey of literature data (see SI of [21,22]). The stability of the catalysts was evaluated by monitoring the change in overpotential needed to keep the current density constant at 10 mAcm⁻² after two hours of operation. The electrodes were rotated with 1600 rpm to get rid of the O₂ formed at the surface, which could otherwise block the parts of the electrode area.

In this work we determine for the first time the specific activity of highly porous α -Mn₂O₃ layers and compare this result with other metal oxide OER catalysts. To this end, α -Mn₂O₃ of different film thicknesses are electrochemically deposited on conductive FTO glass substrates and characterized by cyclic voltammetry (CV) to determine their ECSA and their activity towards the OER. The morphology, crystal structure, optical properties, and stability of the films were also investigated. Despite the modest intrinsic OER activity of α -Mn₂O₃, a surprisingly low overpotential of 340 mV is needed to generate a current density of 10 mAcm². We will explain the origin of this high OER activity, and discuss the potential application and limitations for these electrodeposited α -Mn₂O₃ films in practical water splitting devices.

2. Experimental section

2.1. Materials

MnSO₄·H₂O (≥98%), K₂SO₄ (≥98%), NiSO₄·6 H₂O (≥98%) were obtained from Sigma-Aldrich and 1 M KOH solution from Merck. Conductive glass substrates (F:SnO₂/glass, TEC 7) were purchased from Pilkington and cleaned in an ultrasonic bath in acetone (Sigma-Aldrich, 98%) for 10 min, rinsed with demineralized water and dried under air.

2.2. Film preparation

α -Mn₂O₃-films were deposited on FTO (1 × 1.3 cm²) by galvanostatic deposition at a current density of 0.25 mAcm⁻² in an electrochemical glass cell with a three electrode arrangement, consisting of an Ag/AgCl reference electrode (+0.199 V vs. NHE) and a commercial coiled platinum wire as a counter electrode. The deposition was carried out in a solution of 0.5 M MnSO₄ and 0.5 M K₂SO₄ (pH ≈ 5.5) using a VersaSTAT 3 potentiostat from Princeton Applied Research. Afterwards the films were thoroughly rinsed with demineralized water and dried in air. In order to obtain the crystalline α -Mn₂O₃ phase, the samples were annealed at 773 K in air for 1 h.

2.3. Electrochemical measurements

Evaluation of the OER-activity of the films was performed using cyclic voltammetry measurements in an electrochemical cell with a three-electrode arrangement consisting of an Ag/AgCl reference electrode (+0.199 V vs. NHE), a commercial coiled platinum electrode as counter electrode and the respective deposited films as working electrode. The potential of the working electrode was controlled with a Versastat 3 potentiostat from Princeton Applied Research. The evaluation of the OER activity of the films was conducted in 1 M KOH with a sweep rate of 5 mV/s directly after a potentiostatic pre-oxidation step at a potential of 1.45 V vs. RHE for t = 0.5 h. As it is well known that KOH solutions can contain impurities (e.g. Fe) which could be deposited and influence the activity of OER catalysts, we tested our KOH solution by ICP-MS [23]. No impurities could be found within the detection limit of our ICP-MS system (e.g. 0.6 μ g/l for Fe). Nevertheless, incorporation of impurities cannot be ruled out entirely. The measurements were manually corrected for iR-drop after measuring the total cell resistance with an impedance measurement from 100 kHz to 10 Hz with an amplitude of 10 mV at the open-circuit potential.

Galvanostatic stability measurements of the films were performed at a current density of j = 10 mAcm⁻² for t = 2 h in 1 M KOH with a three-electrode arrangement using an Ag/AgCl reference electrode, a coiled platinum wire as a counter electrode and a rotating working electrode (~400 rpm). The rotation axis was in line with the substrate plane. The measured potential was again corrected for the iR-drop, as described above.

The differential capacitance C_d of the α -Mn₂O₃ films was determined by fast potential sweep curves in a potential range from 1.2–1.3 V vs. RHE, where the Faradaic currents are negligible. The electrolyte was 1 M KOH, the sweep rates varied from 10 to 50 mV/s.

All potentials were referred to RHE calculated from the experimental potential E_{measured}, the potential of the reference electrode E_{Ag/AgCl} = +0.199 V and the pH of the electrolyte solution according to the formula E_{RHE} = E_{measured} + E_{Ag/AgCl} + 0,059·pH. The overpotential η for the OER was determined using the equation $\eta = E_{RHE} - 1.23$ V.

2.4. Structural and morphological characterization

XRD patterns of the α -Mn₂O₃ films were obtained with a Bruker D8 Advance diffractometer with a CuK α ($\lambda = 1.5406$ Å) x-ray tube in Bragg – Brentano geometry and a Sol-X energy dispersive detector. The measurements were performed in the 2-theta angle range of 20°–70° with a step size of 0.02° and an integration time of 10 s/step. Scanning electron microscopy (SEM) images were recorded using a Zeiss LEO 1530 Gemini.

3. Results and discussion

3.1. Electrochemical deposition and film morphology

Amorphous MnOOH_x films with different thicknesses were deposited onto conducting FTO substrates via galvanostatic deposition from a Mn²⁺ containing solution (deposited charge Q = 1–400 mCcm⁻²). Fig. S1a shows the current voltage curve of a FTO working-electrode immersed in the Mn²⁺ solution from which an onset of the deposition current at about E ≈ 1.1 V vs. RHE can be identified. The E-Q curve of the galvanostatic deposition process (Fig. S1b) shows a sharp increase of the potential in the first two minutes, before a constant deposition potential E_D = 1.41 V is reached. Obviously, the growth mode changes as the deposition onto the FTO is energetically favored compared to the growth on an already formed MnOOH_x seed layer. Within the applied potential range the current is exclusively caused by the oxidation of Mn²⁺, resulting in the formation of a MnOOH_x film. The OER activity of both the FTO substrate as well as the formed MnOOH_x layers are negligible small at pH 5. The constant deposition potential indicates

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