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APPLICATION OF POTASSIUM BIRNESSITE THIN FILM/FTO MODIFIED ELECTRODES AS NONENZYMATIC SENSORS FOR HYDROGEN PEROXIDE

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1. INTRODUCTION

The scientific interest in the development of electrochemical sensors for hydrogen peroxide based on transition element substances, especially manganese compounds modified electrodes is very attractive nowadays.

There are different kinds of electrochemical methods for determination of H_2O_2 published in the literature due to the materials that are used for modification of the working electrodes. The most simple classification of the electrochemical methods is described as follows [1-7]:

A) General classification

Enzymatic (based on peroxidase enzymes):

Advantages: low detection limit; high sensitivity, selectivity, wide range of linear response…

Disadvantages: instability, high cost, complicated immobilization, denaturation, limited lifetime and poor reproducibility…

Nonenzymatic:

Advantages: sufficiently low det. lim., high sensitivity, selectivity, wide linear range, reproducibility, robustness…

Disadvantages: sometimes with complex design and expensive if noble and/or rare elements are used…

B) Classification of sensors according to type of materials used for electrode modification:

Metal Hexacyanoferrates; Heme Proteins; Carbon Nanotubes; Graphene; Metal Oxides; Metalloporphyrins…

→ Mn-compounds based amperometric sensors in our main interest from this group!

2. SYNTHESIS OF $MnCO_3$ THIN FILMS ON FTO-COATED GLASS SUBSTRATES

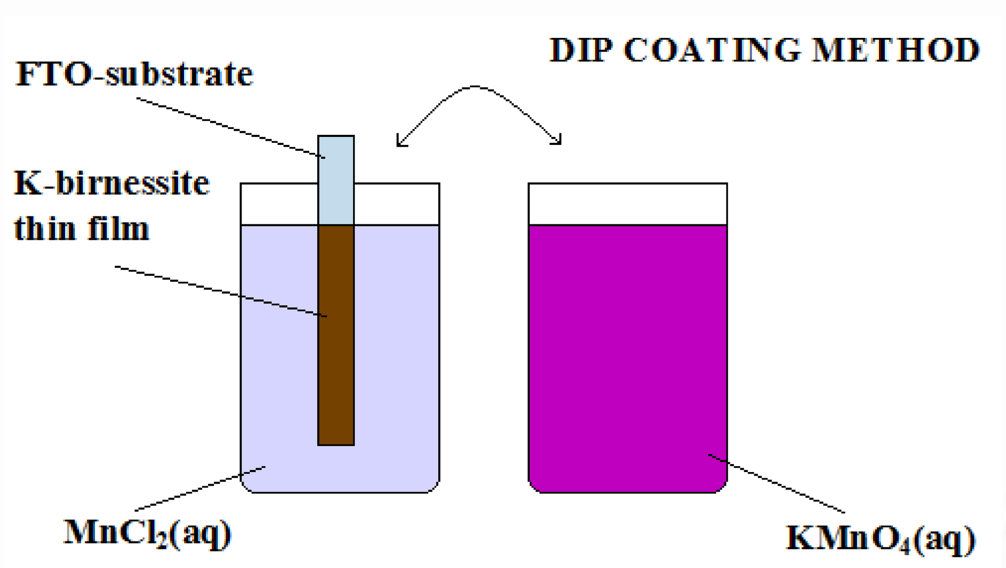
Precursors: $MnCl_2 \cdot 4H_2O$ and $KMnO_4$

Chemical background of the synthesis [8]:

$$0.54K^+(aq) + Mn^{2+}(aq) + MnO_4^-(aq) + 2xH_2O(aq) \longrightarrow 2K_{0.27}MnO_2 \cdot xH_2O(s)$$

where $x \approx 0.54$

Apparatus for Chemical Deposition



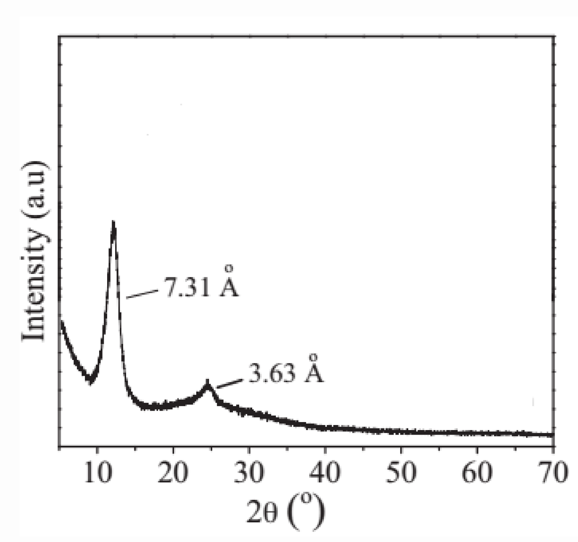
Simple successive immersion of the FTO [fluorine doped tin(IV) oxide] coated glass substrate in the two solutions for 10 times (2-3 s in each solution)

FTO-fluorine doped tin(IV) oxide

3. CHEMICAL AND STRUCTURAL ANALYSIS

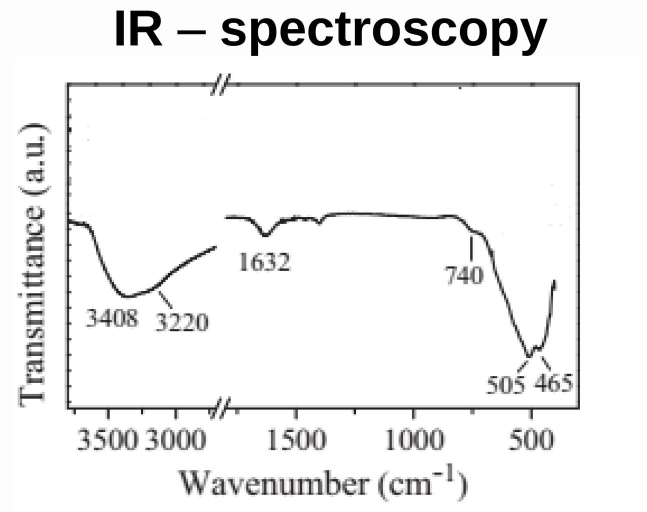
The XRD pattern of the as-deposited thin film exhibits a high background typical of poorly crystalline phase and only two very broad peaks are visible. The positions of these peaks agree well with the two strongest peaks characteristic of hexagonal K-birnessite with composition $K_{0.27}MnO_2 \cdot 0.54H_2O$ (JSPDS 86-666). More probably, our sample has very similar composition. Birnessite-type structure with monoclinic or hexagonal symmetry consists of single sheets of edge-sharing MnO_6 octahedra (usually Mn^{4+}/Mn^{3+} ions) as there is a vacancy in one over every six octahedral sites [8]. The MnO_6 octahedral layers are separated from each other by a distance of around 7 Å [8]. The interlayered space contains mono-potassium cations and water molecules. In our K-birnessite the d-spacing between the MnO_6 layers is 7.31 Å [8].

XRPD



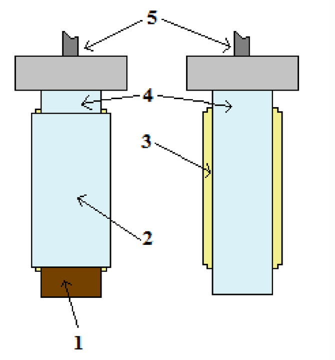
The birnessite-type structure is characterized in the IR spectra by three prominent bands at around 518–510 cm^{-1}, 480–470 cm^{-1} and around 420 cm^{-1} [8]. The frequency positions of these bands are little changed on variation of the type of the incorporated metal ions. The sharpness of the band at 420 cm^{-1} indicates the crystalline order of the birnessite compound [8]. The highest frequency band is related with the asymmetric stretching vibrations of MnO_6 (Mn^{4+}/Mn^{3+}) octahedral involving the displacement of manganese ions in direction perpendicular to the MnO_4 plane [8]. The bands below 500 cm^{-1} can be assigned mainly to the deformation modes of the MnO_6 octahedral [8].

IR – spectroscopy



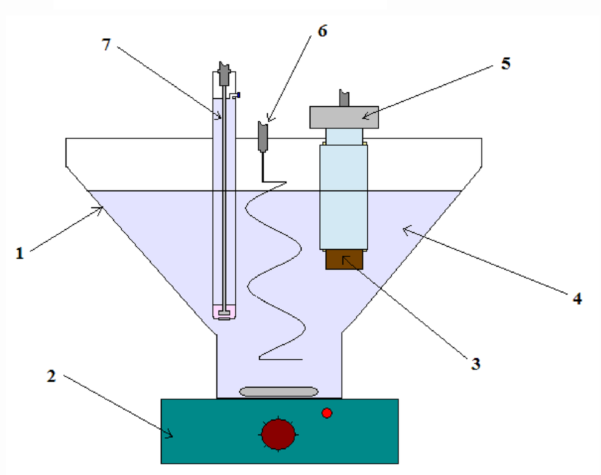
4. APPARATUS FOR ELECTROCHEMICAL MEASUREMENTS

Setup of the $K_{0.27}MnO_2 \cdot xH_2O$/FTO thin film modified electrode



1. $K_{0.27}MnO_2 \cdot xH_2O$ thin film;
2. Microscopic slide;
3. Silicon glue;
4. FTO-substrate;
5. Electrical contacts

Original idea for providing constant surface area of the thin film that is dipped into the electrolyte!



1. Electrochemical cell;
2. Electromagnetic stirrer;
3. $K_{0.27}MnO_2 \cdot xH_2O$ thin film;
4. Electrolyte: phosphate buffer (KH_2PO_4/K_2HPO_4) with pH = 7.5;
5. WE – working electrode ($K_{0.27}MnO_2 \cdot xH_2O$/FTO modified electrode);
6. CE – counter electrode (Pt-wire);
7. RE – reference electrode (Ag/AgCl)

Construction of the electrochemical three-electrode system

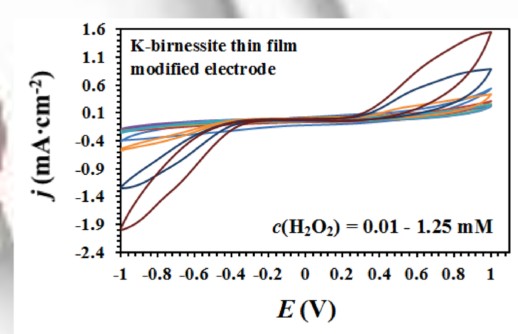
5. EXAMINATION OF THE ELECTROCHEMICAL PROPERTIES WITH CYCLIC VOLTAMMETRY (CV) AND CHRONOAMPEROMETRY (CA)

CV – measurements

Potential window: from -1 to +1 V

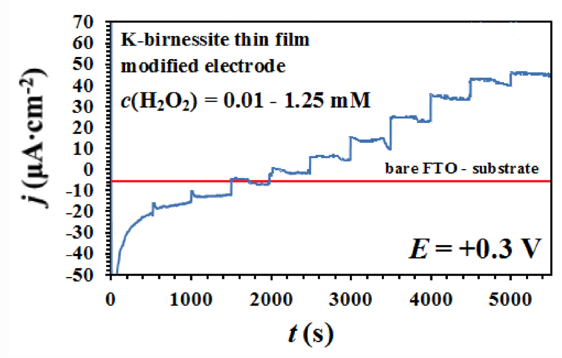
Scan rate: 20 mV·s^{-1}

- Slight Ox and Red peaks are observed



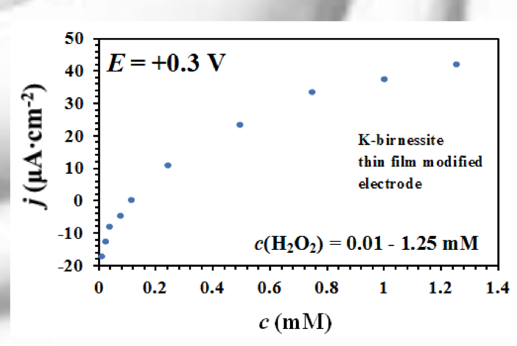
Applied potential during CA: +0.3 V

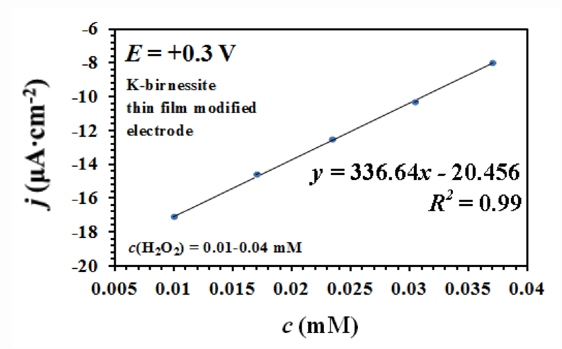
CA – measurements



There is no observed amperometric response from the bare FTO substrate

The total amperometric dependence in the whole examined concentration interval actually represents a curved line





The amperometric function is linear in small concentration intervals

Detection limit: 10 µM

Sensitivity: 336.64 · 10^3 µA·cm^{-2}·M^{-1} in c = 0.01-0.04 mM

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CONCLUSION:

The best results are obtained under oxidation potential in concentration range of H_2O_2 from 10 up to 1500 µM. The lowest detection limit was 10 µM and the sensitivity of the sensor is 353 µA·cm^{-2}·mM^{-1} (in concentration range 10-50 µM). The calibration plot is associated with a linear regression line and coefficient of R^2 = 0.99.