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DESIGN OF NONENZYMATIC AMPEROMETRIC SENSOR FOR H_2O_2 BASED ON ELECTRODES MODIFIED WITH NANOSCALED $MnCO_3$ THIN FILMS

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1. INTRODUCTION

The present study is related to the development of nonenzymatic amperometric sensors for electrocatalytic detection and quantification of (H_2O_2) based on manganese compounds modified electrodes. It is widely known that hydrogen peroxide finds use as a strong oxidizer, bleaching agent, disinfectant, propellant, in chemical industry, also in medicine, pharmacy, food and beverage industry and etc., so its accurate and precise detection and quantification is very important especially in micromolar quantities [1-7].

There are numerous methods for detection and quantification of H_2O_2. These include redox titration methods, chemiluminescence, fluorescence and fluorimetry methods, spectrophotometry, chromatography and electrochemical methods based on sensing the reduction or oxidation of H_2O_2 on an working electrode. All these methods are characterized by distinct advantages and disadvantages. For example, some of these are more and/or less complicated, expensive and sometimes insufficiently selective. However, the electrochemical sensing methods, which are based on transition metal compounds modified electrodes offer most satisfactory level in terms of low detection limits; selectivity, simplicity and cost-effectiveness [1-7].

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

Precursors: $MnCl_2 \cdot 4H_2O$ and $(NH_2)_2CO$

Chemical background of the synthesis [8]:

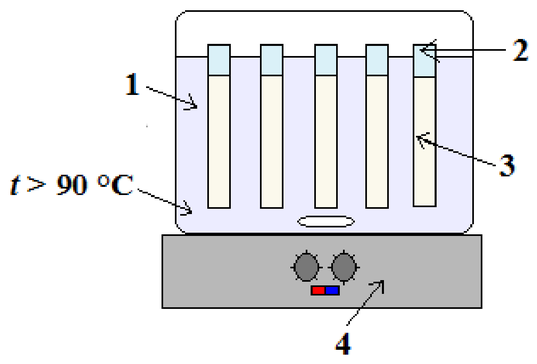
$Mn^{2+} + xH_2NCONH_2 \longrightarrow [Mn(H_2NCONH_2)_x]^{2+}$

$[Mn(H_2NCONH_2)_x]^{2+} + (x+y+1)H_2O \longrightarrow MnCO_3 \cdot yH_2O + (x-1)CO_2 + 2NH_4^+ + 2(x-1)NH_3$

where x = 4 and/or 6

1. **Aqueous solution of precursors;**
2. **Electroconductive FTO – coated glass substrate;**
3. **$MnCO_3$ thin films;**
4. **Electromagnetic stirrer and heater**

Apparatus for Chemical Bath Deposition

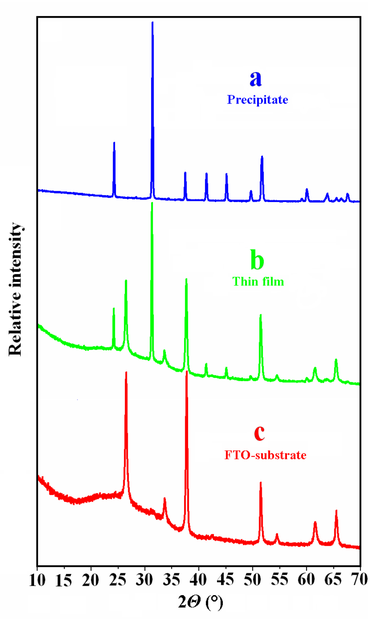


FTO-fluorine doped tin(IV) oxide

The synthesized thin films are with three different thicknesses of 75, 100 and 150 nm.

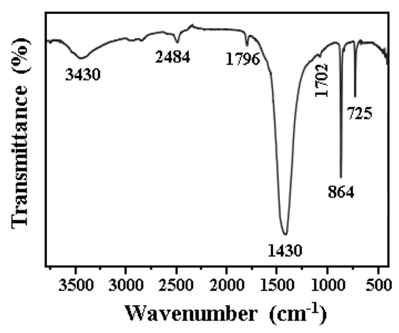
3. CHEMICAL AND STRUCTURAL ANALYSIS

XRPD



- The chemical composition and the structure of the as deposited thin films and the chemical bath precipitate corresponds to well crystalized rhodochrosite phase manganese(II) carbonate (JCPDS 83–1763);
- The XRD patterns **(b)** of the $MnCO_3$ thin film deposited on the substrate are overlapped with the patterns of the FTO (fluorine doped SnO_2 – JCPDS 46–1088);
- The distinguishing of the reflections is resolved by separately recording the precipitate from the CBD beaker and a bare FTO – coated glass substrate, as shown on **(a)** and **(c)**, respectively.

IR – spectroscopy

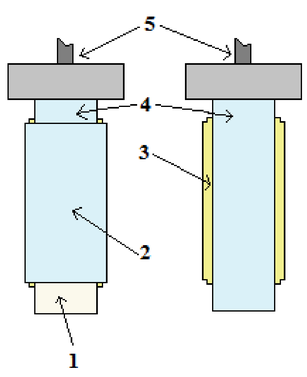


The IR spectrum of the thin films is dominated by the characteristic vibrations of the carbonate ions [8]: stretching C=O vibrations at 1072 (v_1) and 1430 cm^{-1} (v_3); bending OCO vibrations at 864 (v_2) and 725 cm^{-1} (v_4). The weak bands at 1796 and 2484 cm^{-1} arise from the combination vibrations like (v_1+v_4) and ($2v_2+v_4$), respectively.

In addition, a weak broad band centered at 3430 cm^{-1} with a shoulder at around 3530 cm^{-1} are also visible in the ν(OH) mode region. More probably, they are due to water molecules adsorbed on the surface [8].

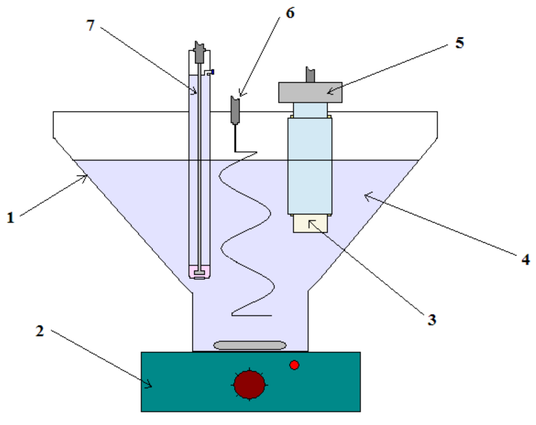
4. APPARATUS FOR ELECTROCHEMICAL MEASUREMENTS

Setup of the $MnCO_3$/FTO thin film modified electrode



1. **$MnCO_3$ thin film;**
2. **Microscopic slide;**
3. **Silicon glue;**
4. **FTO-substrate;**
5. **Electrical contacts**

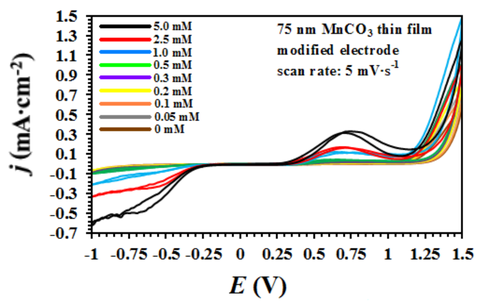
Original idea for providing constant surface area of the $MnCO_3$ thin film!



1. **Electrochemical cell;**
2. **Electromagnetic stirrer;**
3. **$MnCO_3$ thin film;**
4. **Electrolyte: phosphate buffer (KH_2PO_4/K_2HPO_4) with pH = 7.5;**
5. **WE – working electrode ($MnCO_3$/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)



The sensing mechanism is examined with CV in the potential window from -1.0 up to 1.5 V and concentrations of H_2O_2 from 0 up to 5.0 mM

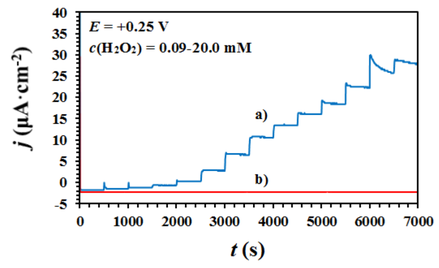
MOST PROBABLE CHEMICAL BACKGROUND OF THE ELECTROCATALYTIC SENSING MECHANISM

The processes in the diffusion layer of the working electrode are described with the following equations:

Eq. 1: $MnCO_3 \rightarrow Mn^{2+} + CO_3^{2-}$
Eq. 2: $Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2$
Eq. 3: $2Mn(OH)_2 + 2OH^- \rightarrow Mn_2O_3 + 3H_2O + 2e^-$
Eq. 4: $Mn_2O_3 + 2OH^- \rightarrow 2MnO_2 + H_2O + 2e^-$
Eq. 5: $Mn_2O_3 + H_2O_2 \rightarrow 2MnO_2 + H_2O$
Eq. 6: $2MnO_2 + 2H_2O_2 \rightarrow 2Mn(OH)_2 + 2O_2$
Eq. 7: $2MnO_2 + H_2O_2 \rightarrow Mn_2O_3 + H_2O + O_2$

Net equation from Eq. 3, 4, 5, 6 and 7:
$2H_2O_2 + 3OH^- \rightarrow 3H_2O + {}^3/_2O_2 + 2e^-$

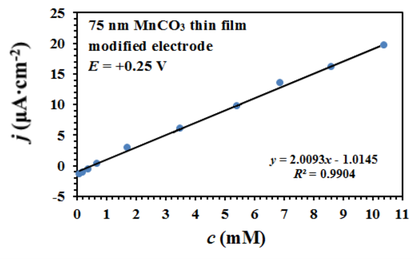
The amperometric response *vs* analyte concentration is examined with CA (as current vs time)



a.) $MnCO_3$/FTO – modified electrode → linear amperometric response;
b.) Bare FTO coated substrate → no response!

The current (or current density) is linearly dependent from H_2O_2 concentration:

$j(\mu A \cdot cm^{-2}) = a(\mu A \cdot cm^{-2}) + b(\mu A \cdot cm^{-2} \cdot mol^{-1} \cdot dm^3) \cdot c(mol \cdot dm^{-3})$
sensor sensitivity



Detection limit: 90 μM
Sensitivity: 2.01 $\mu A \cdot cm^{-2} \cdot mM^{-1}$
in concentration range 0.1-10 mM
Response time: 3 s

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CONCLUSION:

The best sensing properties towards hydrogen peroxide are obtained under oxidation potential of +0.25 V when using modified electrode with 75 nm thickness of the $MnCO_3$ thin film and concentrations of H_2O_2 from 0.1 up to 10 mM. The lowest detection limit is 90 μM and the sensitivity of the sensor is 2.01 $\mu A \cdot cm^{-2} \cdot mM^{-1}$ with response time od 3 s. The calibration plot is associated with a linear regression line and coefficient of $R^2 = 0.99$.