ELECTRODEPOSITED NANOSTRUCTURED POLYFUNCTIONAL TIN-BASED ELECTROCATALYST

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Abstract
The tin-based materials are widely used in sensor technology and also for the catalyst formation. The obtaining of materials with the highest specific surface area, which the volume-porous nano-ordered and structured material can provide, is an important task. In this investigation the electrodeposition of compact nanostructured cathodic tin deposits from sulfate solution with the additive OP-10 has been proposed. The presence of appropriate type of additives in the solution and significant deposition time caused the formation of nanostructured tin surface. It has been established that the highest productivity of CO₂ electroreduction was achieved on electroformed tin electrodes whose deposition time was two hours. In the open type membrane cell at CO₂ bubbling rate of 5 ml/min in a potentials range −1.5...−1.8 V the current efficiency varies between 11...12.5 %. It has been shown that the maximal rate of sodium formate formation on the deposited nanostructured catalyst was observed at the electrode potential −1.8 V and was twice higher than on polished tin.

Keywords: sulfate solution; tin-based catalyst, open type cell, sodium formate, current efficiency.

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Introduction

The tin-based materials are widely used in sensor technology and also for the catalyst formation [1–3]. In metallic form tin is used as a catalyst for carbon dioxide electroreduction due to high hydrogen overvoltage [4–6]. The electrochemical reduction of CO2 to the formic acid or in the alkaline medium to formates – effective liquid fuel – is of major concern [7–11].

One of the most significant parameters which determines the expediency of catalyst application except selectivity is the rate of the target product formation. The rate or productivity of the process, as it is known, rises with the increase in the specific surface area of the catalyst. Catalysts with bulk porous nanoscale structured surface have the highest catalytic activity [12–16].

Electrodeposition of metal on the constant or pulse current is one of the processes of metal catalysts formation. This process, in particular, is used for obtaining tin-based catalytic electrode materials with a nanoscale structure [10; 13–19].

As already noted, the obtaining of materials with the highest specific surface area, which the volume-porous nano-ordered and structured material can provide, is an important task as well. Such structures are also called capillary porous surfaces (CPS). Production of CPS by copper electrodeposition was described in the works of M. I. Donchenko and A. N. Aleksandrovsky, where the achievement of the necessary properties of the deposition was realized by veering of the working current density, the solution composition and a certain kind of additives [20–22]. In the present work, the approach that was previously proposed and used for the electrodeposition of copper CPS, is applied for the preparation of tin nanostructured catalytic materials.

Experimental Section

The surface morphology of tin deposits was examined by ZEISS EVO 50XVP scanning electron microscope equipped with an INCA450 energy dispersive analyzer and INCApent-FETx3 detector and the HKL CHANNEL-5 system for the diffraction of reflected electrons from OXFORD.

The electrodeposition of tin catalysts was carried out in solutions containing (g/l): №1 SnSO4 – 40, H2SO4 – 70, gelatin – 2; №2 SnSO4 – 40, H2SO4 – 70, gelatin – 2, phenol – 30; №3 SnSO4 – 40, H2SO4 – 70; gelatin – 2; additive OP-10 – 1.

Tin catalyst electrodeposition, voltammetric and chronopotentiometric measurements were taken in a three-electrode cell with a PI-50-1 potentiostat. Cathode polarization curves were obtained at a scan rate of 10 mV/s. Current and potential values were registered with a Hantek DSO 6022be USB oscilloscope. Potentials were measured relative to a saturated silver-chloride reference electrode (Ag/AgCl).

Electroreduction of CO2 was carried out in potentiostatic conditions using an open type two compartment membrane cell with cation exchange Nafion 117. An aqueous solution of 0.1 M NaHCO3 pH 6.8 was used as an anolyte, 0.5 M NaHCO3 was used as an anolyte. The acidity of the catholyte was regulated by addition of minute quantity of saturated sulfuric acid. As a cathode, rectangular plates of copper foil on
which a tin catalyst was deposited were used, the cathode working area was 3.5 cm². A stainless steel plate was used as an anode. A catholyte was saturated with CO₂ by bubbling for one hour before electrolysis. CO₂ gas at a flow rate of 5 ml·min⁻¹ was supplied continuously to the catholyte using glass capillary throughout the electroreduction experiments. The Kipp apparatus with a Drexel flask filled with distilled water for gas purification was used as a source of CO₂. The amount of formate and current efficiency (FE) were determined by permanganometric titration using the following method. In a conical flask to 5 ml of a sample of a formate containing solution a saturated sodium carbonate solution was added to pH 11 and then 5 ml of 0.1 M KMnO₄ was added. Then, the resulting mixture was heated up to 50 °C to accelerate the oxidation reaction, after 5 minutes 2 ml of 1.5 M H₂SO₄ was added to create the acidic medium. After which the remainder of the permanganate was titrated with 0.1 M H₂C₂O₄. The amount of formate was calculated from the difference in the volumes of H₂C₂O₄, which was consumed for the titration of the sample and 5 ml of the original 0.1 M KMnO₄. All the solutions were prepared from CP or analytical grade reagents (Khimlaborreaktiv) in distilled water. Fixed channels were used for the preparation of standard solutions H₂C₂O₄ and KMnO₄.

Results and its discussion

Tin catalysts electrodeposition. As a result of the electrodeposition of tin from sulphate electrolytes with various types of organic additives, compact deposits without vickers and dendrites were obtained, and the SEM images of the surface are shown in Fig.1.

As can be seen from Fig. 1a, macrocrystalline deposits with a smoothed surface are obtained from an electrolyte containing phenol and gelatin. Externally, such coatings are semi-bright. A velvet like deposits were obtained from the electrolyte containing gelatin and OP-10, the surface microstructures of which are shown in Fig. 1 b, c. As it can be seen (Fig. 1, b, c), the crystals have a more pronounced pyramidal shape than in Fig. 1 a, with the same thickness. In addition, on the surface of deposits Fig. 1 b, there are nanoscale (about 100 nm thick) grooves. With an increase in deposition time (Fig. 1c), the deposit structure changes: the number of pyramidal crystals decreases, but they become more elongated (needle-shaped), in addition, nanoscale grooves are smoothed. Externally, deposits obtained from electrolytes №. 2, 3 (Fig. 1b, c) are compact. The intensity of their color depends on the angle of the sun's rays. In addition, deposits are well wetted and absorbed water, which indicates their capillary properties.

Fig. 1. SEM-image of Sn deposits obtained from sulfate electrolytes: a – №2; b, c – №3. Deposition time, hours: a – 1; b – 2; c – 4. Current density, A/dm²: a – 1; b, c – 0.5.
The OP-10 additive is a wetting agent that has the gross formula \(O(CH_2-CH_2-O)_{10}CH_2-CH_2-OH\) and is used in this work. OP-10 belongs to the class of additives that, for the first time, was proposed by M.I. Donchenko and A.N. Aleksandrovsky for the deposition of copper capillary-porous coatings. According to their works \([20; 21]\), the necessary conditions for electrodeposition of coatings with high capillary properties and a developed microstructured surface are: the presence of additives of the appropriate type in the solution, diffusion limitations during metal electrodeposition, significant (several hours) deposition time.

To explain the effect of additives on the deposit structure and the cathodic tin deposition process, the current-voltage curves were obtained (Fig. 2).

![Fig.2. Cathodic potentiodynamic (1 – 3) and chronopotentiometric at 0.5 A/dm\(^2\) (4) polarization curves of Sn electrodeposition in sulfate electrolytes: 1 – №1; 2 – №2; 3, 4 – №3](image)

From the potentiodynamic cathodic polarization curves, it can be seen that the electrodeposition of tin from solution with gelatin (Fig. 2, curve 1) in the current density range up to 1 A/dm\(^2\) proceeds with a characteristic low polarization. Additional introduction of phenol into the solution (Fig. 2 curve 2) leads to a shift of the equilibrium potential to negative values and a decrease in the value of the limiting current density, apparently due to phenol adsorption. This is consistent with \([15;23;24]\).

With the introduction of OP-10 into the solution, a limiting current appears in the region of low current densities (about 0.1 A/dm\(^2\)), which associated with the adsorption of the additive. The next wave of the curve (current density range of 0.1...1.2 A/dm\(^2\)) and the second limited current density with a further transition to the hydrogen evolution process are observed after the first limiting current. During the electrodeposition of tin from a solution №3 at a constant current density of 0.5 A/dm\(^2\) (Fig. 2, curve 4), the magnitude of the stationary potential, which was established after 0.17 hours, corresponded to the polarization curve (Fig. 2, curve 3). This can be explained by the fact that at the electrodeposition process the working surface area remains almost unchanged. Thus, during the electrodeposition of tin from the solution with OP-10, the current is distributed mainly along the tops of the pyramid crystallites, on which the deposit grows, mainly in the normal direction to the substrate, which is consistent with the nature of the structure modification (Fig.1 b, c). Also, by the optical method, focusing the microscope on the tops of the crystallites and in the hollows (with an increase of x40000) the following was established. With the estimated deposit thickness 27.5 \(\mu\)m (Fig. 1b), the height of the crystallites is 15 \(\mu\)m; with a calculated deposit thickness 55 \(\mu\)m (Fig. 1c), the crystallite height is 21 \(\mu\)m. All the above facts are consistent with \([20–22]\) and explain the formation of structured dendritic capillary-porous deposits.

**Evaluation of catalytic properties of the obtained materials.** Tin, as a metal with significant hydrogen overpotential, is used as a catalyst for the hydrogenation of organic compounds, as well as for the reduction of carbon dioxide to formic acid or formates according to the total reaction \([6; 14]\):

\[
\text{CO}_2 + \text{HCO}_3^- + 2e = \text{HCOO}^- + \text{CO}_3^{2-}.
\]

(1)

In particular, it was shown in \([6]\) that the surface structure of a tin catalyst significantly
affects the current efficiency of potassium formate. In addition, in a number of works [4–8; 14], it was shown that pH, cathode potential, type of indifferent cation have a significant effect on current efficiency of formate formation. Also, it was shown that in 0.1 KHCO₃, the maximum formate yield is observed at pH 6.85 and a potential of about −1.48 V (NHE) or −1.7 V (vs. Ag/AgCl) [4].

For a comparative evaluation of the catalytic activity of tin-based materials, obtained in this work, it was proposed to use 0.1 M NaHCO₃ [14] with an initial pH 6.8.

The potentiostatic current-voltage curves, which were obtained on the studied materials, indicate the following (Fig. 3.).

On the polished tin electrode and on the electrode with the surface structure shown in (Fig. 1 c), the current density values in the potential range of −1.5...−1.8 V are approximately the same. On the electrode with the structure (Fig. 1 b), the current density in the potential range of −1.6...−1.8 V is 20...40 % higher than on the other tested samples. This may indicate that the electrode material (Fig. 1 b) has a greater true working surface area than polished tin and the material (Fig. 1 c).

The maximum current or Faradaic efficiency (FE) of formate obtained on the studied electrode materials does not exceed 12.5 % (Fig. 4). This may be due to the nature of the cation [8], low volumetric flow rate of CO₂ (5 ml / min), and cell design features (the cell is not hermetic).

As follows from Fig. 4, curves 1, 3, the maximum FE for polished tin and tin with the structure (Fig. 1c) is observed at the potential of −1.7 V (vs. Ag/AgCl), which is consistent with the data obtained in a solution of 0.1 M KHCO₃ [4–6].
... 30% higher than on the other studied samples of electrodes.

Thus, the electrode material obtained in the present work with the surface structure (Fig. 1b) has the highest catalytic efficiency with respect to reaction (1) at a potential of −1.8 V (vs. Ag/AgCl). At the same time, the rate of formate formation is 2...2.5 times higher than on other test samples. This can be explained by the peculiarities of the electrode material structure, the pyramidal crystallites of which have nanoscale grooves on their surface. With excessively long electrodeposition, the structure is modified (Fig. 1c). The number of crystallites decreases, their size increases, and the surface becomes smoother, while the catalytic activity decreases.

Conclusion

Electrodeposition of tin-based electrode material with a nanostructured highly developed surface from a sulphate solution with the addition of organic additives has been proposed. It has been shown that the structure of tin deposits obtained from the proposed electrolyte has nanoscale grooves.

The current efficiency of formate on electrodes with obtained developed structure is 1.3...1.8 times higher than that of polished tin. It has been established that the highest rate of formate formation (0.75 mg/cm²/h) is observed on nanostructured tin electrodes with an electrodeposition duration of 2 hours at the potential of −1.8 V (vs. Ag/AgCl).

References


