

R. KOWALIK*[#]**ANALYSIS OF THE UNDERPOTENTIAL DEPOSITION OF CADMIUM ON COPPER****ANALIZA PROCESU PODPOTENCJAŁOWEGO OSADZANIA KADMU NA MIEDZI**

In this study the process of deposition of cadmium on polycrystalline copper electrode in sulfate solution was investigated. The process of underpotential and bulk deposition was analyzed by classical electrochemical method: cyclic voltammetry(CV), anodic stripping voltammetry(ASV) and electrochemical quartz crystal microbalance(EQCM). The obtained results were compared with electrochemical impedance spectroscopy(EIS) measurements. CV, EQCM and EIS results suggest that the UPD of cadmium starts below potential -0.4 V vs Ag/AgCl. Additionally the stripping analysis indicates the formation of cadmium monolayer with different density of deposited atoms depending on the applied potential. The transition from UPD to bulk deposition occurs below potential -0.7 V.

Przeprowadzono badania dotyczące procesu podpotencjałowego osadzania kadmu na polikrystalicznej elektrodzie miedzianej w roztworach siarczanowych. Zjawiska podpotencjałowego oraz nadpotencjałowego osadzania były badane z wykorzystaniem klasycznych metod elektrochemicznych: cyklicznej woltamperometrii, anodowej woltamperometrii inwersyjnej i elektrochemicznej mikrowagi kwarcowej. Otrzymane rezultaty były porównane z wynikami otrzymanymi podczas badań za pomocą elektrochemicznej impedancji spektroskopowej. Na podstawie wyników zauważono, że proces podpotencjałowego osadzania kadmu na miedzi zaczyna się od potencjału -0.4 V względem elektrody Ag/AgCl. Ponadto anodowa woltamperometria inwersyjna wskazuje, że w zależności od stosowanego potencjału zmienia się gęstość upakowania atomów kadmu na miedzi w zakresie od -0.4 do -0.7 V względem elektrody Ag/AgCl. Proces nadpotencjałowego osadzania kadmu rozpoczyna się poniżej potencjału -0.7 V względem elektrody Ag/AgCl.

1. Introduction

The underpotential deposition(UPD) phenomena is very interesting not only because of its fundamental importance but also due to its noticeable growing impact on the material science. The amazing possibility of control the deposition process down to monolayer results in new kind of materials with different properties than bulk ones embracing they catalytic, electronic or magnetic properties. Excellent reviews embracing theoretical considerations and different UPD systems are given in[1-5]. The systems related with cadmium attracted in the last years due to their application in the electrochemical atomic layer epitaxy (ECALE) process[6-9] and synthesis semiconductor compounds[10]. Moreover the modification of electrode surfaces through underpotential deposition enables to improve their catalytic properties, like in case a Cd-Au system[11, 12]. It also play a crucial role in the deposition of alloy coatings by electrochemical method[13].

Up-to-date, only few papers analyzed the problem of

Cd UPD on Cu[13-19]. The formation of Cd UPD layer on Cu has been analyzed by conventional electrochemical techniques: cyclic voltammetry and potentiostatic measurements. Additionally the structural studies were carried out by X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS), low energy electron diffraction (LEED), atomic force microscopy(AFM) and scanning tunneling microscopy (STM).

The aim of this work was to study the process of deposition of cadmium on polycrystalline copper electrode in sulfate solution. The process of underpotential and bulk deposition was analyzed by classical electrochemical method: anodic stripping voltammetry(ASV), cyclic voltammetry(CV) and electrochemical quartz crystal microbalance(EQCM). The obtained results were compared with electrochemical impedance spectroscopy(EIS) measurements. The last technique indicates the range of potentials where underpotential and bulk deposition occurred. The obtained results are in very good accordance with previous ones obtained by ASV, CV and EQCM.

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2. Experimental

The electrochemical measurements were carried out in the Teflon® three electrode cell. The working electrode was freshly evaporated copper on glass by magnetron sputtering technique [20]. Deposition began with a 10 nm adhesion layer of Ti, followed by 300 nm of Cu deposition. The working electrodes for EQCM measurements were 10 MHz AT-cut quartz crystals with evaporated and unpolished copper electrodes. Pt-wire as counter electrode and Leakless Miniature Ag/AgCl Reference Electrode as reference electrode were used. All the potentials below are given with respect to this electrode.

Before each experiment the sample surface was electrochemically pretreated by cyclic voltammetry in the range of potentials from -0.1 to -0.8 V in the solutions 0.1 M H₂SO₄, and afterwards in 0.1 M Na₂SO₄ at pH=2. Then the electrolyte was changed for a solution containing a different concentration of cadmium ions. The electrolyte was exchanged by the flow system and substrate did not have any contact with air. All chemicals used in this work were of analytical grade. Concentrations of solutions varied from 0.001 to 0.002 M CdSO₄, with 0.1 M Na₂SO₄ as a supporting electrolyte. The pH was adjusted to 2.0 by sulfuric acid addition. The solutions were purged by argon to remove oxygen. An Autolab PGSTAT30 was used for cyclic voltammetry and electrochemical impedance spectroscopy measurements. Oscillation frequency changes were registered by the electrochemical quartz crystal microbalance (UELKO Type M106) connected with the potentiostat. Electrochemical impedance spectroscopy measurements were obtained from a frequency range of 10 kHz to 0.1 Hz and 10 mV amplitude. The impedance spectra were recorded step by step at different potentials within the range from -0.1 to -0.8 V, every 0.025 V. The electrode was kept at the corresponding potential for 60 seconds before every step.

3. Results and discussion

3.1 Cyclic voltammetry and electrochemical quartz crystal microbalance

Fig. 1 shows the current and frequency response for a polycrystalline Cu quartz crystal oscillator obtained in two solutions with various concentrations of CdSO₄. The cathodic current insignificantly increased from potential -0.2 V in both cases and is probably related with the double layer charging or the residuals of oxygen reduction. No mass variation is observed up to potential -0.5 V. The process of deposition is signaled from the potential -0.5 V and the decreasing of the frequency of the resonator is recorded. The mass change of the electrode is the same in solutions with 0.001 and 0.002 M CdSO₄ up to potential -0.7 V, although the higher cathodic current is registered when higher concentration of Cd²⁺ was applied. It can be assumed that underpotential deposition of cadmium on copper starts from potential -0.5 V. This process is not signaled by sharp peaks on voltammograms due to the polycrystalline structure of the substrate, grain boundaries and surface roughness. Additionally, the formation of the ordered adlayers with an increasingly higher packing density is possible when the potential was swept in negative direction, which also

effects on the broadening of the UPD peak. Below potential -0.7 V the intensive increase of cathodic current is observable. The cathodic current and the increment of mass of electrode is higher in this range of potentials when solution with higher concentration of Cd²⁺ was applied. It can be assumed that below potential -0.7 V bulk deposition of cadmium starts.

On the revers scan the wide anodic peak appeared on the voltammogram and the dissolution of the deposited cadmium is observed from -0.7 V to -0.4 V. The UPD and bulk anodic peaks are superimposed on each other.

3.2 Anodic stripping voltammetry

To define better the conditions for the Cd UPD on Cu, further tests were carried out. The anodic stripping voltammetry after Cd deposition at constant potentials and at different accumulation times were conducted in the flow cell. The voltammetric experiments were preceded by the process of cadmium deposition for 30, 60, 120 and 240 s. Subsequently the electrolyte was exchanged for 0.1 M Na₂SO₄ with pH=2 and the stripping was carried out without the presence of Cd²⁺. The shape of anodic peaks is presented in Fig. 2. The first anodic peak related with dissolution of underpotentially deposited cadmium appeared when the potential -0.5 V was applied. The size of the anodic peak do not depend on the time of deposition and the voltammetry scans are not distinguishable. In turn, the anodic peaks after deposition at potential -0.6 V is bigger and also the second anodic peak appeared on the voltammetry curves when potential -0.7 V was applied. This assumes that more densely packed structure of cadmium is deposited on the copper electrode. As was mentioned previously it is due to the formation of the ordered adlayers with an increasingly higher packing density of cadmium atoms. The area under the anodic peaks increased systematically after holding the potential at -0.8 V, when different accumulation times were applied and thereby it confirms the bulk deposition of cadmium.

3.3 Electrochemical impedance spectroscopy

Very good technique which confirmed the process of underpotential deposition of metals is electrochemical impedance spectroscopy [21]. For this the electrochemical impedance spectroscopy was conducted in the 0.1 M Na₂SO₄ solution with and without 0.002 M CdSO₄ (Fig. 3 and Fig. 4). The capacitive loops obtained in the 0.1 M Na₂SO₄ solution become much smaller below the potential -0.4 V, when cadmium ions were present in the electrolyte. This characteristic effect is observable in the whole range of frequencies and is connected with the underpotential deposition of cadmium on copper. Following the spectra obtained at the more negative potentials, the characteristic local maximum appeared at the potential -0.6 V, and right after the capacitive loop decreased again. The characteristic local "saddle" visible on the 3D-graph appeared at the potential -0.7 V and this is connected with the more dense "huddled" atoms of cadmium deposited on the surface of the copper electrode. This second local minimum is related with the second anodic peak, which appeared during the anodic stripping voltammetry after polarization at -0.7 V. It can

be assumed that coverages of the copper surface is increasing when potential is shifted to the more negative direction and two structures of Cd monolayer with different density of atoms are possibly deposited.

The bulk deposition of cadmium is indicated at a minimum of around -0.75 V clearly visible on the impedance spectra in the whole range of the applied frequencies and agree with the CV and EQCM measurements.

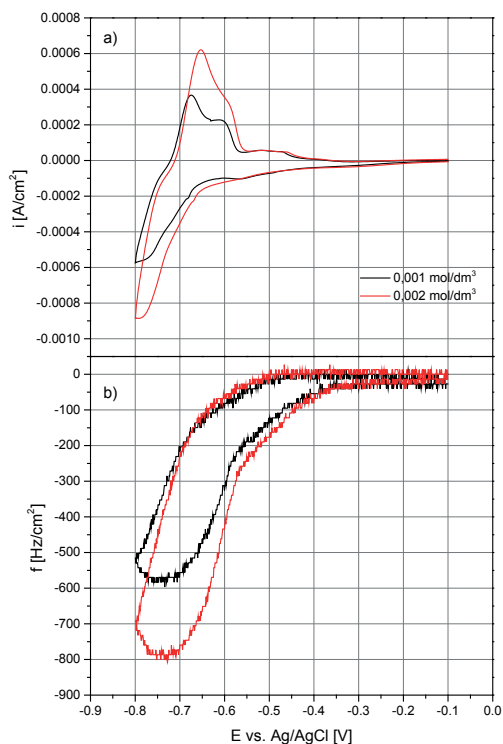


Fig. 1 Cyclic voltammograms and frequency response measured for copper substrate at 50 mV/s scan rate in electrolytes: (black) 0.001 M CdSO_4 , (red) 0.002 M CdSO_4 , 0.1 M Na_2SO_4 , pH 2

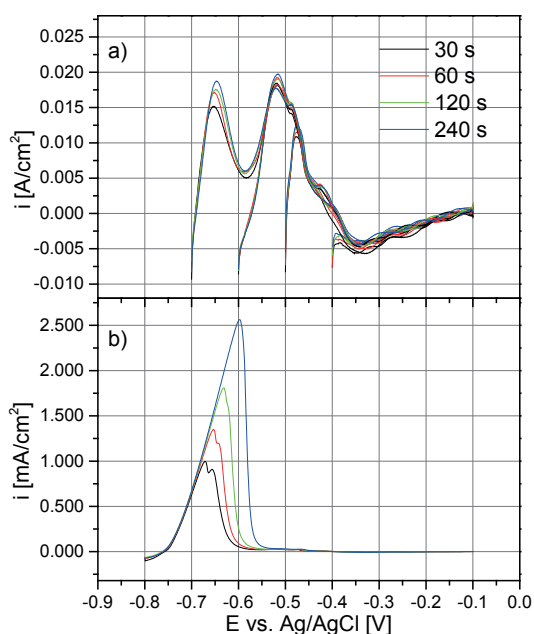


Fig. 2 Anodic stripping curves of Cd deposited at constant potentials for different times

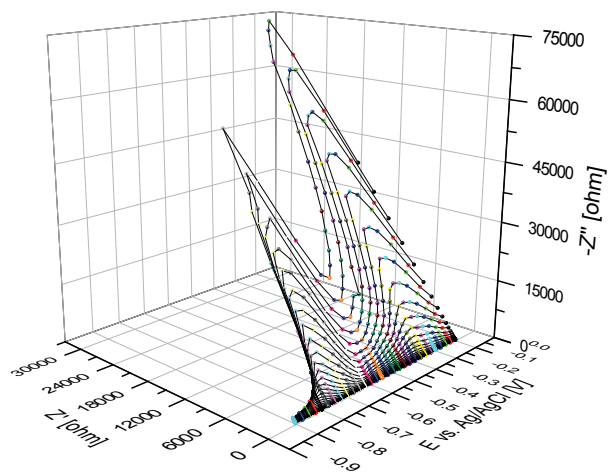


Fig. 3. Electrochemical impedance spectra for copper substrate in electrolyte: 0.1 M Na_2SO_4 , pH 2

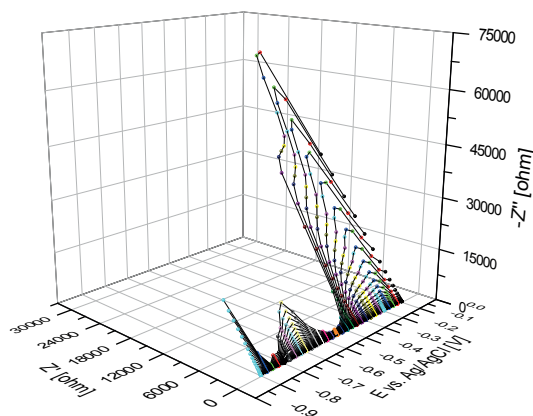


Fig. 4. Electrochemical impedance spectra for copper substrate in electrolyte: 0.002 M CdSO_4 , 0.1 M Na_2SO_4 , pH 2

4. Conclusion

These classical electrochemical techniques clearly distinguish the underpotential and bulk deposition of cadmium on copper. Formation of UPD layer of Cd on polycrystalline Cu electrode from sulfate solutions starts from -0.5 V. The voltammetric measurements do not show clearly peaks related with the UPD process but the EQCM undoubtedly signals the mass increment of the electrode. Anodic stripping voltammetry confirmed the surface limited process of cadmium deposition at range of potentials from -0.5 to -0.7 V. The stripping curves reveal two anodic peaks after polarization at -0.7 V and indicate the higher degree of coverages of copper surface when compared them with stripping curves obtained after polarization at more positive potentials. Moreover the electrochemical impedance spectroscopy measurements also indicate the two stages of Cd UPD on Cu and bulk deposition at -0.75 V and they show a high level of accordance with stripping analysis, voltammetry and electrochemical quartz crystal microbalance results.

Acknowledgments

This work was supported by the Polish National Center of Science under grants 2011/01/D/ST5/05743, 2011/01/N/ST5/05509 and AGH University of Science and Technology contract no. 11.11.180.509.

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Received: 20 October 2014.