

Electrochemical analysis of the underpotential deposition of cadmium and zinc on different substrates
Remigiusz Kowalik, Piotr Zabiński, Krzysztof Mech
 AGH University of Science and Technology, Faculty of Non-Ferrous Metals, Department of Physical Chemistry and Metallurgy of Non – Ferrous Metals
 al. A. Mickiewicza 30, 30-059 Krakow

The underpotential deposition phenomenon is very intensively analyzed in the recent years due to its very high impact in the material science. The crucial role in the alloy and compounds electrodeposition[1-5] and the unique possibility to obtain a control over a monolayer or even sub-monolayer amount of atoms on metal substrates as well as the increasing interest in the new properties of such a coatings identify UPD as an excellent candidate for resolving current issues of fundamental and practical importance. 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[3, 5]. The phenomena is successfully adopted for deposition of ultrathin films of different metals[6, 7] or compounds[8, 9].

The electrochemistry offer not only the possibility to precisely control the process of deposition but also enable to analyze this phenomenon by the various well-known electroanalytical techniques. Among them the electrochemical quartz crystal microbalance and electrochemical impedance spectroscopy are perfect ones for investigation such a complicated process on the electrolyte-electrode interface[10, 11].

These studies are interesting not only from fundamental point of view but also due to the potential application of UPD processes in the analytical chemistry[12], alloy electrodeposition[1], electrochemical atomic layer deposition (ECALD)[8, 9], surface limited redox replacement[13] or selective electrodesorption based atomic layer deposition (SEBALD)[14] methods. In this study the process of deposition of cadmium and zinc on polycrystalline metal substrates in sulfate solution was investigated. We present electrochemical impedance spectroscopy studies supported by voltammetry and electrochemical quartz microbalance on polycrystalline substrates.

The electrochemical measurements were carried out in a three electrode cell made by Teflon®. Pt-wire as counter electrode and Leakless Miniature Ag/AgCl Reference Electrode as reference electrode were used. The working electrode for EIS measurements was freshly evaporated metals on microscope glass slides by magnetron sputtering technique. The working electrodes for EQCM measurements were 10 MHz AT-cut quartz crystals with evaporated metal electrodes. All chemicals used in this work were of analytical grade. Concentrations of cadmium and zinc in the solutions varied from 0.001 to 0.002 M, 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. The electrochemical impedance spectroscopy were obtained from 10 kHz to 0.1 Hz frequency range and 10 mV amplitude.

These relatively simple experiments clearly distinguish the underpotential and bulk deposition of cadmium on silver. This phenomena are visible in the whole applied range of frequencies obtained during dc impedance spectroscopy measurements and they are in very good relation with cyclic 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.

References:

- [1] A. Budniok, *Journal of Electroanalytical Chemistry*, 123 (1981) 365.
- [2] R. Kowalik, K. Fitzner, *Journal of Electroanalytical Chemistry*, 633 (2009) 78.
- [3] R. Kowalik, K. Szaciłowski, P. Zabiński, *Journal of Electroanalytical Chemistry*, 674 (2012) 108.
- [4] R. Kowalik, P. Zabiński, K. Fitzner, *Electrochimica Acta*, 53 (2008) 6184.
- [5] J. Switzer, *Science (New York, N.Y.)*, 338 (2012) 1300.
- [6] J. Nutariya, M. Fayette, N. Dimitrov, N. Vasiljevic, *Electrochimica Acta*, (2013).
- [7] D.K. Gebregziabihier, Y.G. Kim, C. Thambidurai, V. Ivanova, P.H. Haumesser, J.L. Stickney, *J Cryst Growth*, 312 (2010) 1271.
- [8] B.W. Gregory, J.L. Stickney, *Journal of Electroanalytical Chemistry*, 300 (1991) 543.
- [9] G. Pezzatini, S. Caporali, M. Innocenti, M.L. Foresti, *Journal of Electroanalytical Chemistry*, 475 (1999) 164.
- [10] B.B. Balázs, M. Artjom, S. Wolfgang, S.B. Alexander, *The Journal of Physical Chemistry C*, 115 (2011).
- [11] R. Kowalik, P. Zabiński, K. Mech, *Electrochemistry Communications*, 31 (2013) 49.
- [12] Y. Bonfil, E. Kirova-Eisner, *Anal Chim Acta*, 457 (2002) 285.
- [13] C. Thambidurai, Y.G. Kim, J.L. Stickney, *Electrochimica Acta*, 53 (2008) 6157.
- [14] M. Innocenti, S. Bellandi, E. Lastraioli, F. Loglio, M.L. Foresti, *Langmuir*, 27 (2011) 11704.