

Cobalt electrodeposition from electrolyte containing
 $[\text{CoCl}_x(\text{H}_2\text{O})_{6-x}]^{2-x}$ ($x = 0, 1, 2$) complexes

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Cobalt and its alloys enjoy a lot of interest from many research centres in the world, mainly due to the interesting magnetic properties. Electrodeposition is one of the most commonly applied techniques of producing thin layers of cobalt and its alloys used in constructing spin valve devices [1], magnetic data carriers [2], heterogeneous catalysers [3], or materials of low overpotential of hydrogen evolution [4]. The mechanism and kinetics of electrode reactions, nucleation and deposition processes in the electrolytes containing Co^{2+} ions have been discussed in many works [5-10]. Alloys of cobalt and elements such as W [11], Ni [12], Mo [4, 13] Fe [14], Cu [15], Pt [16] obtained through electrodeposition are the subject of many studies based on the optimization of the electrolysis process according to the electrocatalytical properties of these alloys. Recently, particular attention has been focused on the studies of the phenomenon of underpotential deposition of cobalt (UPD) [8, 9]. It is commonly known that the properties are tightly connected with the structure, composition and morphology of the synthesized alloys which, in turn, depend on the synthesis conditions, i.e. temperature, concentration of metal ions, the potential of the working electrode, current density, addition of complexing agents, surface active agents and electrolyte pH. One of the significant problems accompanying the electrodeposition of cobalt or its alloys is co-evolving hydrogen, which causes considerable lowering of current efficiency and local increase of the pH value.

The work comprises results of the studies of the mechanism and kinetics of the co-reduction of hexaaquacobalt(II) and pentaquachlorocobalt(II) complexes in chloride solutions at $\text{pH} = 3$. The studies were preceded by the thermodynamic analysis of the electrolyte. Electrolyte stability was determined by UV – Vis absorbance measurements. Electrochemical examinations were performed by cyclic voltammetry (CV) combined with Electrochemical Quartz Crystal Microbalance (EQCM). The M/z values determined by electrogravimetric measurements indicated that the reduction process occurs in one step 2-electron reduction reaction. Although the low pH value ($\text{pH} = 3$) electrogravimetric tests also indicate the process of $\text{Co}(\text{OH})_2$ precipitation. Deposition of Co takes place only in the overpotential deposition range. The examined reactions were diffusion controlled. The diffusion coefficient of Co^{2+} ions was determined by using the Berzins – Delahay equation.

The electrolyte was prepared by dissolution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (analytical grade reagent) in deionised water. The concentration of Cl^- ions in electrolyte was controlled by addition of NaCl. The pH was adjusted by adding HClO_4 . The tests were performed in a Teflon measurement cell. The working electrode (WE) in CV combined with EQCM measurements was a gold – covered quartz crystal with a basic oscillation frequency of 10 MHz, while in the classical electrochemical test it

was a cross-section of Au wire. It should be underlined that, in voltammetric tests, the electrode was positioned horizontally at the top, while during electrogravimetric tests it was positioned horizontally at the bottom. The counter electrode (CE) was platinum wire (Pt). An Ag/AgCl (3 M KCl) electrode was used as the reference electrode. The measurements were conducted at a constant temperature of 298 K. Oscillation frequency changes were registered by the electrochemical quartz crystal microbalance (UELKO Type M106) connected with the Autolab PGSTAT30 potentiostat. A UV-Vis spectrometer Agilent Model 8453 was used for absorbance measurements. The UV-Vis measurements were performed within the range of wave length 190–1100 nm.

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