Influence of tetrabutylammonium chloride on the electrodeposition of indium from chloride solution on a glassy carbon electrode

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ABSTRACT
In this paper, the electrochemical reduction of indium on a glassy carbon electrode (GCE) in a chloride electrolyte in the presence of tetrabutylammonium chloride (TBACh) was studied using the rotating disk electrode method, chronoamperometry and scanning electron microscopy. It was found that the addition of TBACh inhibits the electrodeposition of indium by increasing the activation energy of the process by 17 kJ mol⁻¹, and also shows leveling action at its low concentrations. The diffusion coefficient of indium (III) ions found from Levich equation at 25°C, was 4.93 × 10⁻⁶ cm² s⁻¹. The In³⁺ diffusion coefficient determined using the Levich equation are consistent with the values determined by the Cottrell law and universal Stokes-Einstein equation. The addition of 10⁻⁴ M TBACh to the electrolyte reduces the diffusion coefficient to 2.13 × 10⁻⁶ cm² s⁻¹.

The type of crystallization corresponding to the progressive 3D nucleation with diffusion control has been established. Using the Scharifker-Hills, Scharifker-Mostany and Mirkin-Nilov-Heerman-Tarallo models nucleation parameters were calculated, which correlate well with the results of scanning electron microscopy. Addition of TBACh increases the nucleation rate at −0.90 V from 9.19 × 10⁶ cm⁻² s⁻¹ to 48.09 × 10⁶ cm⁻² s⁻¹ and reduces the average radius of grains of indium coatings from 18.0 μm to 6.8 μm.

1. Introduction
Electrodeposition of indium has been comprehensively investigated on solid electrodes such as platinum, glassy carbon electrode, nickel, tungsten, molybdenum and copper [1–7]. This great interest is due to the practical application of indium, namely, the production of an ultrapure metal with subsequent use in the preparation of various semiconductor alloys. The most complete review of the electrodeposition of indium on various electrodes is given in [8,9]. Recently, in the electrodeposition of indium, ionic liquids were used as an electrolyte, which makes it possible to obtain compact coatings of indium and its alloys [10–14]. This effect is explained by the increase of the number of active sites during electrodeposition of indium on tungsten and glassy carbon electrodes [4]. From aqueous chloride electrolytes, high purity indium is obtained, but forms dendritic coatings [15].

Earlier studies [16,17] have established the influence of chloride ions on the electrocrystallization of indium on a glassy carbon electrode, and the limiting stage of electrochemical reduction of indium and the nucleation mechanism were determined. It has been established that as the concentration of chloride ions increases, the nucleation rate increases too.

To improve the quality of the coatings, it is necessary to add surfactants to the electrolyte, which have a leveling action in indium electrodeposition. In [18–21], additions of quaternary ammonium salts were used to inhibit dendritic formation during electrodeposition of zinc, copper and silver; these additives showed a high leveling effect. Formation of compact coatings is possible when surfactants are added to the electrolyte. So, in [22,23], for electrodeposition of zinc on carbon steel (AISI 1018), additives of quaternary ammonium compounds were used to obtain compact coatings. N-benzyltriethylammonium chloride and tetrabutylammonium hydroxide additives inhibit the growth of dendrites and can be used as a leveling additive, whereas in the case of tetrabutylammonium hydroxide this effect is negligible [24].

In this paper, we studied the electrodeposition of indium on a glassy carbon electrode in the presence of tetrabutylammonium chloride (TBACh) using a rotating disk electrode and chronoamperometry. In addition, the kinetics of the initial stages of electrocrystallization and local deposition of fragments of a new solid phase has been studied.

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