Electrodeposition of Indium on Glassy Carbon from Tetrabutylammonium Chloride Containing Solutions

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Abstract

The effectiveness of tetrabutylammonium chloride (TBACl) as inhibition additive of dendritic growth of indium has been investigated by means of cyclic voltammetry and chronoamperometry methods. The rotating disk electrode (RDE) method allowed the calculation of the diffusion coefficient of In\(^{3+}\) ions using the Levich equation, at 25 °C is \(4.41 \times 10^{-6}\) cm\(^2\)/s. Diffusion coefficient of indium ions determined by chronoamperometry using the Cottrell law (\(6.63 \times 10^{-6}\) cm\(^2\)/s) is in consistent with the value calculated by the Levich equation. The addition of tetrabutylammonium ions to the electrolyte reduces the diffusion coefficient and inhibits the cathodic process by increasing the activation energy from 10.5 kJ/mol to 20.7 kJ/mol. The indium nucleation and growth on glassy carbon in chloride solutions was studied by single potentiostatic pulse techniques. The nucleation mechanism was evaluated by analyzing the influence of different TBACl ion concentration and applied potentials. The electrocrystallization mechanisms were determined by fitting the experimental non-dimensional current transients on the basis nucleation and growth model developed by Scharifker-Hills. The type of nucleation corresponding to the progressive three-dimensional nucleation with diffusion control is determined. Based on theoretical models of 3D multiple nucleation from the potentiostatic current transients were calculated nucleation characteristics, such as the stationary nucleation rate, saturation nucleus density and the average grains radius of indium deposits. The leveling action of TBACl on the electrodeposition of indium at concentration of \(10^{-4}\) M was found.

Keywords

Indium
Tetrabutylammonium chloride
Electrocrystallization
Stationary nucleation rate
Saturation nucleus density
Average grains radius

1. Introduction

Electrodeposition is used in various technologies including production of high-purity metals. Among them indium, whose practical application depends on thorough purification, requires basically the electrorefining method. The problem is discussed in a large number of research papers on indium electrodeposition on solid electrodes [1–13]. Papers [14–17] provide profound description of electrochemical reduction of indium at different electrodes from aqueous electrolytes. Electrodeposition of indium from chloride electrolytes often leads to the formation of dendritic deposits [18], which requires the use of inhibitors of dendritic formation. The authors of [19–23] used additive quaternary ammonium salts in electrochemical reduction of zinc, copper and silver, and the additives effected in high inhibition action of dendritic growth. This kind of additives with good chemical stability could be alternatives of leveling additives for electrochemical deposition of indium from aqueous chloride solutions.

This research deals with the study of phase formation in electrochemical reduction of indium on a glassy carbon (GC) electrode from chloride solutions in the presence of tetrabutylammonium chloride ions. The research results were obtained using cyclic voltammetry with a rotating disk electrode and chronoamperometry. The kinetics of electrocrystallization processes resulting in formation of a new phase takes its origin from the concept of formation.
nucleation. At present, there are models for a detailed quantification of the nucleation process [24–26]. The current transients allow to give a general description of the process and choose the model of nucleation and growth. In this paper, all calculations for the study of nucleation have been carried out using the three-dimensional Scharifker-Hills model [27–31].

2. Experimental

All electrochemical measurements were carried out in a three-electrode cell using Autolab PGSTAT 302N potentiostat-galvanostat (Metrohm®, the Netherlands). The working electrode was a GC electrode produced by Metrohm® with a surface area of 0.07 cm². The GC RDE is a solid-state electrode with a stationary, planar surface (disk diameter is 3 mm). During use, surface of GC electrode becomes increasingly contaminated with the products of the electrode redox processes. Therefore, the surface of the electrode tips was regenerated and then by mechanically cleaning it with finest aluminum oxide powder. As an auxiliary electrode a platinum plate was used, and the reference electrode was a silver chloride electrode (Metrohm®). The basic electrolyte (B.E.) consisted of a 2 M sodium chloride solution and 0.1 M indium (III) chloride with a pH of 1.5. The concentration of the surfactant additive of TBACh (Sigma Aldrich, 99.99%) was 10⁻⁴ and 10⁻³ M. The InCl₃ solution was obtained by the interaction of indium metal with mark of In²⁺ (99.98%, Kazzink Ltd., Kazakhstan) with 37% hydrochloric acid solution (Sigma Aldrich, 99.99%). During the experiments temperature, overvoltage and angular speed of the rotating disk electrode were varied.

Before each measurement, the surface of GC electrode was mechanically trimmed and then thoroughly washed with twice distilled water. To assess reproducibility of results, each measurement was repeated no less than 3 times.

3. Results and discussion

3.1. Study of kinetics

The study of the effect of tetrabutylammonium on the kinetics of the electrodeposition of indium on a glassy carbon electrode from a chloride electrolyte was carried out by the cyclic voltammetry method. The cyclic voltammograms (CV) of the discharge-ionization process of indium are shown in the Fig. 1. Limiting diffusion current density for the electrochemical reduction of indium is observed in the range of potentials – 0.8 V ... – 1.2 V (Fig. 1).

To determine the rate-limiting stage of the reaction, the RDE method was used. With an increase in the rotation speed of the glassy carbon disc electrode in the range from 100 to 500 rpm, the cathodic limiting current density (j_l) increases. This is connected with an increase in the mass transport rate and a decrease in the thickness of the Prandtl’s hydrodynamic layer, which is directly proportional to the thickness of the diffusion layer. The reduction of indium ions at an electrode rotation speed of 1500 rpm and above the increase of the limiting current density is not observed, due to the change in the nature of the rate-determining stage of the process, when the rate constant of the charge transfer stage is equivalent to the rate constant of mass transfer. Apparently, under these conditions, the discharge of indium ions proceeds in a mixed mode. Using the Levich equation, which is applicable to processes with diffusion limitation, the values of the diffusion coefficient of indium ions at the electrode rotation speeds of 100–1500 rpm were calculated. The values of kinematic viscosity of chloride solutions for calculating the diffusion coefficient of indium ions are taken from ref. [32].

From the CV (Fig. 2), it can be seen that the addition of tetrabutylammonium (10⁻⁴ M) to the electrolyte leads to a marked decrease in the cathodic currents, in the potential range −1.0 V ... −1.2 V,
which indicates its inhibitory effect on the electrochemical reduction of indium ions. With an increase in the concentration of TBACh by one order, the effect of inhibition of the discharge rate of indium ions is somewhat higher, due to the increase in the concentration of tetrabutylammonium molecules in the near-electrode layer, which inhibits the cathodic reaction.

The limiting stage of the electrode process can be established by the voltammetry method under study at different temperatures. With increasing temperature, an increase in the \( j/l \) is observed, which is associated with an increase in the diffusion coefficient of \( \text{In}^{3+} \) ions (Table 1).

To determine the limiting stage of the electrochemical reduction of indium, was used the potentiostatic current transients of indium electroreduction (Fig. 3), which indicates the course of the process in the diffusion regime. Figure 3 shows the good correlation between the obtained experimental chronoamperogram and theoretical dependence.

Also, it allows to calculate the values of the diffusion coefficient of indium ions using the Cottrell equation and activation energy on the basis of the Arrhenius equation for various temperature (Table 1).

Thus, it has been established that the electrochemical reduction of indium ions on the surface of the glassy carbon takes place in the diffusion regime, and the transition from the diffusion control region to the mixed regime is observed on a rotating disk glassy carbon electrode at a disk rotation speed of 1500 rpm and higher. The values of the activation energy of the process correspond to the diffusion restrictions in the non-stationary regime. Addition of tetrabutylammonium chloride to the solution inhibits the electrochemical reduction of indium, as evidenced by an increase in the activation energy and a decrease in cathodic current on cyclic voltammograms.

### Table 1

<table>
<thead>
<tr>
<th>T, °C</th>
<th>( D, 10^6 \text{ cm}^2 \text{s}^{-1} )</th>
<th>( D, 10^6 \text{ cm}^2 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ch.A</td>
<td>RDE</td>
</tr>
<tr>
<td>25</td>
<td>6.63</td>
<td>4.41</td>
</tr>
<tr>
<td>35</td>
<td>8.33</td>
<td>5.46</td>
</tr>
<tr>
<td>45</td>
<td>9.39</td>
<td>5.68</td>
</tr>
<tr>
<td>55</td>
<td>10.76</td>
<td>6.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>B.E.</th>
<th>B.E. + ( 10^{-4} \text{ M TBACh} )</th>
<th>B.E. + ( 10^{-3} \text{ M TBACh} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a, \text{ kJ mol}^{-1} )</td>
<td>10.5</td>
<td>20.7</td>
<td>28.9</td>
</tr>
</tbody>
</table>
3.2. Nucleation study

A study of the parameters of the nucleation process during the electrodeposition of indium on a glassy carbon electrode was carried out by the single potentiostatic pulse techniques in a B.E. and B.E. solution with TBACl additives (Fig. 4 (a), (b)). On the chronoamperograms, when the potential is varied, electrodeposition of indium is observed, which corresponds to cathodic peaks (current density maxima $j_{max}$). The further course of the current transients indicates the diffusion regime (Fig. 4 (a)). In the basic electrolyte containing $10^{-4}$ M TBACl, a slight shift of the maximum is observed in the direction of small times (in this case we mean the time maxima $t_{max}$). The addition of $10^{-3}$ M TBACl to the solution shifts the maximum on the chronoamperogram into the region of large times, which apparently is due to the adsorption and blocking of the electrode surface by tetrabutylammonium ions (Fig. 4 (b) curve 3). Formation of dendritic deposits was visually observed precisely at this concentration of surfactant.

The adsorption of TBACl at the cathode occurs as a result of electrostatic attraction forces between the plus charged hydrophilic head group ([N(C$_4$H$_9$)$_2$H]$^+$) and the negatively charged surface of the GC, which depends on the polarization values. At a lower concentration of the N(C$_4$H$_9$)$_2$H$^+$, the alkyl chain of these quaternary ammonium cations may be oriented toward the electrolyte [21]; however, they may also be arranged horizontally to the cathode [33], involving the displacement of water molecules from the surface of GC electrode. At the beginning of the adsorption process the hydrophobic chains may be arranged horizontally, what could entail the decreasing of the surface area available for the electoreduction of In$^{3+}$ ions. As the concentration of TBACl reaches the critical micelle concentration value [34], the [N(C$_4$H$_9$)$_2$H]$^+$ ions start to arrange vertically and the formation of hemi-micelles or ad-micelles or surface aggregation of [N(C$_4$H$_9$)$_2$H]$^+$ is expected to start. In this manner, these micelles are highly charged and, because of, the higher electrostatic attraction, adsorption of the surfactant increases faster with a consequent reduction of the indium electoreduction rate by blocking the cathode surface [35]. The above-mentioned effect of the formation of dendrites, needle structures at a high concentration of TBACl is apparently due to the presence of an adsorption layer with a vertically arranged alkyl groups.

The nature of the limiting stage of the process and the type of nucleation are determined from the non dimensional potentiostatic curves ($j/j_{max}^2$ vs. $t/t_{max}$). The use of the Scharifker-Hills model for nucleation with diffusion limitation made it possible to calculate the basic parameters of indium nucleation on a glassy carbon. The experimental potentiostatic transients were normalized to dimensionless form ($j/j_{max}^2$ vs. $t/t_{max}$), and then compared with theoretical ($j/j_{max}^2$ vs. $t/t_{max}$) curves, it was calculated based on Scharifker-Hills model [27] for the instantaneous and progressive 3D nucleation models presented by the Eqs. 1 and 2, respectively:

$$
\left(\frac{j}{j_{max}}\right)^2 = \frac{1.9542}{t/t_{max}} \left[1 - \exp\left(-1.2564\left(\frac{t}{t_{max}}\right)^2\right)\right] \tag{1}
$$

$$
\left(\frac{j}{j_{max}}\right)^2 = \frac{1.2254}{t/t_{max}} \left[1 - \exp\left(2.3367\left(\frac{t}{t_{max}}\right)^2\right)\right] \tag{2}
$$

Figure 5 shows the experimental and theoretical non dimensional plots for instantaneous and progressing 3D nucleation.
Fig. 5. Non dimensional plots obtained at – 0.84 V potential, $(j/j_{max})^2$ vs. $t/t_{max}$ experimental and theoretical for instantaneous and progressive for the indium nucleation on glassy carbon electrode, in a B.E. solution (dot line), B.E. in containing $10^{-4}$ M TBACh solution (solid line), in B.E. containing $10^{-3}$ M TBACh solution.

Dimensionless form of potentiostatic transients for the basic electrolyte and with the addition of TBACh ($10^{-4}$ M) are located between the theoretical curves for progressive and instantaneous nucleation. At the initial and final sections, a shift toward progressing nucleation is observed. With a larger content of TBACh ($10^{-3}$ M) in the electrolyte, the experimental curve shifts significantly from the theoretical curve, which makes it impossible to characterize the type of nucleation.

The stationary nucleation rate ($AN_{∞}$) and the saturation nucleus density ($N_s$) formed for progressive nucleation with diffusion control are calculated from the maximum values of current density ($j_{max}$) and time ($t_{max}$) on chronoamperograms (potentiostatic transients), according to Eqs. 3 and 4:

$$AN_{∞} = \frac{0.1004(zFc)^{1/2}D}{(j_m^{1/2}t_m)} \left( \frac{3}{4(8\pi V_m)^{1/2}} \right)$$

(3)

Where $AN_{∞}$ is the nucleation rate ($s^{-1}$ cm$^2$), $c$ is the bulk concentration of In$^{3+}$ ions (mol cm$^{-3}$), $D$ is the diffusion coefficient of In$^{3+}$ ions (cm$^2$ s$^{-1}$), $V_m$ molar volume of indium (cm$^3$ mol$^{-1}$), while $z$, $F$ have their usual meaning.

$$N_s = \sqrt{\frac{3AN_{∞}}{8(8\pi V_m)^{1/2}D}}$$

(4)

From the value of $N_s$, the average radius of the individual nuclei – $r$, can be estimated by the equation [15]:

$$r = \frac{N_s}{\pi}^{1/2}$$

(5)

where $N_s$ is the saturation density of active sites (cm$^{-2}$); $r$ is the average radius of the individual nuclei (cm).

The calculated values of the stationary nucleation rate, the saturation density of active sites and the average grain radius of indium deposits during electocrystallization of indium on glassy carbon in the basic electrolyte and with the addition of TBACh $10^{-4}$ M at different potentials are given in Table 2.

It can be seen that during electrochemical reduction of indium on a glassy carbon electrode, the rate of nucleation and the saturation density of active sites increase with increasing overvoltage. The addition of tetrabutylammonium enhances the growth effect. From the found values of $N_s$, the average grains radius (Eq. 5) of electrodeposited indium was calculated.

During electrodeposition of indium in the basic electrolyte and in a solution with the addition of TBACh, the average radius of the cathode deposits decreases noticeably with increasing polarization. These results show the leveling effect of tetrabutylammonium chloride at a concentration of $10^{-4}$ M, which leads to the formation of dense indium deposits on the surface of the glassy carbon electrode.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>B.E.</th>
<th>B.E. + $10^{-4}$ M TBACh</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$, V</td>
<td>$AN_{∞}$, $10^6$ s$^{-1}$ cm$^2$</td>
<td>$N_s$, $10^6$ cm$^2$</td>
</tr>
<tr>
<td>–0.72</td>
<td>0.075</td>
<td>1.46</td>
</tr>
<tr>
<td>–0.79</td>
<td>0.265</td>
<td>2.75</td>
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<tr>
<td>–0.84</td>
<td>0.515</td>
<td>3.83</td>
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<tr>
<td>–0.89</td>
<td>2.282</td>
<td>8.06</td>
</tr>
<tr>
<td>–0.94</td>
<td>6.341</td>
<td>13.44</td>
</tr>
</tbody>
</table>

Table 2
Calculated values of $AN_{∞}$, $N_s$ and $r$ for the progressive nucleation according to Eqs. 3–5 at 25 °C.
4. Conclusions

The influences tetrabutylammonium chloride on the kinetics of electroreduction, nucleation mechanism of indium electrodeposition from the acidic chloride solution were investigated. At large cathodic potentials, the current is diffusion-limited. On the basis of Levich equation, the values of the diffusion coefficient of In^{3+} ions are determined. In the presence of TBACh, the values of the diffusion coefficient are reduced, due to the inhibition of TBACh in the amount of 10^{-3} M to the electrode process by adsorbed [N(C_{8}H_{18})_{4}]^{3-} ions. The inhibition of the indium electroreduction at presence of TBACh is confirmed by a significant increase in the activation energy of diffusion. Addition of TBACh in an amount of 10^{-3} M to the electrolyte, activation energy increases from 10.5 to 28.9 kJ mol^{-1}.

Chronoamperometry made it possible to determine the type of nucleation corresponding to three-dimensional progressive nucleation with diffusion control, according to the Scharifker-Hills model. It is established that as the polarization increases, the nucleation rate and the saturated nucleus density increase. The addition of TBACh in the amount of 10^{-4} M to the electrolyte enhances this effect, leading to a decrease in the average grains radius of the electrodeposited indium at a potential of – 0.94 V from 15 μm to 8 μm and to obtaining dense cathodic deposits on the electrode surface.

Acknowledgments

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References


[34]. M. Benraou, B.L. Bales, R. Zana, J. Phys. Chem. B 107 (203) 13432–13440. DOI: 10.1021/jp021714u