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# Cathodic reaction of saccharin and N-methylsaccharin during nickel electrodeposition in electrolytes containing different anions

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The behaviour of saccharin and N-methylsaccharin during Ni electrodeposition in electrolytes containing different quantities of sulphate, chloride and hydroxycarboxylic acids anions was investigated by determining consumption rates ( $V_c$ ) of additives and accumulation rates ( $V_a$ ) of cathodic reaction products. The hydroxycarboxylic acids and/or chloride anions in comparison with anions of Watts electrolyte increase  $V_c$  of saccharin and N-methylsaccharin by accelerating either one or both cathodic reduction reactions of carbonyl group (with and without hydrogenolysis of endocyclic C–N bond). The mixtures of the cathodic reaction products of both additives in all-chloride electrolyte differ from that of Watts electrolyte, and only the corresponding mixture of saccharin differs in the presence of hydroxycarboxylic acids at concentrations 0.04–0.10 mol dm<sup>-3</sup> used. The increase of  $V_a$  of o-toluene sulphonamide, N-methyl-o-toluene sulphonamide and N-methylbenzyl sultame shows that the adsorption of additives by a carbonyl group was increased. A decrease of  $V_a$  of corresponding benzamides allows to suggest the opposite influence of investigated anions on the adsorption of additives by a sulphonyl group. The mechanism of the action of additives under study is performed by their cathodic reactions. The transformation process of additives on the cathode depends on their nature, electrolyte and electrodeposition properties and on the competition of all compounds and ions during adsorption on the electrode and in it.

**Key words:** nickel electrodeposition, saccharin, N-methylsaccharin, Watts-type electrolyte, all-chloride electrolyte, electrolytes containing hydroxycarboxylic acids

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## INTRODUCTION

Saccharin (SAC) additive of class I, which decreases internal stresses caused by additives of class II or other compounds in electrolytes during metal or alloy electrodeposition have been used till now [1–24]. The articles about SAC in Ni electrodeposition published earlier are reviewed in [25]. The influence of N-methylsaccharin (NMS) on electrodeposition of Ni [26, 27], Ni–TiO<sub>2</sub> [28] and Ni–Fe [29] are investigated. The main cathodic reactions of SAC [25] and NMS [30–32] in Watts-type electrolytes are the same (desulphuration, reduction of carbonyl group with and without endocyclic C–N bond hydrogenolysis), but the accumulation rates ( $V_a$ ) of the products formed differ markedly.

The electrodeposition of Ni may be carried out in electrolytes containing different anions and is anion-dependent [33–41]. Chloride ions are adsorbed on Ni cathode [42] and serve as a bridge for Ni<sup>2+</sup> electrodeposition [43]. The activity of Ni<sup>2+</sup> in

chloride electrolytes is higher than in sulphate ones [34, 44]. The electrodeposition potential of Ni is lower in electrolytes containing a high concentration ( $c$ ) of Cl<sup>-</sup> [33, 34] or citric acid [37] than in sulphate one. Organic acids (including hydroxycarboxylic) serve as buffers in electrolytes [35, 45]. The appearance of electrodeposits and their internal stresses ( $\sigma$ ) show that SAC are more suitable than benzene derivatives containing only a sulphonyl group in all-chloride electrolytes [45].

The direct methods of analyzing adsorbed organic compounds as SERS are not applied for Ni cathodes. The above methods are used for Ag, Cu and several other cathodes. The adsorption of o-, m- and p-isomers of nicotinic acid on Ag cathode from sulphate and chloride solutions may be given as an example [46]. All three isomers are adsorbed from a sulphate solution and only p-nicotinic acid from chloride one. The second example may be the mode of adsorption of 1-octyne-3-ol on Fe electrode [47]. The measurements of layer thickness show that

chloride ions exhibit a pronounced effect on the adsorption and reorientation of 1-octyne-3-ol on the electrode in acidic solutions.

The investigation of consumption rates ( $V_c$ ) of additives and  $V_a$  of cathodic reaction products in electrolytes containing different anions may help to reveal the changes in the mechanism of additive action during formation of electrodeposits.

## EXPERIMENTAL

Investigations were carried out in the electrolytes containing (mol dm<sup>-3</sup>): 1. NiSO<sub>4</sub> · 7H<sub>2</sub>O – 1, NiCl<sub>2</sub> · 6H<sub>2</sub>O – 0.19, H<sub>3</sub>BO<sub>3</sub> – 0.48; 2. NiSO<sub>4</sub> · 7H<sub>2</sub>O – 0.27, NiCl<sub>2</sub> · 6H<sub>2</sub>O – 0.31, H<sub>3</sub>BO<sub>3</sub> – 0.48, citric acid – 0.10; 3. NiCl<sub>2</sub> · 6H<sub>2</sub>O – 1.25, H<sub>3</sub>BO<sub>3</sub> – 0.48; 4. N1 + citric acid – 0.04; 5. N1 + citric acid – 0.04, gluconic acid – 0.02, glucose – 0.04. Reagents and solvent chloroform were of analytical pure grade. Organic compounds with the following melting points were used as the additives: saccharin (SAC), 225 to 226 °C, and NMS, 130 to 131 °C. The concentrations of the additives were selected according to recommendations for electroplating solutions. Ni was electrodeposited in a two-chamber cell made of acrylic plastic with a porous glass diaphragm. A brass foil was used as the cathode and Ni of N1 grade served as the anode.

NMS and cathodic reaction products of both additives were analyzed by liquid chromatography af-

ter their extraction with chloroform from electrolytes at pH ~ 5 [25, 48]. Determination of SAC was carried out by UV spectra of diluted Watts and all-chloride electrolytes and after extraction at pH 1 of electrolytes containing hydroxycarboxylic acids [25].

## RESULTS AND DISCUSSION

The five electrolytes used in the study contain different quantities of sulphate, chloride and hydroxycarboxylic acid anions. All electrolytes were proposed for electroplating, and electrodeposits were formed in them. The potential of cathode and its properties depend on electrolyte composition [33–44].

The cathodic reaction of SAC and NMS in Watts electrolyte (N1) has been investigated earlier (Figs. 1a, 2a) [31, 49]. An increase of chloride anions  $c \sim 1.5$  time in the presence of citric acid in electrolyte N2 accelerates the consumption of SAC (Fig. 1a, b, curve 1) and increases  $V_a$  of o-toluene sulphonamide (curve 2) and benzyl sultame (curve 4)  $\sim 2$  times, but decreases  $V_a$  of benzamide  $\sim 20\%$  in comparison with the corresponding data of Watts electrolyte. Both cathodic reactions of carbonyl group reduction in SAC with (o-toluene sulphonamide) and without (benzyl sultame) endocyclic C–N bond hydrogenolysis were accelerated by the composition of electrolyte N2. The above reactions of SAC in all-chloride (N3) electrolyte (Fig. 1c) are less influenced than in electrolyte N2 (Fig. 1b). Only the  $V_a$  of o-toluene

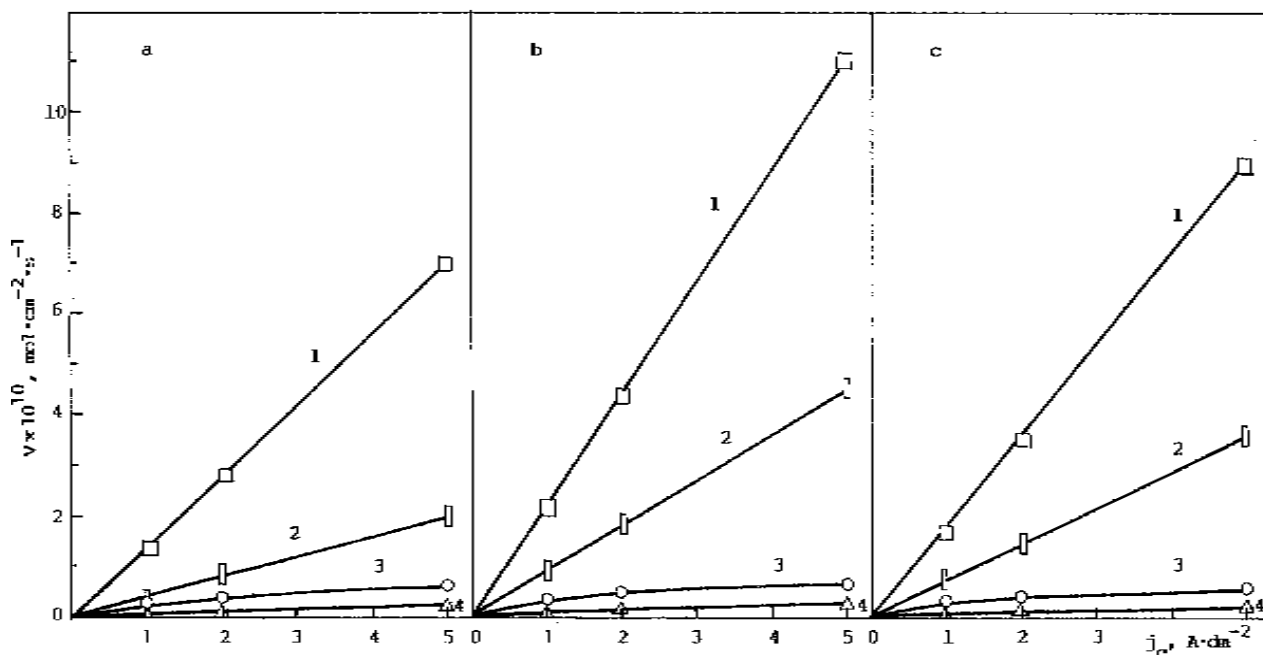
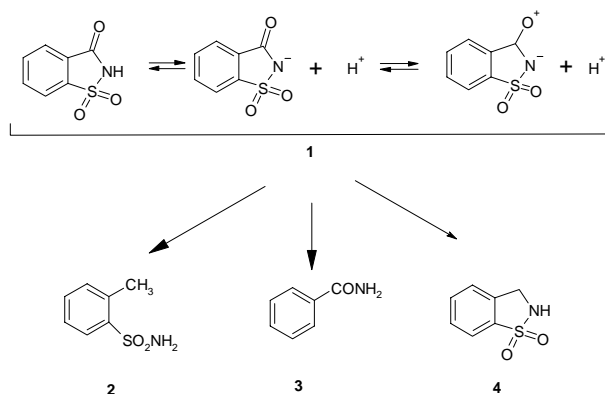


Fig. 1. Dependency of saccharin consumption rate (1) and accumulation rates of o-toluene sulphonamide (2), benzamide (3) and benzyl sultame (4) on  $j_c$  of cathode at 20 °C and pH 3 in electrolytes containing (mol dm<sup>-3</sup>): 1) NiSO<sub>4</sub> · 7H<sub>2</sub>O – 1, NiCl<sub>2</sub> · 6H<sub>2</sub>O – 0.19, H<sub>3</sub>BO<sub>3</sub> – 0.48 (a); 2) NiSO<sub>4</sub> · 7H<sub>2</sub>O – 0.27, NiCl<sub>2</sub> · 6H<sub>2</sub>O – 0.31, H<sub>3</sub>BO<sub>3</sub> – 0.48, citric acid – 0.10 (b); 3) NiCl<sub>2</sub> · 6H<sub>2</sub>O – 1.25, H<sub>3</sub>BO<sub>3</sub> – 0.48 (c)

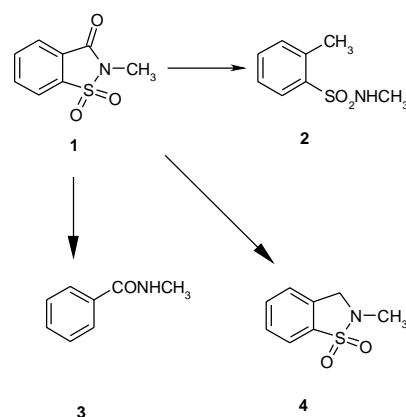
sulphonamide is higher than that in Watt's electrolyte (N1) (Fig. 1a), but it is lower than in electrolyte N2 (Fig. 1b). The above results show that chloride and citric acid anions favour the adsorption of SAC by a carbonyl group.

Different dependencies of SAC and NMS behaviour at the cathode on electrolyte composition were noticed. They might be caused by a different behaviour of C–N–H (SAC) and C–N–C (NMS) bond systems of additives in electrolytes (Schemes 1, 2; Fig. 1, 2). SAC are dissociated in electrolytes at  $\text{pH} > 2$  (Scheme 1) when NMS are stable. The  $V_a$  of N-methyl-o-toluene sulphonamide is 4–8 times lower than the  $V_a$  of o-toluene sulphonamide, and the  $V_a$  of N-methylbenzylsultame is 2–10 times higher than the  $V_a$  of benzylsultame (Fig. 1, 2). The anions of electrolyte N2 in comparison with Watts electrolyte change the behaviour of SAC on the cathode (Fig. 1 a, b), but exert no marked influence on NMS cathodic reactions (Fig. 2 a, b). The opposite behaviour of additives was determined in all-chloride electrolyte (Fig. 1, 2 a, c). Chloride anions increase the adsorption of NMS by a carbonyl group. A simple reduction of it with the formation of N-methylsultame increases  $>3$  times (Fig. 2 a, c, curve 4). The reduction of carbonyl group with hydrogenolysis of endocyclic C–N bond and formation of N-methyl-o-toluenesulphonamide increased  $\sim 2$  times (Fig. 2 a, c, curve 2). A decrease in  $V_a$  of N-methylbenzamide (which is more stable than benzamide in electrolytes) in all-chloride electrolyte informs about poor conditions for adsorption of NMS by sulfonyl group (Fig. 2, curve 3). The above effect was noticed for SAC (Fig. 1, curve 3). The decrease of adsorption of additives under study by a sulphonyl group may explain the reason for a slight influence on electrodeposition by benzene derivatives with only one sul-

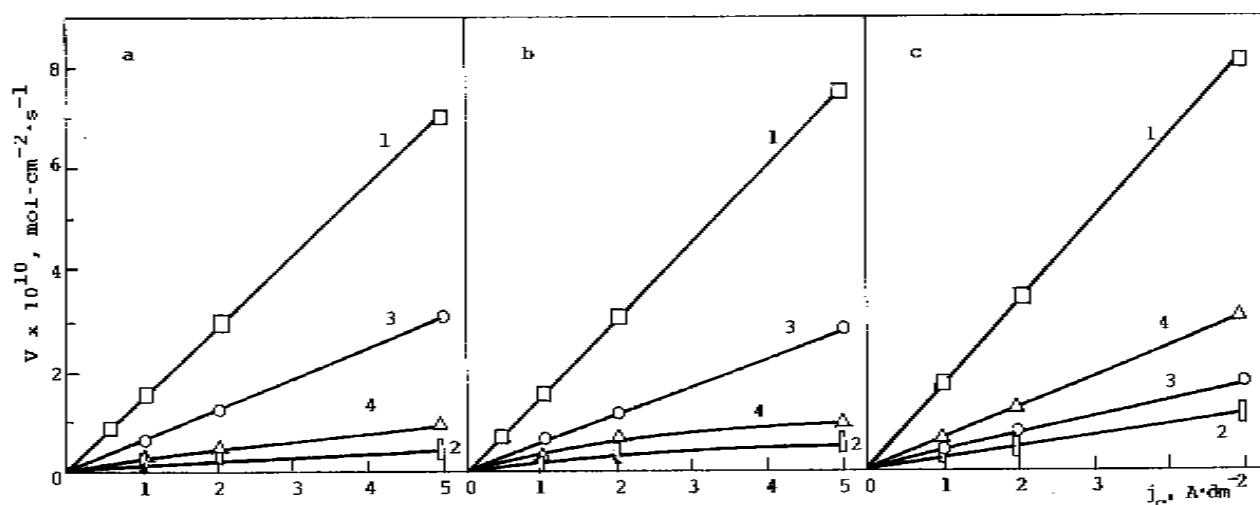
fonyl group (benzene sulphonamide, benzene sulfonic acid, etc.) in highly chloride electrolytes [45].



**Scheme 1.** Schematic representation of saccharin (1) dissociation, electron dislocation and transformation on the cathode (2 – o-toluenesulphonamide, 3 – benzamide, 4 – benzylsultame)



**Scheme 2.** Schematic representation of N-methylsaccharin(1) transformation on the cathode (2 – N-methyl-o-toluenesulphonamide, 3 – N-methylbenzamide, 4 – N-methylbenzylsultame)



**Fig. 2.** Dependency of N-methylsaccharin consumption rate (1) and accumulation rates of N-methyl-o-toluenesulphonamide (2), N-methylbenzamide (3) and N-methylbenzylsultame (4) on  $j_c$  of cathode. Conditions of electrodeposition and composition of electrolytes are the same as in Fig. 1

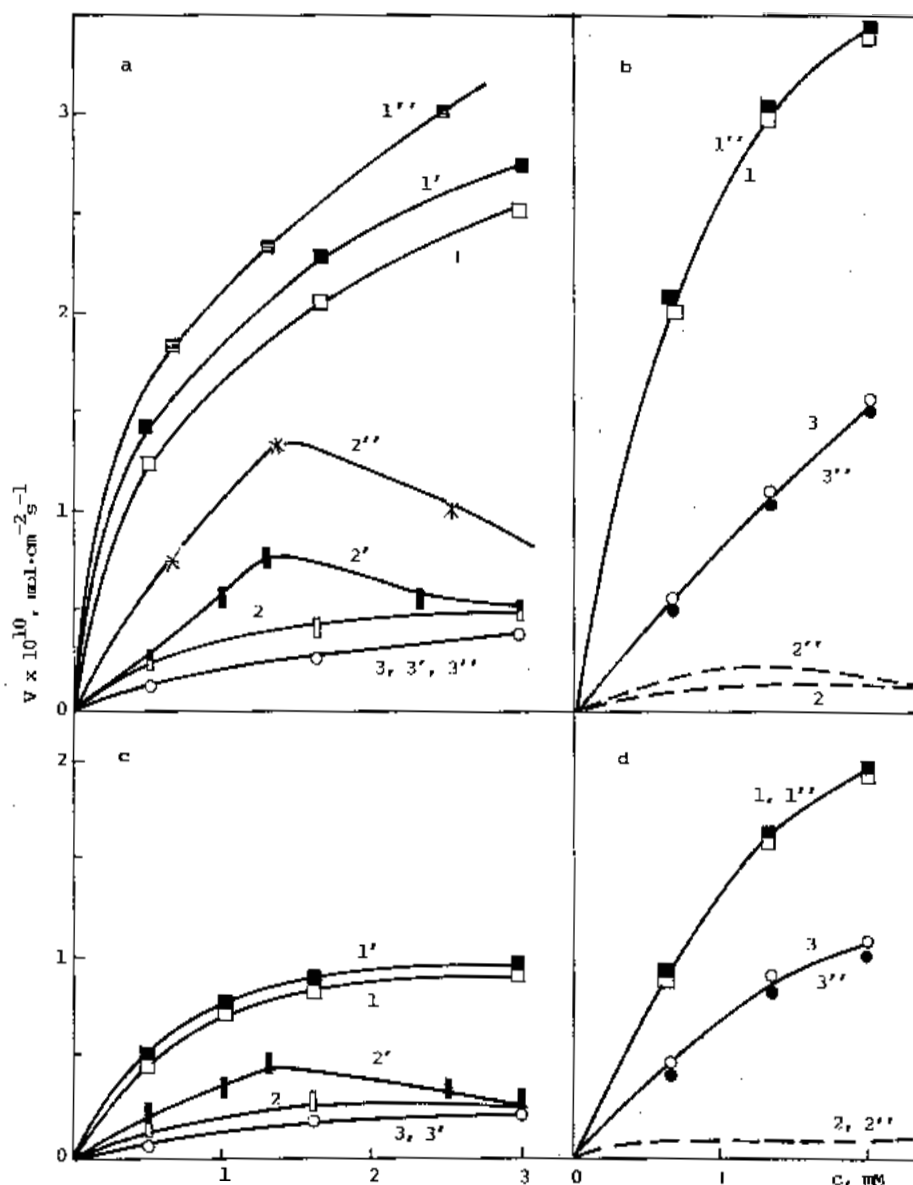


Fig. 3. Dependency of consumption rate (1, 1', 1'') of saccharin (a, c) and N-methylsaccharin (b, d) and accumulation rates of corresponding o-toluene sulphonamides (2, 2', 2'') and benzamides (3, 3', 3'') on the concentration ( $c$ ) of additives at 20 °C (a, b) and 55 °C (c, d), pH 4.5 and  $j_c = 2 \text{ A dm}^{-2}$  in electrolytes containing (mol  $\text{dm}^{-3}$ ): 1, 2, 3 -  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O} - 1$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} - 0.19$ ,  $\text{H}_3\text{BO}_3 - 0.48$  (N1); 1'2'3' - N1 + citric acid - 0.04 (N4); 1''2''3'' - N1 + citric acid - 0.04, gluconic acid - 0.02, glucose - 0.04 (N5)

The influence of citric acid and a mixture of glucose, citric and gluconic acids (stabilizer in Ni-Fe electroplating) on SAC behaviour during Ni electrodeposition have been investigated earlier in Watts electrolyte (N1) (Fig. 3 a, c) [53, 54]. The dependency of cathodic reactions on  $c$  of additive informed about more complicated processes on the cathode than competition of all components of electrolyte during adsorption. The highest value of  $V_a$  o-toluene sulphonamide at  $\sim 1.25 \text{ mM}$  of SAC ( $j_c = 2 \text{ A dm}^{-2}$ ) in comparison with higher and lower  $c$  of additive makes it possible to suggest that

the catalytic activity of electrodeposits formed depends on the ratio of adsorbed compounds. The cathodic reaction of o-toluene sulphonamide synthesized from SAC is mostly dependent on Ni electrodeposit properties in comparison with other reactions (Fig. 3 a, c, curve 2, 2', 2''). The greatest influence on  $V_a$  of o-toluene sulphonamide had the mixture of glucose, citric and gluconic in the solutions under study. The above mixture had no such a marked influence on the behaviour of NMS in Watts electrolyte (Fig. 3 b, d) as citric acid in electrolyte N2 (Fig. 2 a b). The nature of additive is of less influence in all-chloride electrolyte, but, on the contrary, greater changes in the cathodic process were determined in electrolyte with NMS than with SAC (Fig. 1, 2 a c).

The differences in  $V_a$  of cathodic reaction products in electrolytes under study will be followed by changes in the influence of additives on electrodeposits formation. The mechanism of action of SAC and NMS is performed by cathodic reactions [50, 51]. Changes of internal stresses mainly depend on desulphuration

reaction and sulphur incorporation. The appearance of electrodeposits is probably more dependent on carbonyl group reduction reactions (with and without C-N bond hydrogenolysis). The above proposals are made in comparison with the data on SAC cathodic reactions (Figs. 1-3) with the influence of p-toluene sulphonamide and SAC on the reflectivity of submicrorough surface of cathode [52]. The four hydrogen atoms are used in the synthesis of o-toluene sulphonamide from SAC as in hydrogenation of levelling additive 2-butyne-1,4-diol to 1,4-butanediol. The o-toluene sulphonamide synthesis (scheme 1,

Figs. 1–3) may have a levelling influence on sub-microroughness of cathode surface and increase the reflectivity of electrode as has been determined in [52].

## CONCLUSIONS

Hydroxycarboxylic acids and/or chloride anions increase consumption of SAC and NMS by accelerating only one or both cathodic reactions of carbonyl group reduction (with and without C–N bond hydrogenolysis). The mixtures of the cathodic reaction products of both additives in all-chloride electrolyte differ from that of Watts electrolyte, and only the corresponding mixture of saccharin differs in the presence of hydroxycarboxylic acids at used concentrations 0.04–0.10 mol dm<sup>-3</sup>. Increase of  $V_a$  of o-toluene sulphonamide, N-methyl-o-toluenesulphonamide and N-methylbenzylsultame shows that the adsorption of additives by carbonyl group is increased. The decrease of  $V_a$  of the corresponding benzamides allows to suggest the opposite influence of the anions investigated on the adsorption of additives by the sulphonyl group. The transformation process of additives on the cathode depends on their nature, on the properties of electrolytes and electrodeposits and on the competition of all compounds and ions during adsorption on the electrode.

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**SACHARINO IR N-METILSACHARINO KATODINĖS REAKCIJOS ELEKTROLITIŠKAI IŠSKIRIANT NIKELĮ IŠ ELEKTROLITŲ SU ĮVAIRIAIS ANIJONAIS**

S a n t r a u k a

Sacharino ir N-metilsacharino elgsena elektrolitiškai išskiriant Ni elektrolituose, kurių sudėtyje buvo įvairūs kiekiai sulfato, chlorido ir hidroksikarboksirūgščių anionų, buvo tirta analizuojant priedų išsekimo ( $V_{is}$ ) ir katodinių reakcijų produktų susikaupimo greičius ( $V_s$ ). Priedų  $V_{is}$  elektrolituose su hidroksikarboksirūgščių ir/ar chlorido anijonais padidėjo pagreitėjus susikaupimui produktų tik vienos ar dviejų karbonilinės grupės redukcijos reakcijų (su ir be C–N jungties skilimu penkianaryje žiede), palyginus su Uotse elektrolitu. Abiejų priedų katodinių reakcijų produktų mišiniai chloridiniame elektrolite skiriasi nuo gauto Uotso elektrolite ir tik sacharino minėtas mišinys skiriasi esant tirtiems hidroksikarboksirūgščių kiekiams (0,04–0,10 mol dm<sup>-3</sup>). o-Toluolsulfamido, N-metil-o-toluolsulfamido ir N-metilbenzilsulfamo  $V_s$  padidėjimas rodo, kad tiriami anijonai palengvina priedų adsorbciją ant atsinaujinančio katodo karboniline grupe. Benzamidų  $V_s$  sumažėjimas rodo apsunkintą priedų adsorbciją sulfoniline grupe. Tiriamų priedų veikimas for-

muojant Ni elektrolitines nuosėdas pasireiškia per katodines reakcijas. Priedų kitimo procesą ant katodo sąlygoja jų kilmė, elektrolito ir elektrolitiškai nusodinto Ni savybės bei konkurencija visų junginių, esančių elektrolituose adsorbuojantis ant elektrodo.

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**КАТОДНЫЕ РЕАКЦИИ САХАРИНА И N-МЕТИЛСАХАРИНА ПРИ ЭЛЕКТРООСАЖДЕНИИ НИКЕЛЯ В ЭЛЕКТРОЛИТАХ, СОДЕРЖАЩИХ РАЗНЫЕ АНИОНЫ**

Р е з ю м е

Поведение сахараина и N-метилсахарина при электроосаждении Ni в электролитах, содержащих разные количества сульфатных, хлоридных и оксикарбоновых кислот анионов, исследовалась определяя скорости расходования ( $V_p$ ) добавок и скорости накопления ( $V_n$ ) продуктов катодных реакций Анионы оксикарбоновых кислот и хлоридные по сравнению с анионами электролита Уоттса увеличивает  $V_p$  сахараина и N-метилсахарина за счет одной или обеих реакций восстановления карбонильной группы (с разрывом и без разрыва C–N связи в пятичленном цикле). Смеси продуктов катодных реакций обеих добавок в хлоридном электролите отличаются от такой смеси в электролите Уоттса и только соответствующая смесь продуктов сахараина отличается в присутствии использованных концентраций (0,04–0,10 моль дм<sup>-3</sup>) оксикарбоновых кислот. Увеличение  $V_n$  o-толуолсульфамида, N-метил-o-толуолсульфамида и N-метилбензилсультама показало, что количество молекул добавок адсорбированных карбонильной группой, увеличилось. Уменьшение  $V_n$  соответствующих бензамидов позволяет предполагать о противоположном влиянии исследуемых анионов на адсорбцию добавок сульфонильной группой. Влияние сахараина и N-метилсахарина на формирование электроосадков в основном осуществляется с помощью катодных реакций, скорости которых зависят от природы добавки, свойств электролитов и катодов, а также конкуренции между всеми соединениями, присутствующими в электролите при их адсорбции на обновляющемся Ni катоде.