MultiScience - XXX. microCAD International Multidisciplinary Scientific Conference
University of Miskolc, Hungary 21-22 April 2016, ISBN 978-963-358-113-1

THE EFFECT OF TIN CONCENTRATION ON THE ELECTRODE PROCESSES OF TIN ELECTRO-REFINING IN HCl SOLUTIONS

Tibor Kulcsár[1], Zsolt Dobó[2], Tamás Kékesi[3]
[1] PhD student, [2] research fellow [3] Professor
[1,3]Institute of Metallurgy, [2]Institute of Energy and Quality Affairs,
University of Miskolc, Hungary,
kekesi@uni-miskolc.hu

ABSTRACT

Tin refining in solutions containing just the necessary concentration of HCl for stability (1 mol/dm^3), has been investigated in different types of electrolysis cells. A rotating cathode with a centrally placed vertical axis was used to demonstrate the importance of the cathode crystal structure. A computer controlled special potentiostat and current supply was developed for the purpose of potentiostatic and galvanostatic experiments. The virtually even surface of the rotating cathode could offer a uniform conditions over also the anode surface. Cathodic and anodic current densities vs. overpotential were plotted and analysed, as well as cathode potential vs. time at different current densities, applying different tin concentrations. At low tin concentrations, the diffusion limiting current sets in early at the, followed by a shift of the dominant cathodic process for hydrogen evolution, whereas at higher tin concentrations tin deposition was undisturbed. Anodic processes were found virtually unaffected by any of the applied conditions. The optimum energy requirement was found at 30-90 g/dm^3 Sn in the 1M HCl solution at ~ 300 A/m^2 anodic current density.

1. INTRODUCTION

Conventional electrolytes applied for tin electrorefining in the industry have been based on sulphuric media containing great amounts of inorganic components and additives for stability and controlled electro-crystallization[Halsall, 1989]. In our laboratory, we have developed a method to produce and apply pure hydrochloric - tin chloride electrolytes, which offer low costs of materials and high purity of the cathodes[Rimaszéki, 2011]. These solutions are stable, allow high solubility and high conductivity even with low HCl concentrations applied. However, changes in the structure of the cathode deposit and in the stability of the solution require a closer examination of the electrode processes. Although the introduction of periodic compression of conventional planar cathodes or the continuous compression of the rotating cylindrical cathode provide practical operation for long time[Kulcsár, 2014] changes in the state of the anode may still affect the conditions of tin electrorefining significantly. The anode potential may change significantly even on clean surfaces, causing changes in the characteristic valence states and concentration of dissolved tin species and even the process of cathodic deposition. At higher anode potentials Sn(IV) may be primarily generated, but the slime layer containing basically metallic tin particles may reduce it to the Sn(II) state preferred as predominant in the bulk

DOI: 10.26649/musci.2016.015

solution for stability and for the ease of cathodic reduction [Rimaszéki-1, 2011, Kulcsár 2014]. With the rotating cathode, further oxidation by air at the solution surface can take place more, but the analysed Sn(IV) concentration may not be a direct indicator as direct or electroless contact reduction at the electrode surface may remove it continuously. However the decrease in the current efficiency is an evident indirect indicator. As tin forms chloride complexes readily, and by conversion of the ions, their mobility and their redox properties are affected, electrodes may be also influenced by the changes in the concentrations of the HCl background. According to thermodynamic simulation,[Rimaszéki-2, 2011] complex ions of high coordination can be formed even at a level of 1 mol/dm^3 HCl. Electrode processes are practically indicated by changes in the potential and the – also measurable – current efficiency. The solution should contain Sn(II) species predominantly which species form stable solution and can be readily reduced at the cathode at moderate potentials, [Toth, 2014] which is however shifted slightly in the negative direction by the concentration of complexing chloride ions.[Kulcsár, 2014] We have developed a data acquisition system to record both these important characteristics continuously. [Kulcsár, 2014]

For a steady current to evolve, it is required to supply overpotential to the electrode too. Not considering the macroscopic concentration changes at the electrode surfaces, the current density (i, A/dm^2) depends on the activation type overvoltage (η_{akt}, V) [Erdey-G.T 1969, Kékesi 1993] for the Sn^{2+}/Sn couple:

$$i = |i_{\mathrm{a}}| - |i_{\mathrm{c}}| = |i_{\mathrm{o}}| \left\{ \exp\left[\frac{\alpha_{\mathrm{a}} 2\mathrm{F}\eta_{\mathrm{akt}}}{\mathrm{R}T} \right] - \exp\left[-\frac{\alpha_{\mathrm{c}} 2\mathrm{F}\eta_{\mathrm{akt}}}{\mathrm{R}T} \right] \right\} \tag{1}$$

where i_{a} – anodic partial current density, A/dm^2, i_{c} – cathodic current density, A/dm^2, T – temperature, K, R – molar gas constant, J/mol K, F – Faraday constant, determining the molar charge in combination with the average change of charge as 2·96500 As/mol. The system is characterized by the transfer coefficients (α_{a}, α_{c}), and the exchange current density, i_{o} (A/dm^2) can be expressed as:

$$i_{\mathrm{o}} = z\mathrm{F}c_{\mathrm{Sn^{2+}}}\mathrm{B}_{\mathrm{red}} \exp\left(-\frac{\varepsilon^{\neq}_{\mathrm{red}} + \alpha_{\mathrm{red}} 2\mathrm{F}E_{\mathrm{Sn^{2+}/Sn}}}{\mathrm{R}T} \right) \tag{2}$$

where $\mathrm{B}_{\mathrm{red}}$ is the pre-exponential coefficient in the kinetic equation of the cathodic process, $\varepsilon^{\neq}_{red}$ is the activation energy of the cathodic process and $E_{\mathrm{Sn^{2+}/Sn}}$ is the equilibrium electrode potential. [Erdey-G.T 1969].

At higher resultant currents ($|i|$>1 A/dm^2) the partial current densities opposite to the dominant process (anodic deposition or cathodic dissolution) can be neglected from expressions (1) and (2) with good approximation. The activation overvoltage develops virtually simultaneously with the launched current[Kékesi, 1993]. With a set current, the concentration of the tin species are shifted, which in turn generates diffusion transport and also a potential shift – diffusion overvoltage – according to the Nernst-equation. The corresponding transient period can however take as long as dozens of seconds.[Kékesi, 1993] This voltage component is stabilized by the increased transport of active species by diffusion and natural/forced convection.

Applying the specifically developed rotating cylinder cathode and continuous compacting,[Kulcsár, 2015] the surface conditions at the cathode could be stabilized during the measurement. This allowed to investigate the optimum set of conditions in terms of tin concentration and current density. A major indicator is the potential development of the anode, primarily responsible for changes in the in the electrolyte. Besides the pressed rotating cathode, a special potentiostatic equipment was also required to detect the quickly changing potential profiles of the tin electrode. Facilitated by these special technical developments, it was possible to obtain characteristic polarization curves both in the cathodic and anodic direction, revealing the nature of electrode processes in tin refining.

2. EXPERIMENTAL PROCEDURE

The safe minimum of HCl concentration of 1 mol/dm^3 was applied throughout the experiments, as suggested by basic studies.[Rimaszéki-1, 2011] In order to avoid the changes in the cathode surface in long term runs, the cell was equipped with a rotating cylindrical cathode and a pressure bar continuously compressing the loose crystals into a smooth layer at the cathode surface. In this case, the anode and the cell was also constructed with a cylindrical geometry. Similar electrorefining experiments were also carried out with the conventional stationary planar electrodes. However in this case the electrodes were suspended from a digital scales connected to a data acquisition system to record the weight changes. The potentiodynamic experiments were carried out with a small working electrode with a circular active surface of 0.125 cm^2 area and a pure tin counter electrode, as well as a calomel reference electrode connected to the detection point by a Luggin-capillary tube. The cell constructions devised for the refining experiments with two different cathode types and for the potentiodynamic studies are shown in Fig. 1.

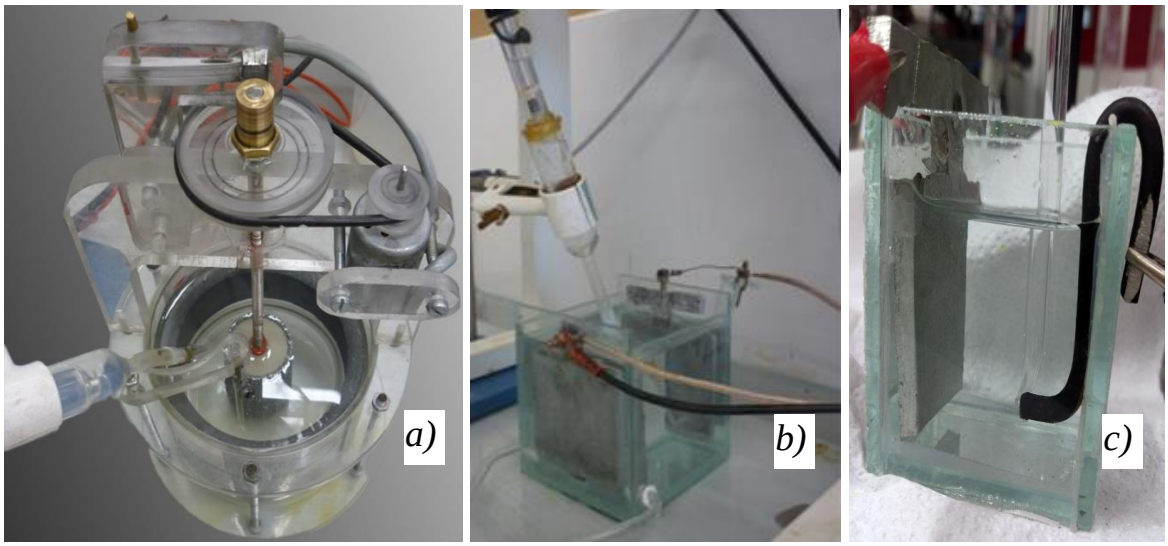

Fig. 1 Refining cells with compressed rotary cylindrical cathode (a) with conventional suspended electrodes (b), and the potentiodynamic cell (c).

The potentiodynamic experiments were carried out in the conventional way in the three-electrode arrangement in stationary solutions, however with an extremely short cycle time usually lasting for 10 seconds with the 100 mV steps applied. During this short time, the surface roughness of the mechanically prepared working electrode did not change so much as to make the polarisation curves unrealistic. However, because of the tendency of tin deposition to form loose dendritic crystals, the effective surface of the electrode may quickly grow. Therefore, constant potential may result in fast increasing currents. At the Institute of Metallurgy of the University of Miskolc, we have developed a special computer controlled potentiostat that was capable to produce rapid current increments, suitable also for the investigation of the cathodic processes under rapidly changing conditions.

We used two different techniques for the investigations of electro-refining. By the galvanostatic experiments, the changes in the potential were recorded in time, using constant currents. The potentiodynamic experiments, on the other hand, showed the evolution of current as the potential was set at constant levels, increased continually with 100 mV/s rate without any time intervals. The reference electrode was saturated calomel, connected to the point of detection through a tightly fitted connection tube filled with the electrolyte. The tip of the tube was a bent Luggin-capillary (as seen in Fig. 2*a*), placed less than 1 mm apart from the electrode surface.

For the galvanostatic experiments, we have developed another special computer controlled power supply capable of setting different current shapes, including the smooth direct current and optionally reversed impulse currents of short (milliseconds range) periods too. The interface between the electrolytic cell and the computer was provided by the NI USB-6212 multi-function converter unit supplied by National Instruments.

The arrangement of the detection point, where the Luggin-capillary is set, also influences the absolute potential results measured, as the current distribution is usually not uniform over the electrode surface. The Luggin arrangements at the anode of the cell operated with the conventional planar electrodes and that operated with the cylindrical rotating cathode are shown in Fig.2.

Fig. 2 Reference electrodes and deposit structures in the conventional (a) and the rotating cathode operated cylindrical (b) cells.

It is seen that the deposit structure is very rough at the conventional cathode, especially at the lower edge, where the supply of the tin ions is the highest. Consequently, the current is also concentrated more to the lower section of the opposite anode. However, due to the continuous cathode compression and the agitation of the electrolyte, a virtually homogenous deposit structure could be assured by the rotating cathode. The difference in the operating conditions is expressed by the comparison of the respective anode potentials shown in Fig. 3.

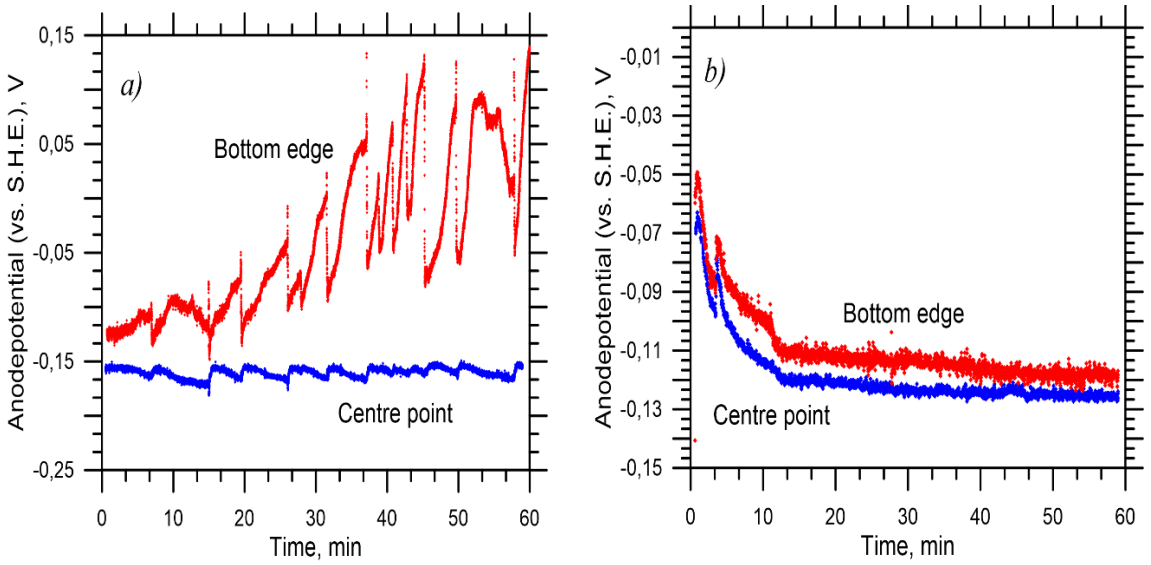

Fig. 3 Potentials at different points on the anodes of a conventional cell (a) and of the cylindrical cell equipped with a rotating and compressed cathode (b).

The rest potential of the tin anode was generally – 0.252 V vs. the standard Hydrogen Electrode (S.H.E.) on the average. The potential at the bottom edge was consistently higher than that in the centre of the anode. This is caused primarily by the preferential growth of the opposite cathode at the bottom. Thereby the shorter inter-electrode distance caused a higher local current density at the bottom sections of the anodes. This potential difference is further increased by the higher tin concentration at the lower segments of the cell, due to stratification of the electrolyte induced by the conditions of natural convection. Whereas the potential – and the current overload – at the bottom of the anode in the conventional cell is continually increasing – with irregularities caused by the intermittent cathode compression by hand – that at the bottom of the cylindrical anode in the cell equipped with the rotating and continuously compressed cathode is stable or even slightly decreasing in time. This indicates an undisturbed and regular operation in the latter case.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The cathodic processes showed significant differences at the potentiostatic investigations in solutions of different tin concentrations. The slopes and the break points in the polarisation curves of Fig. 4*a* correspond to the characteristics of the relevant electrode processes.

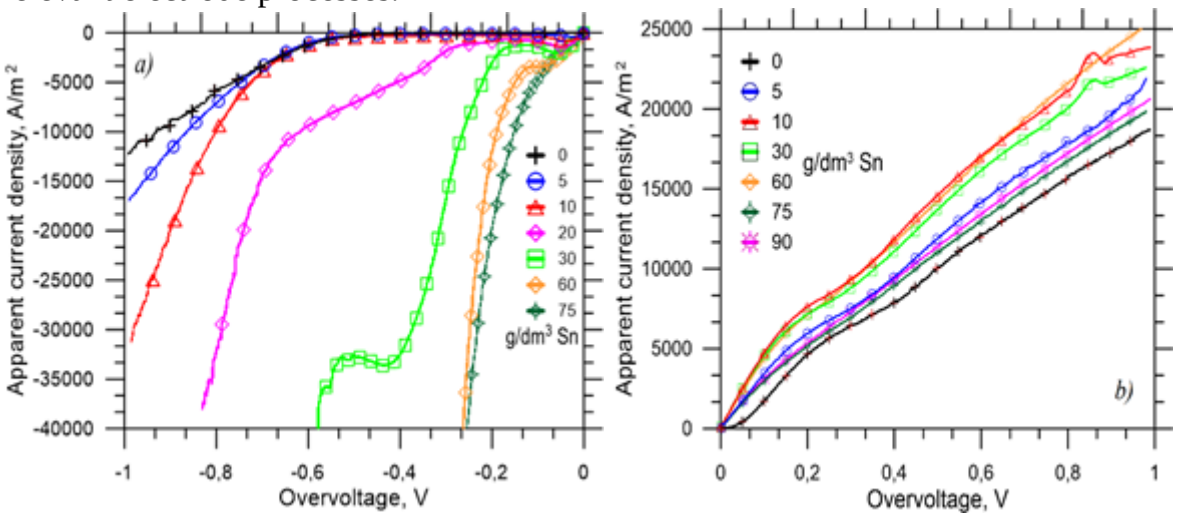

Fig. 4. Cathodic (a) and anodic (b) polarization curves in 1M HCl solutions of different tin concentration.

The current curves generally show an initial increase with polarising the electrode in the negative direction, according to Eq. (1), which is however quickly stopped by the depletion of the surface film in the electroactive Sn(II) species. Considering also Eq. (2), it is understood that this change may reduce the current at the same overpotential significantly. This is followed by a relatively stable range exhibiting a very low limiting current with further increased cathodic polarization. This flat section of the current profile changes into a second increase as the cathode surface becomes rougher by the deposited crystals. In solutions of 30 g/dm^3 or lower tin concentration, this secondary rising section of the current curve declines again as the crystal growth and the surface roughness becomes practically uniform and stable. With further increased cathodic overvoltage, forcing the overpotential below approx. 0.6 V, the evolution of hydrogen starts and causes a steeper third increasing segment in the current profile. This is however not recognised in solutions of higher tin concentration than 30 g/dm^3, because the fast growing crystals may get enough supply of electroactive Sn(II) species. This, in turn, may cause a continually increasing surface roughness with long crystals projecting towards the counter electrode, thereby developing very high currents before the potential could reach the value of starting hydrogen evolution. With stationary solutions of as low bulk Sn(II) concentration as 5 g/dm^3, significant currents could only develop by a steady hydrogen evolution. This indicates that the supply of the electroactive tin species is strongly limited by the diffusion transport, which is in direct correlation with the tendency of dendritic electro-crystallization.[Kékesi 1993]

On the other hand, as shown by Fig. 4*b*, the anodic currents build up relatively smoothly as the overvoltage is increased in the positive direction. The anodic process seems stable in the entire examined range. In the 1 M HCl solution containing 0 – 90 g/dm^3 tin as Sn(II), equally high anodic currents can be produced by the same mechanism. The maximum anodic currents are reached in the 1 M HCl solution of 60 g/dm^3 (i.e. ~ 0.5 M) Sn(II) concentration. At higher tin concentration there are no more free chloride ions for complexation and the hydroxo-chloro species arise, slowing the transport and to hydrolysis, therefore may hinder the anodic process.

The effects of the tin and the HCl concentrations on the anodic dissolution are compared in Fig. 5. It is seen that changing the tin concentration in the 10 – 120 g/dm^3 range (corresponding to 0.08 – 1 mol/dm^3) in a 1 M HCl solution does not influence the anodic process. However, increasing the HCl concentration from 0.5M to 3 M accelerates the anodic dissolution of tin significantly. At 1 V anodic overvoltage the current density was approx. 7500 A/m^2 in the 0.5 M HCl solution, which is practically higher than usually required. This high value was even doubled in the 1 M HCl solution, and in 3 M HCl it was more than 5 times higher. It indicates that the chloro-complex formation may have a significant effect on the dissolution and the stability of tin in the solution. The galvanostatic experiments, with different current densities revealed the development of overpotentials over time of electrorefining (Fig. 6).

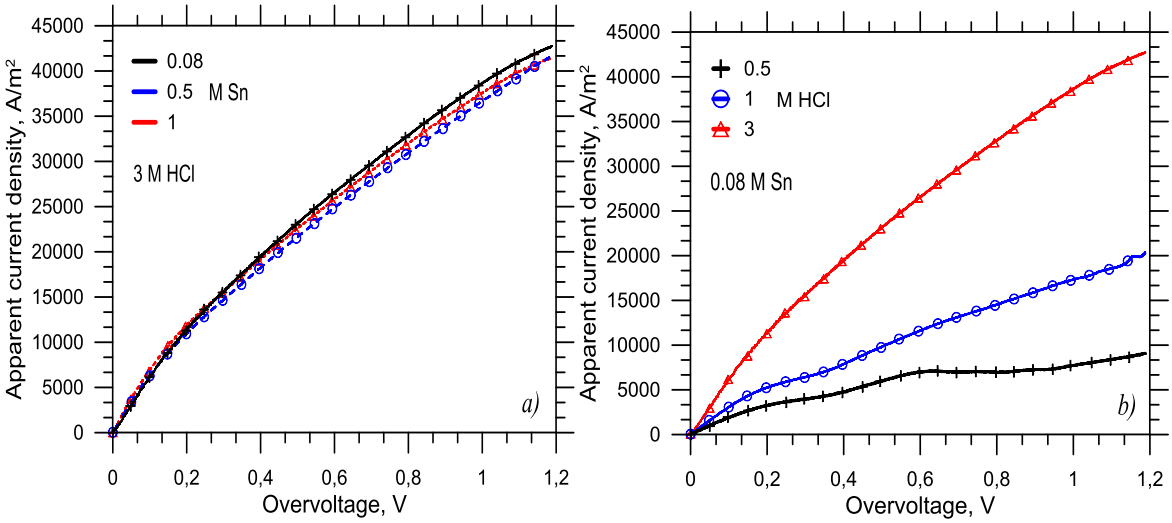

Fig. 5. Anodic polarization curves in solutions of different tin (a) and different HCl (b) concentrations.

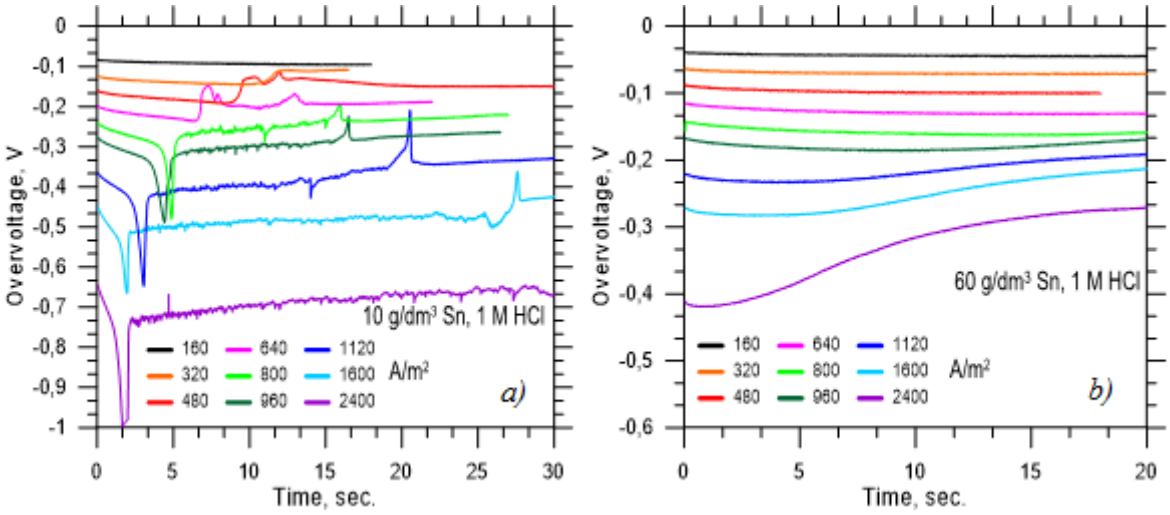

Fig. 6 Development of cathodic overvoltages with different current densities in 10 g/dm^3 (a) and 60 g/dm^3 (b) Sn (1 M HCl) solutions.

In the solution of lower (10 g/dm^3) tin concentration, the cathode surface film is depleted in electroactive tin species shortly after starting the current and the cathodic overpotential sharply increases (in the negative direction). It also triggers hydrogen evolution, which in turn blocks part of the active cathode surface by attached gas bubbles and thereby further increases the overpotential needed to keep the set current. As the bubbles get detached, as verified by visual observations, the current is maintained by a sharply reduced cathodic overpotential. In the continuation, hydrogen evolution subsides and the deposited tin crystals appear visibly when the cathodic overpotential drops again. Further deposition of tin takes place with a slightly decreasing cathodic overpotential as the surface gets rougher (and its area effectively greater) with the developing crystals. In the solution of higher (60 g/dm^3) tin concentration, hydrogen evolution is excluded by a higher rate of tin ion supply to the cathode surface. At the highest examined current densities, the initial cathodic overpotential is significantly reduced by the relatively faster growing rough crystals.

If the solution is in contact with air, the oxidation of the Sn(II) species to the Sn(IV) state can also take place. We have examined the effect of oxidation in the solution on the cathodic process by adding increased amount of hydrogen peroxide to a solution originally containing 32 g/dm^3 tin in the Sn(II) form. Figure 7 shows that the cathodic currents generated at the same overpotentials are reduced as more of the dissolved tin is converted into the Sn(IV) state.

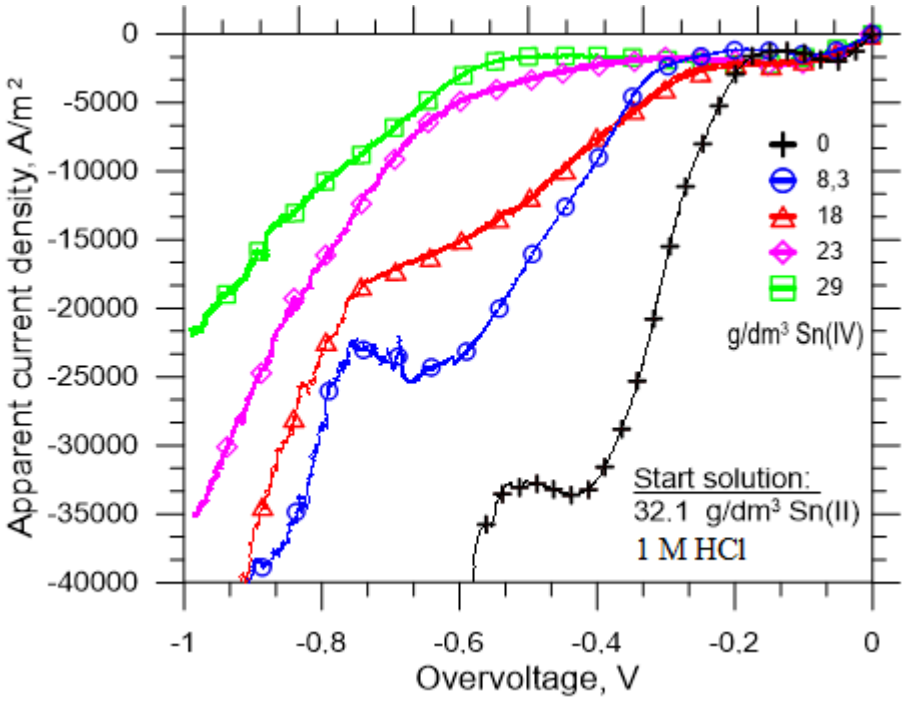

Fig. 7 The effect of converting different portions of the tin concentration into the Sn(IV) state by oxidation in a 30 g/dm^3 Sn electrolyte (1 M HCl).

It is seen that as more tin is oxidised into the Sn(IV) state, the same cathodic overpotentials can generate significantly lower currents. This indicates that the Sn(IV) species are less active to take part in the cathodic process. The current profiles approximately replicate those in Fig. 4 obtained with similar Sn(II) concentrations in the solution, but in this case the currents are slightly higher because of the additional reduction of Sn(IV) at the cathode. The mechanism shifts finally to the evolution of hydrogen at relatively higher overpotentials as the cathode surface is modified by the different overall deposition process. Another effect of Sn(IV) generation is the gradual loss of solution stability, as Sn(IV) species are especially prone to precipitation if hydrated SnO_2 may be formed.

In order to determine the specific energy requirement of the tin electro-refining process as a function of the Sn(II) concentration in the electrolyte and the applied apparent (geometric) current density of the cathode, it was necessary to use the rotating cathode. The uniform and practically constant cathode surface allowed the use of longer electrolysis runs without interference from irregular electro-crystallization. As shown in Fig. 8, the cylindrical cell equipped with the rotating cathode was best operated with lower current densities and higher tin concentrations.

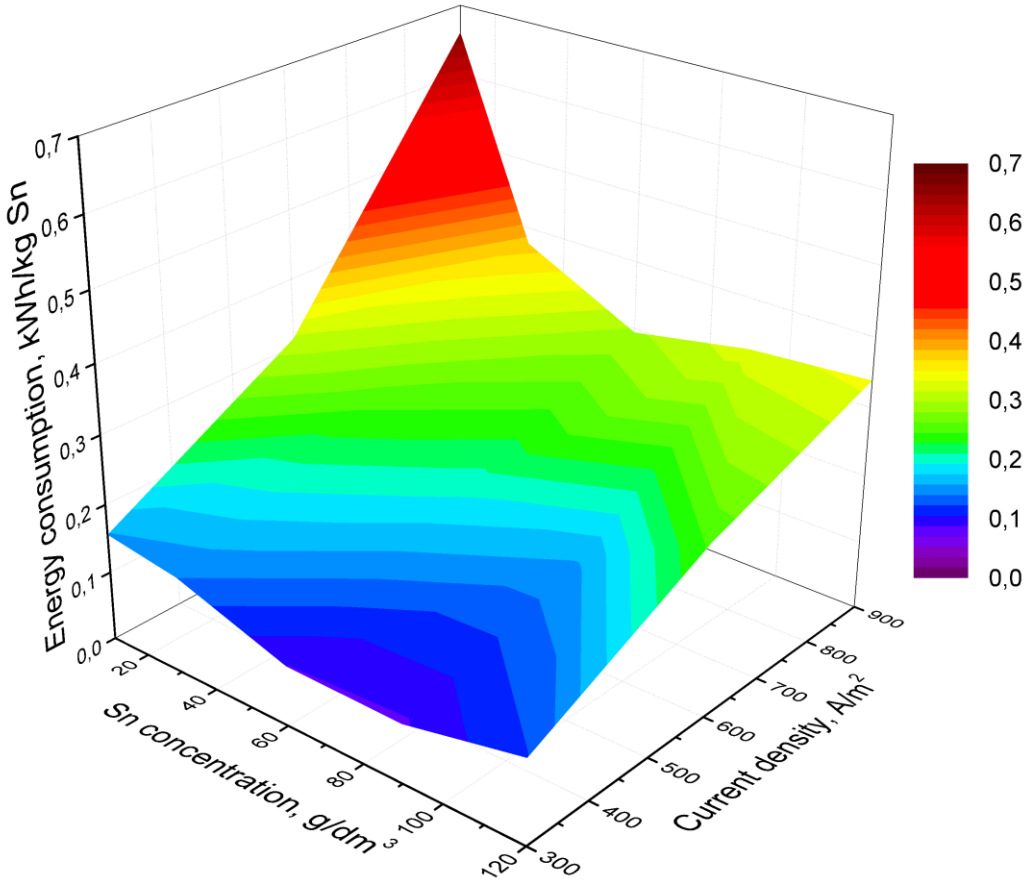

Fig. 8 Specific energy consumption of the cell equipped with the rotating cylinder cathode (1 M HCl)

By increasing the current, the energy requirement of the cell increases considerably because of the greater voltage drop at the resistance of the electrolyte and the increased overpotentials of the electrodes. This effect is strongest in the range above 500 A/m^2. On the other hand, increasing the tin concentration of the solution, especially in the range below 50 g/dm^3, strongly decreases the energy requirement.

The optimum conditions of tin electro-refining in the 1 M HCl solution (already assuring chemical stability) and with the rotating cathode is with less than 600 A/m^2 cathodic current density and approximately 60 g/dm^3 tin concentration in the Sn(II) state. This is different from the optimum conditions expressed merely to the cathodic current efficiency in conventional cells and stationary electrolytes of 1000 A/m^2 current density and 10 g/dm^3 Sn(II) concentration.[Rimaszeki, 2011]

The decrease in the current efficiency at low current densities is not attributed to hydrogen evolution, but it may be primarily caused by the oxidation of the Sn(II) species in the solution, which will in turn cause partial re-dissolution of the cathode by the reaction of Sn(IV) and metallic tin. This effect may be enhanced by the rotation of the cathode also enhancing the superficial oxidation processes of the electrolyte solution by the agitating effect. However the process of re-dissolution also leads to the reduction of the Sn(IV) species, also prone to hydrolysis, thereby assuring the chemical stability of the electrolyte solution.

4. CONCLUSIONS

The special electrolysis control and data acquisition system developed for the examination of tin electrorefining could allow the determination of the major characteristics of the involved electrode processes and the optimum of the operating conditions. The slow transport of the dissolved tin species result in the fast growth of rough crystals at the cathode, which change the surface very soon. To copy with this difficulty we have devised such measuring technique and equipment which made it possible to handle fast changes in the current in response to potential increments. Potentiodynamic experimental results pointed out the great importance of tin concentration in the electrolyte in determining the cathodic processes at different overpotentials. However, anodic processes were virtually unaffected by this parameter, but responding sensitively to the HCl concentration. Although higher 1 M HCl can allow higher anodic currents, it is not required to increase acidity beyond this level, which has proved to be enough for solution stability. Low tin concentration may result in strong cathode polarization and considerable interference of the principle process by hydrogen evolution. It is however changed for a dominant process of tin deposition as the deposited crystals make the cathode surface rougher. Oxidation of Sn(II) ions effectively reduces the concentration of the electroactive species and the current efficiency of the electrolysis. The rotating cylinder cathode could efficiently assure homogeneous cathodic deposit structure and even current distribution also on the anode, thereby suitable conditions for long term operation. The optimum conditions for specific energy requirement were established as less than 600 A/m^2 cathodic current density and approximately 60 g/dm^3 tin concentration in the Sn(II) state, applying the 1 M HCl solutions at room temperature. Under these conditions, the electro-refining of tin in the experimental cell required only ~ 0.2 kWh/kg specific electric energy.

ACKNOWLEDGEMENT

The research work presented in this paper was based on the results achieved in the Centre of Applied Materials Science and Nano-Technology at the University of Miskolc and within the TÁMOP-4.2.2.A-11/1/KONV-2012-0019 project, and carried out as part of the TÁMOP-4.2.2.D-15/1/KONV-2015-0017 project in the framework of the New Széchenyi Plan. The realization of this project is supported by the European Union, and co-financed by the European Social Fund.

REFERENCES

Erdey-Grúz 1969, T.: Elektródfolyamatok kinetikája, Akadémiai kiadó, Budapest.

Halsall 1989, P.: The Refining of Tin, Metall, 43., 131-136

Kékesi-1 1993, T.: Polarization taking place during electrolytic refining of copper, possibilities of its reduction ,Acta Technica Acad. Sci. Hung., 105 (3), pp. 153-172

Kulcsár 2014, T.: Sósavas oldatokban folyamatos tömegméréssel felszerelt álló elektródokkal, valamint forgó katóddal végzett ónraffinálás folyamatainak meghatározása, Diplomamunka, Metallurgiai Intézet,

Kulcsár 2015, T., Kékesi, T.: Nagytisztaságú ón előállításának lehetősége forrasztási ónhulladékból vizes közegű speciális elektrolizáló rendszerben, XVII. Bászányászati, Kohászati és Földtani Konferencia (17th Mining, Metallurgy and Geology Conference), Deva, Románia, 55-60.

Rimaszéki-1 2011, G, Kulcsár, T., Kékesi, T.: Elektrolitos ónraffinálás sósavas oldatokban. BKL-KOHÁSZAT, 144, 5, 18-22.

Rimaszeki-2 2011, G.; Kulcsar, T.; Kekesi, T.: The characteristics of electrolytic refining of tin soldering scrap in hydrochloric acid solutions, Proc. 50th Ann. Conf. Met. CIM – Waste Proc. Recycling –VI, Ed. Rao, S.R.; et al.; Montreal, QC, Canada. 2-5. October, 137- 145.

Tóth 2014, G. B., Uchikoshi, M., Kékesi, T.: Polarization Characteristics of Tin Electrorefining in Chloride Solutions, Materials Science and Engineering, 39, 2 (2014) 103-113.