ELECTROREFINING IN AQUEOUS CHLORIDE MEDIA FOR RECOVERING TIN FROM WASTE MATERIALS

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Abstract

Recycling of the impure tin generated by the hot dip tinning and wave soldering technologies widely applied in modern electronic industry can be carried in a flexible and economical way even at relatively low production rates by electrorefining. In order to avoid the economical disadvantages of the alkali stannate or the sulphuric acid – cresylic phenylic sulphonic acid baths, the hydrochloric acid tin chloride electrolyte solutions can be applied. The major difficulties of solution stability, cathode corrosion and rough electro-crystallization can be overcome by optimizing the solution composition and the current parameters. Strong chloro – complex formation in the hydrochloric acid solution enhance stability of the Sn(II) species and the consequent natural inhibition promotes a cathodic deposition of acceptable quality. The virtual current efficiency and the morphology of electro-crystallization were improved by applying periodically reversed (PCR) current. Although cathode corrosion could be depressed to a negligible level, dendritic crystal growth remains to be dominant, therefore special cell arrangement and cathode handling should be applied. The cathode deposit is easily removed and melted, allowing to obtain a recycled tin of high purity.

1 Introduction

The rapidly developing electronic industry produces a growing amount of basically lead free tin containing waste material. Considering the high price of tin (~ 25 USD/kg) the entrained impure metal is usually recovered from the dross by simple hot pressing at the sites of production. However, the hot lead – free molten tin bath is aggressive for the copper contacts, thus the copper concentration is steadily increasing – and becoming critical – during use. The impure tin also contains alloying elements, for example silver at various concentration levels. Recycling primarily requires the elimination of the dissolved Cu. Although the removal of iron by controlled heating/ cooling can be really efficient, a simple treatment of liquefaction of the raw material may allow reducing the Cu concentration to only ~ 0.7 % if the eutectic temperature is closely approached. On the other hand, electrolytic refining is capable of eliminating practically all the important impurities from lead–free tin scrap in one step, implying a relatively simple operation and low cost equipment [1]. Impurities with relatively high electrode potential (among them the most important elements are Cu, Ag and Bi) practically do not dissolve from the tin based anode. They tend to build a fine slime layer at the surface, in the elemental or oxide form [2]. Due to the uneven dissolution, the slime also contains a significant amount of tin powder.

Metals of relatively negative electrode potential, less characteristic in the tin scrap, can dissolve without depositing at the cathode, unless their concentration increases beyond a limit dependent on the actual concentration of tin.

The main characteristics of tin electrorefining are strongly dependent on the type of solution applied as the electrolyte. Alkaline baths are capable of producing relatively dense and regular cathodic deposits, however high temperatures (~ 80 °C) are required and the dominance of the Sn(IV) species arising in alkaline media implies high specific electric charge, and Sn(II) ions – also produced at the anode – disturb the deposition [2, 3]. Therefore, alkaline tin refining is considered as the exception to the general practice [4]. Acid electrolyte solutions, on the other hand, generate more anode slime with high tin content and a dense cathodic deposit can only be obtained at the expense of applying large amounts of special components and additives in the electrolyte [2]. The conventional multi – component baths consist of $SnSO_4$ (30 – 40 g/l tin), cresylic phenylic sulphonic acid (40 – 100 g/l) and free sulphuric acid (40 – 80 g/l) with 1 – 2 g/l β – naftol, or gelatine also added [2, 4]. The acid assures hydrolytic stability, improves conductivity and reduces the solubility of lead. Cresylic phenylic sulphonic acid is extremely expensive, but it is necessary to improve solution stability through more soluble compounds of Sn(IV), whereas β–naphtol, or gelatine promote finer structures of the cathodic deposit.

It seems straightforward to examine the potentials in applying chloride electrolytes. Tin chloride is highly soluble. Chloride electrolysis usually allows higher currents densities. It also suits the production of pure tin, as any tin chloride entrapped in the cathode finally is removed by the final melting step. Stability of the Sn(II) chloride based solution is enhanced and the inherently rapid electric charge transfer at the cathode – causing rough structure – may be partially controlled by the complexing chloride ions [5]. Nevertheless, the stability of the electrolyte solution may be endangered by the oxidation of the Sn(II) species allowing stannic acid precipitation or re-dissolution of deposited tin. Thus it may be important to minimize the oxidizing effects by ambient air or over–polarized anodes by applying proper solution preparation, cell design and current. Cathodic deposition may be improved by supplying short cycle periodically reversed (PCR) or interrupted (PIC) currents, possibly allowing a complete omission of organic additives. The frequent interruption of the current reduces the concentration drop of tin ions at the cathode, thus helping to lessen the harmful effects of the diffusion overpotential and promoting finer grain structure [5, 6].

In order to interpret the possible effects related to the composition of the electrolyte solution, it is necessary to investigate the equilibria of redox and the chloro–complex reactions of tin. Redox potentials and complex stability constants are available in specific databases [7]. The activity of an aquo – ion can be expressed with that of the adjacent lower oxidation state if the potential of the system (E), determined by the applied redox agent, is known:

$$a_{Sn^{(n_{i+1})+}} = a_{Sn^{n_i+}} \cdot 10^{\dfrac{\left(n_{i+1}-n_i\right)\left(E-E^{o}_{Sn^{(n_{i+1})+}/Sn^{n_i+}}\right)}{0.059}} \qquad (n_{i+1} > n_i,\ 0 \le n_i) \qquad (1)$$

Starting from the elemental state, the ion activities of all the possible higher oxidation states can be derived. The activities of the chloro – complex tin species $[SnCl_x]^{(n_i-x)}$ are defined by the activities of the related aquo – ions and the cumulative stability constants of the given oxidation state (n) and coordination number (x):

$$a_{[SnCl_x]^{(n_i-x)}} = \beta_{n_i,x} \left(\gamma_{\pm} \cdot c_{Cl^-} \right)^x a_{Sn^{n_i+}},$$

(2)

where c_{Cl^-} is the concentration of the free chloride ions and $\gamma_{\pm}$ is the mean activity coefficient, determined by the dominance of the HCl in the solution [8]. If tin is completely dissolved, the concentration of a certain species can be obtained from the balance of the all the dissolved species:

$$\sum_i \sum_x c_{[SnCl_x]^{(n_i-x)}} = \sum_i \left\{ \sum_x \frac{a_{Sn^{n_i+}}}{\gamma_{\pm}} \left[1 + \beta_{n_i,x} \left(\gamma_{\pm} \cdot c_{Cl^-} \right)^x \right] \right\} = c_{Sn}$$

(3)

This algorithm has been built into a computer software, ROCC (Reduction – Oxidation – Chloro – Complexation), to assess the formation of the different species of metals dissolved in HCl solutions. The distribution of tin among the various species in contact with the metal or air at varied chloride ion concentrations can be represented by the curves of **Fig. 1 a** and **b**. The Sn(II) solution has a good stability in contact with metallic tin over the entire Cl⁻ ion concentration range, but it may be easily oxidized if the redox potential is determined by oxygen in air.
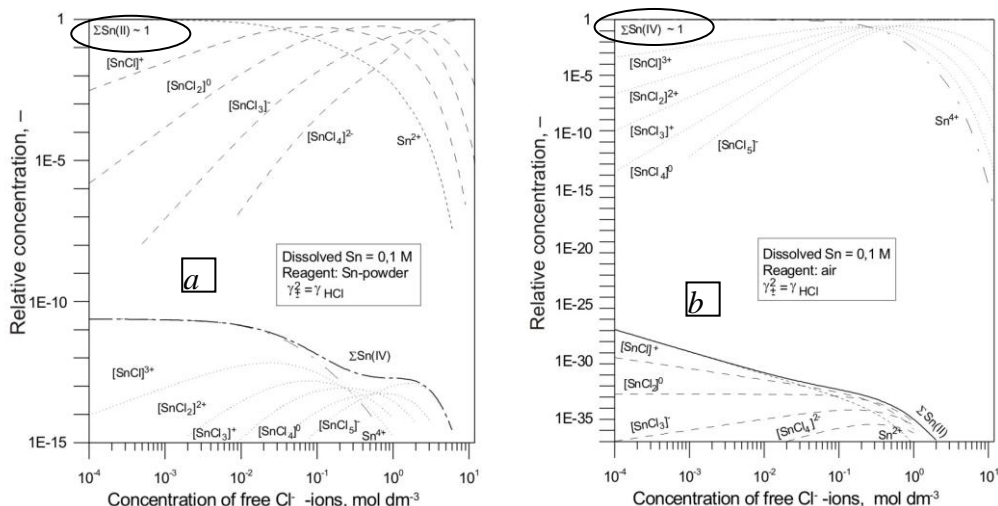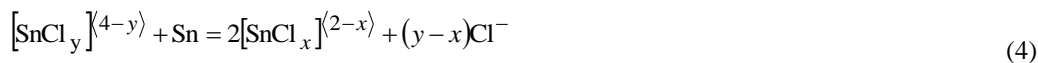

Fig. 1   Equilibrium distribution of Sn among different species dissolved in HCl solutions in contact with *a)* tin metal, or *b)* air

The standard potentials (Sn^{4+}/Sn^{2+} = 0.154V and Sn^{2+}/Sn = -0.136V) suggest that Sn^{2+} can be stabilized in aqueous solutions. The reaction:

$$[SnCl_y]^{(4-y)} + Sn = 2[SnCl_x]^{(2-x)} + (y-x)Cl^-$$

(4)

ensures the stability of the Sn(II) form in contact with metallic tin. This also implies some re – dissolution of the deposited metal, thus reducing the current efficiency too. On the other hand, Sn(IV) ions can be formed by the oxidizing effect of air or the more or less passivated anode:

$$[SnCl_x]^{(2-x)} + 0.5O_2 + 2H^+ + (y-x)Cl^- = [SnCl_y]^{(4-y)} + H_2O$$

(5)
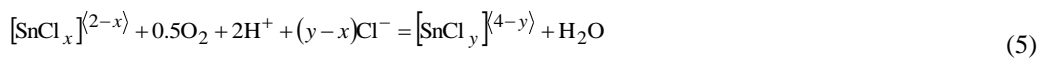
The required conditions for the anodic and the cathodic reactions can be outlined by the potential – pCl$^-$ diagram (**Fig. 2a**) constructed on the basis of the electrode potentials of the aquo – ions and the stability constants of the chloro–complex species. Tin may form oxide or hydroxide compounds, resulting in precipitation. The compound to be first precipitated is SnO_2. At higher pH, the precipitation of $Sn(OH)_4$ and finally $H_2Sn(OH)_6$ can also take place. The possibility of precipitation can be assessed by the relevant potential – pH diagram shown in **Fig. 2b** [9]. Below zero pH – corresponding to the 1 – 2 M HCl range – $Sn(OH)_4$ is not formed, but SnO_2 may arise if the electrode potential is higher than ~ 0.15 V. Therefore formation of stannic oxide precipitation is likely at the area of the anode and the surface of the solution. Comparing Figs. 2a and b suggests that by controlled anode potential the chloro – complex Sn(II) species can be formed and the formation of SnO_2 avoided. The conditions allowing the generation of chloro – complex Sn(IV) species and SnO_2 virtually coincide. Higher pH values than 0 are unfavorable for the danger of SnO_2 formation, however higher acid concentrations are not desired because of the potentially increased cathode corrosion and the decreasing electrode potential of the Sn(II)/Sn couple shown in Fig. 2a, the danger of H_2 evolution, therefore the economy of the operation. Thus ~1M HCl solutions have been in the focus of further attention.
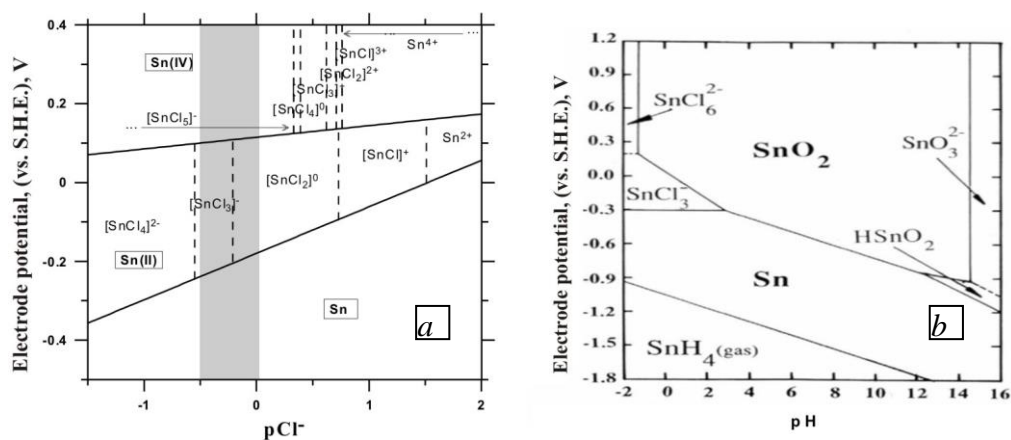

Fig. 2   Stability of the tin species in different aqueous media: *a)* redox potential – pCl$^-$ diagram, *b)* redox potential – pH [9] diagram

As demonstrated in Fig 2*b*, the surface of the polarized anode can be quickly covered by a layer of tin – oxide and hydroxide compounds mixed with detached metal particles.
Oxidation of the originally 10 g dm^{-3} Sn(II) – 1 M HCl solutions with air is illustrated by **Fig. 3**. The concentrations of the Sn(IV) species generated can be indicated by the corresponding changes in the light absorption spectra, using phenylfluorone indicator [10]. The net absorption value is calculated by subtracting that of the HCl – phenylfluorone solution.
As shown in Fig. 3, the oxidation of dissolved Sn(II) by air is slow, even if intensive bubbling is applied. The changes in the absolute concentrations were determined by the direct iodometry of Sn(II) and the analysis of the total tin concentration by the same method after a complete precipitation by aluminium powder and re – dissolution of the precipitated tin content under inert atmosphere in boiling HCl assisted with a platinum catalyst.
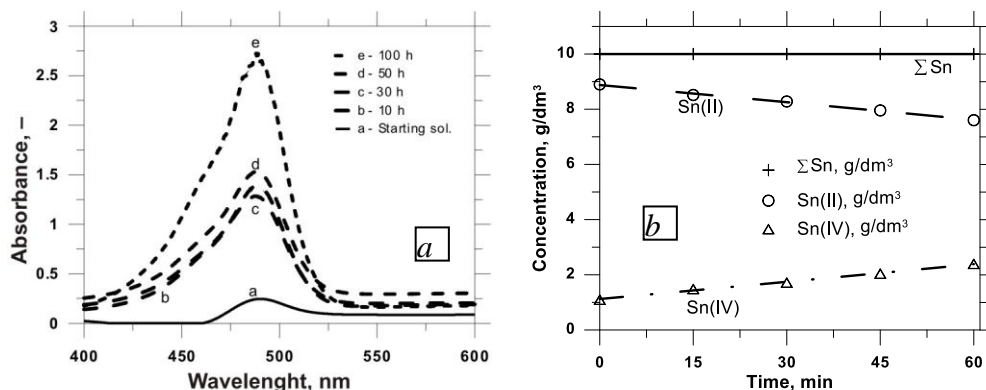
Fig. 3 Oxidation of the originally 10 gdm^{-3} Sn(II) - 1 M HCl starting solution (*a*) light absorption spectra, *b*) analyzed concentrations (50 cm^3)

2 Experimental materials and methods

The Sn(II)/Sn reduction and oxidation processes were studied in a standard thermostated three – electrode experimental cell (**Fig. 4***a*) of 100 cm^3 volume. A tin rod with 1 cm^2 freshly ground open surface was used as the working electrode opposite to a Pt spiral counter electrode. A saturated calomel electrode served as the reference electrode. The apparent current density refers to the geometric surface area. The voltage between the working and the reference electrodes was controlled by an Electroflex EF 435C potentiostat. The current generated between the working and the counter electrodes was recorded by a computer using EF 2105 AD/DA converter and the EMP IEMAS 1.06 software. The voltage was increased gradually by 5 mV steps from the zero – current equilibrium potential. Currrent data were taken after 3 s setting time at each step.

In order to examine the electrorefining process, the anodes were cast from the tin dross obtained from lead – free soldering after liquefaction and skimming. The copper starting cathode sheet was masked and the 9 cm^2 square active surface was coated with a compact layer of tin deposited by pre electrolysis. It was polished to approximately the same surface quality before every run. The electrolyte solution was prepared by dissolving the required amount of reagent grade tin powder in boiling ~6M HCl, followed by setting the concentrations. The refining cell (**Fig. 4***b*) of 150 cm^3 volume was made from polycarbonate. A fine Teflon filter mesh separated the anodic and cathodic compartments, helping to avoid the contact between the roughly growing deposit and the slimy anode surface. Two regulated direct current (DC) supplies were used for the periodic current reversal (PCR) experiments, periodically switched over by a computer controlled electronic device. Voltage and current data were recorded by a computer equipped with a National Instruments NI – USB 6212 AD/DA converter and running the NI Labview software. To determine the cathodic current efficiency, the deposit was removed and measured after washing and drying. Overpotentials were measured with calomel electrodes inserted in the cell with Luggin–capillary junctions (**Fig. 4***c*). The raw material and the product samples were analysed by Inductively Coupled Plasma Optical Emission Spectrometry after dissolution in HCl.

The gross current efficiency expresses the utilisation of the total electric charge, considering the charge transferred by the reverse current also consumed for the cathodic process. The virtual value of the current efficiency was expressed assuming the deposition of the Sn(II) species. Thus for example with the usually applied [8] $t_+/t_- = 20/1$ forward to reverse time periods and constant

absolute currents the maximum gross current efficiency cannot be higher than ~91 per cent, assuming the reduction of Sn(II) species at the cathode. The also occurring Sn(IV) species are considered to cause cathode corrosion, thereby reducing the virtual current efficiency.
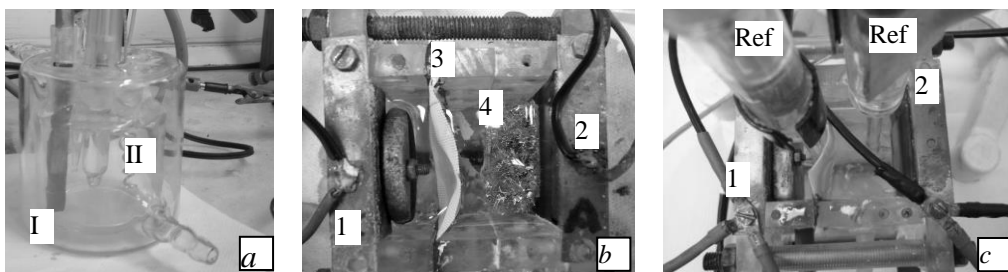

Fig. 4   The experimental equipment, *a* – electrochemical measuring cell (I – working electrode, II) counter electrode)*, b)* refining cell (1 – anode, 2 – cathode, 3 – filter separation, 4 – deposit), *c)* refining cell with reference electrodes (Ref – calomel electrode)

3   Experimental results and discussion

As the major difficulty is related to the cathodic process, tin deposition was primarily examined by the potentiodynamic technique. The polarization curves are shown in **Fig. 5*a*** at increasing tin and hydrochloric acid concentrations. The effect of HCl can be interpreted by the increased mobility of tin ions as the hydration sphere decreases. The polarization curves get steeper also by increasing the Sn concentration. According to **Fig. 5*b*** however, beyond ~ 10 g/dm^3 it has little effect on the current. Therefore, this value may be suitable for a practical application.
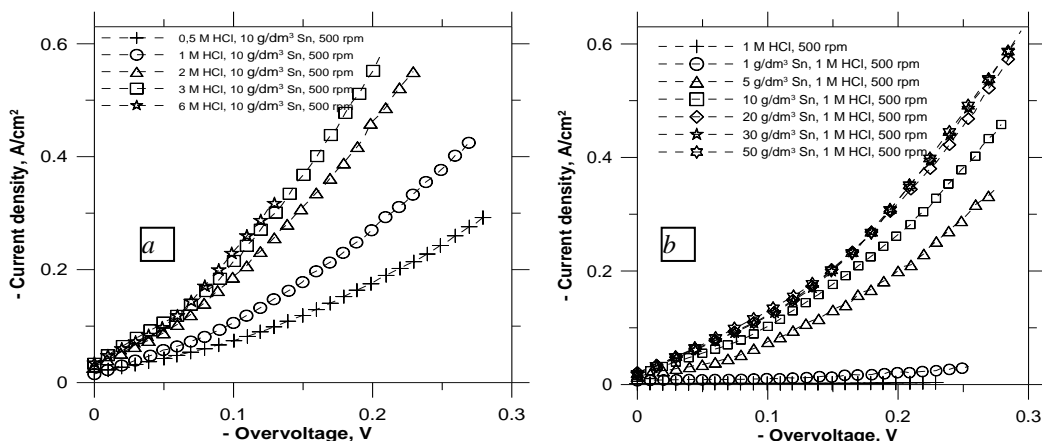

Fig. 5   Cathodic polarization at different concentrations of (*a*) HCl and (*b*) Sn (500 rpm stirring)

The rough dendritic nature of cathodic deposition from acidic electrolytes is usually related to high exchange current densities (i_o) and a relatively slow mass transfer [5]. The asymptotes of the logarithmic polarization curves can be applied for determining the i_o values. **Figure 6** shows the current densities (i, A/cm^2) as functions of the cathodic overvoltage for the tin and copper electrodes in HCl and H$_2$SO$_4$ solutions of virtually identical concentrations.
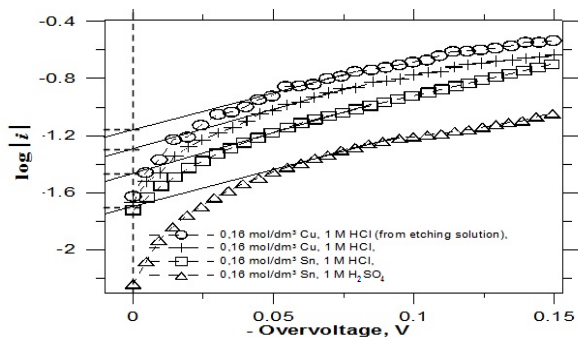
Fig. 6   Determination of the exchange current densities from cathodic polarization curves in electrolyte solutions, containing Sn and Cu (500 rpm stirring)

The copper chloride solutions exhibit the highest exchange current (510 and 690 A/m^2), whereas that of the sulphate tin electrolyte has the lowest (200 A/m^2) value. The tin electrode in chloride solution has relatively higher (300 A/m^2) exchange current density. The differences between the cathodic depositions of these solutions are illustrated in **Figure 7**. Corresponding to the high exchange current density, the cathodic deposition in the copper electrolyte solution has a strongly needle – dendritic nature, growing mostly at the edges, while tin is deposited in larger crystals, growing in a more dispersed planar, spongy morphology. Nevertheless the deposition of tin is basically dendritic, therefore practical application would require optimizing the mass transfer conditions to the electrode surface to avoid the long outgrowing crystals.
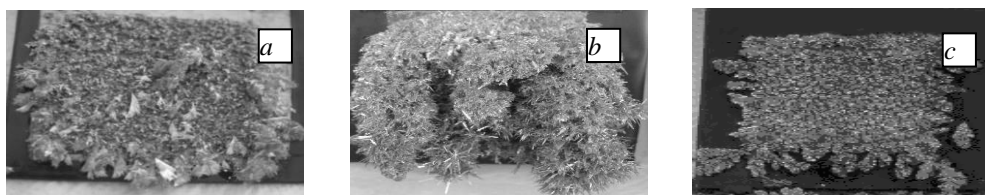

Fig. 7   Cathodic deposits from different electrolyte solutions with 2 h electrolyses *a*) 0.16 mol/dm^3 Sn, 1 M H$_2$SO$_4$, *b*) 0.16 mol/dm^3 Sn, 1 M HCl, *c*) 0.16 mol/dm^3 Cu, 1 M HCl

The application of periodically reversed current instead of the simple DC supply may offer finer crystal structures at the cathode [6]. It has been found efficient also in the case of tin electrodeposition from chloride electrolytes. However, low period time ratios (with relatively longer periods of reversed current) cause low current efficiencies through the forced or spontaneous re–dissolution of the cathodic deposit. Higher period time ratios, with longer normal and shorter reverse current periods, usually results in the expected higher current efficiencies. However, increasing the normal/reversed (t_n/t_r) time ratios beyond the value of 20 does not increase current efficiency further. With relatively shorter reversal of the current, higher anode potentials and rougher cathodic deposit structures enhance the re – dissolution of deposited tin. The practically most important results of the electrorefining experiments are summarized in **Fig. 8**. Confirming the findings of the potentiodynamic studies, the advantage of a 10 g/dm^3 Sn – 1 M HCl solution has been pointed out again. Increasing the apparent current density (referring to the original cathode surface) until ~ 1000 A/m^2 has a marked improving

effect, however beyond this value, hydrogen evolution hinders the further increase of the virtual current efficiency. The effect of temperature is positive for the deposition but also increases the chemical redissolution, thus it has an optimum around the 30 °C level. The presented current efficiencies refer to the freshly prepared or once used $SnCl_2$ –HCl solutions and 2 hours electrolysis time. Repeating the electrolysis with the same solution regularly gave a few per cent higher current efficiencies. This indicates that the inadvertent Sn(IV) concentration is reduced – at the expense of some loss form the deposited tin – during the first electrorefining run.
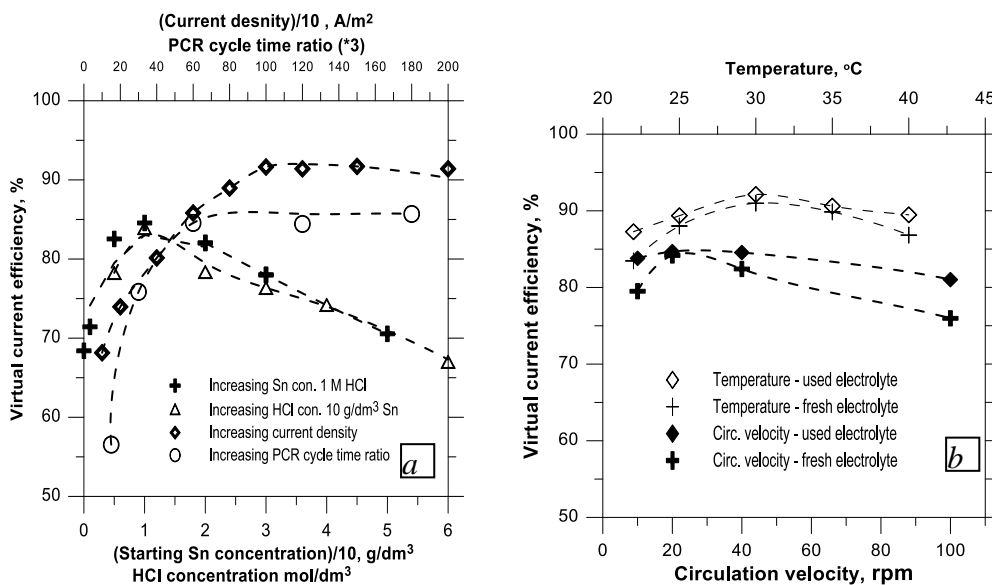

Fig. 8   The change in the virtual gross current efficiency as a function of (*a*) the cathodic current density ($t_n/t_r = 20$, 10 g/dm^3 Sn, 1 M HCl, 25 °C, stationary), PCR cycle time ratio (1000 A/m^2, 10 g/dm^3 Sn, 1 M HCl, 25 ºC, stationary), tin concentration ($t_n/t_r = 20$, 1000 A/m^2, 1 M HCl, 25 °C, stationary), hydrochloric acid concentration ($t_n/t_r = 20$, 1000 A/m^2, 10 g/dm^3 Sn, 25 °C, stationary) in fresh solutions; (*b*) the temperature ($t_n/t_r = 20$, 1000 A/m^2, 10 g/dm^3 Sn, 1 M HCl, stationary) and the relative circulation velocity ($t_n/t_r = 20$, 1000 A/m^2, 10 g/dm^3 Sn, 1 M HCl, 25 °C) in fresh and once used electrolyte solutions.

Increasing the flow rate of forced electrolyte circulation may improve conditions of mass transfer to the cathode surface and thus improve tin deposition, but it also enhances re– dissolution if Sn(IV) species are also present in the solution. Therefore, it also requires optimization, as suggested by **Fig. 8*b***. Forced circulation should mainly be used to maintain the electrolyte conditions at the convenient temperature set by the natural heat balance of the cell.

The addition of gelatine, as the common organic inhibitor, has been found little affecting the nature of electrocrystallization. The morphology of cathodic deposition is generally rough and dendritic. **Fig. 9** shows the typical structures obtained during an 8 h long experimental electrolysis run applying the conditions optimized according to the results given in **Fig. 8**.

In order to control deposit morphology, the concentration polarization of the cathode should also be limited. As shown in **Fig. 10*a***, experiments with inserted reference electrodes have pointed out that reducing the current density in the 1000 – 250 A/m^2 range may have the same effect in

this respect as increasing the tin concentration in the $10 - 50$ g/dm^3 range. Although gelatine addition may improve deposit morphology but an adverse effect is the observed hydrogen evolution and porous initial deposition resulting in lower current efficiencies. It is also reflected in the changes of the overpotentials at the cathode shown in **Fig. 10*b***.
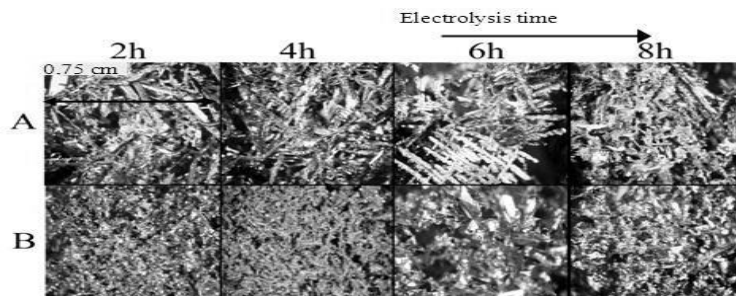

Fig. 9   Deposition in long electrolysis A – with no additives, B – 0.267 g/dm^3 gelatine added (10 g/dm^3 Sn, 1 M HCl, stationary electrolyte, 4:0.2 s PCR current of 1000 A/m^2).
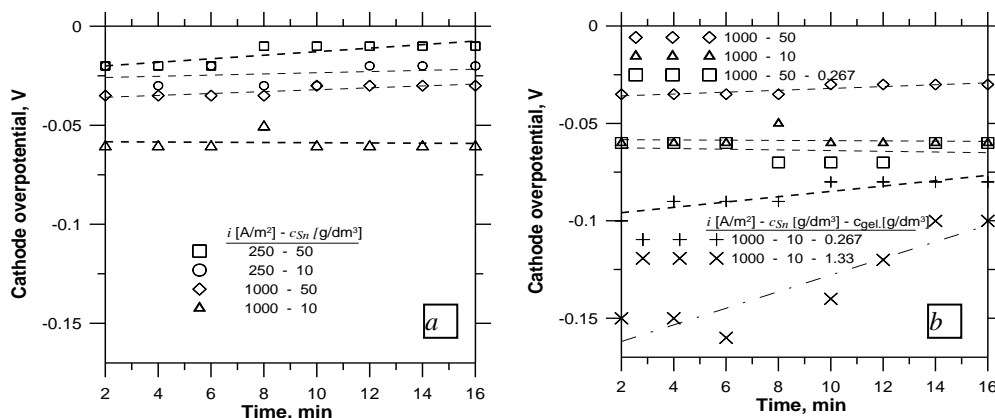

Fig. 10   Cathodic overpotentials during electrolysis *a*) at different current densities and tin concentrations in pure solutions, *b*) with gelatine added (1 M HCl, DC)

At high current densities and low tin concentrations anode passivation may take place, causing oxygen evolution [11]. This in turn results in the excessive formation of Sn(IV) species. In strongly oxidized solutions and at low acid- to- tin concentration ratios a stannic acid type (SnO$_2$.nH$_2$O) precipitation may arise. **Table 1** shows that the tin crystals obtained at the cathode after 8 hours of electrolysis from the lead free soldering waste have a remarkably high purity.

Table 1 Typical analysis of the impure anode and the purified cathode

Source material	Impurity concentration, %								
	Ag	Al	As	Bi	Cu	Fe	Pb	Sb	Total
Anode	0.0805	2.1442	0.0030	0.0414	1.9605	0.0050	0.0187	0.0367	4.29
Cathode	0.0004	–	0.0001	0.0004	0.0063	0.0004	–	0.0003	0.0082

Impurities of high standard electrode potential (Ag, Cu Bi) are retained undissolved in the anode sludge. Due to the uneven dissolution, it also contains a great amount of tin particles.

4   Conclusions

Electrorefining in HCl – SnCl$_2$ solutions may be considered as a flexible and efficient method to extract pure tin from waste materials mostly originating from the electronic industry. The interpreted results of the potentiodynamic and long term electrorefining experiments proved that a pure solution of approximately 1M HCl and 10 g/dm^3 Sn may be applied as the electrolyte and high current efficiencies can be reached with apparent current densities of approximately 1000 A/m^2, applying the PCR technology with a 20:1 time ratio. Solution agitation, increased temperatures and organic additives cannot improve significantly the main characteristics. While gelatin addition increases cathode overpotentials, leading to losses of current efficiency, natural inhibition by chloro–complexation can substitute additives. The cathodic deposit is typically loose and dendritic but it is easily removed and high purity (~ 99.99 %) tin can be produced even after melting.

References

[1]   A. E. Saba, A. S. El Sherief: Neue Hütte, Vol. 32, 1987, No. 3, p. 90-96
[2]   P. Halsall: Metall, Vol. 43, 1989, p. 131-136
[3]   T. Kekesi, T. I. Torok, G. Kabelik: Hydrometallurgy, Vol. 55, 2000, p. 213-222
[4]   T. S. Mackey: Journal of Metals, Vol. 7, 1969, p. 39-45
[5]   T. Kekesi, M. Isshiki: Journal of Applied Electrochemistry, Vol. 27, 1997, p. 982 – 990.
[6]   H. Wöbking, H. Wörz: Erzmetall, Vol. 32, 1979, p. 53-108
[7]   L. G. Sillén, A. E. Martell: *Stability Constants of Metal – Ion Complexes*, Supplement, Special Publication No. 25, The Chemical Society, London, 1964
[8]   J. F. Zemaitis et al.: *Handbook of Aqueous Electrolyte Thermodynamics*, New York, American Institute of Chemical Engineers Inc., 1983
[9]   G. H. Kelsall, F. P. Gudyanga: Journal of Electroanalytical Chemistry and Interfacial Electroche, Vol. 280, 1990, p. 267-282
[10] B. Muller, T. M. Seward: Geochimica et Cosmochimica Acta, Vol. 65, 2001, p. 4187-4199
[11] B. Szesny, U. Landau, R. Kammel: Metall, Vol. 40, 1986, No. 9, p. 868-874

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