Influence of As, Sb, Bi and O on Copper Anode Behaviour – Part 1: Passivation Characteristics

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This article is the first of a three articles series of results from a three year research project funded by the "Sponsor Group Copper Electrorefining". Investigated were dissolution/passivation behaviour, anodic current efficiencies, anode sludge formation and distribution coefficients of impure anodes with varying Sb, As, Bi and O contents processed at three current densities. The design of a copper electrolysis experimental setup is presented using synthetic anodes with linear independent target compositions of As, Sb, Bi and O. Casting of anodes is described, as well as preparation and run of the electrolysis trials. Mathematical modelling of the results showed that an increasing Sb and/or O concentration in the anode and/or higher current densities significantly raises the passivation tendency, whereas an increased anode arsenic concentration significantly lowers the passivation tendency. Using partial least square regression, it was possible to develop a prediction model for the passivation tendency of impure anodes.

Keywords:

Copper refining electrolysis – Anode passivation – Impure anodes – Mathematical modelling – Anode behaviour

Einfluss von As, Sb, Bi und O auf das Verhalten von Kupferanoden – Teil 1: Passivierungserscheinungen

Dies ist der erste von drei Artikeln über die Ergebnisse eines Drei-Jahres-Projekts finanziert von der „Sponsor Group Copper Electrorefining". Untersucht wurde das Auflösungs-/Passivierungsverhalten, die anodische Stromausbeute, die Anodenschlammbildung und die Verteilungskoeffizienten von verunreinigten Anoden mit verschiedenen Sb-, As-, Bi- und O-Konzentrationen bei drei unterschiedlichen anodischen Stromdichten. Das Design eines experimentellen Versuchsaufbaus einer Kupferelektrolyse mit synthetischen Anoden linear unabhängiger As-, Sb-, Bi- und O-Zusammensetzung wird vorgestellt. Beschrieben wird die Herstellung der Anoden sowie Vorbereitung und Durchführung der einzelnen Elektrolyseversuche. Die anschließende mathematische Modellierung der Versuchsergebnisse zeigte, dass ein Anstieg der Sb- und/oder O- Konzentration und/oder ein Anstieg der anodischen Stromdichte die Passivierungsneigung der Anoden erheblich erhöhen, wohingegen ein Anstieg der Arsenkonzentration in der Anode diese verringert. Unter Verwendung von „partial least square"-Regression war es außerdem möglich, ein Modell zur Vorhersage der Passivierungswahrscheinlichkeit verunreinigter Anoden zu entwickeln.

Schlüsselwörter:

Kupfer-Raffinationselektrolyse – verunreinigte Anoden – Verhalten von Anoden – Anodenpassivierung – mathematische Modellierung

Influence de As, Sb, Bi, et de l'oxygène sur le comportement des anodes de cuivre – section 1: Phénomènes des passivation

Influencia del As, Sb, Bi y O en el comportamiento de los ánodos de cobre – Parte 1: Fenómenos de pasivación

1 Introduction

Copper refining electrolysis is the essential process step to produce high-purity copper and to further concentrate precious metals. The anode copper used in the electrolysis process contains always further elements, most frequently Ag, As, Au, Bi, Fe, Ni, O_2, Pt, S, Sb, Se, Te, and Zn. Their content depends on the raw material used (ores or scraps) and process conditions. During electrolysis, many impurities, which are more ignoble than Cu, are dissolved into the electrolyte and the insoluble rest based on more noble or insoluble compounds is collected as anode sludge. The accompanying elements cause different, often negative effects on the electrolysis process by reacting with each other or with electrolyte components. These effects range from anode polarisation, copper losses in precipitation products up to cathode inclusions. Normally the content of certain impurities in industrial copper anodes is correlated as they derive from the same starting material. Therefore it is hard to separate the effects of single impurities on current efficiency, polarisation etc.

The target of the presented study is the systematic investigation of selected impurity interactions in the copper anode in respect to their dissolution/passivation behaviour, anodic current efficiencies and distribution coefficients. Lab-scale-produced anodes with various impurity combinations of the Cu-Ag-Ni-As-Sb-Bi-O-system are tested, with linear independent target contents of Bi, As, Sb and O. The use of synthetic anodes allows to separate the effects of the different elements by using multivariate statistical methods. The trials have been carried out parallel in six electrolysis cells with three different anode current densities.

This publication is a first part of presented results from a three years research project, funded by the "Sponsor Group Copper Electrorefining". It focuses on preparation and setup of the electrolysis trials and on the dependency between anode composition and passivation behaviour.

2 Experimental setup

In order to investigate the "interaction of anode impurities", 87 anodes are cast, 81 of them with linear independent compositions. Among the seven alloying elements, which can exist in each anode, the contents of Bi, Sb, As and oxygen are altered. Target oxygen contents are 1000 ppm, 2000 ppm and 4000 ppm, Bi contents are 0, 250 and 500 ppm, Sb contents are 0, 500 and 1000 ppm and As contents are 0, 1500 and 3000 ppm. The silver concentration is kept constant at 1000 ppm for all trials, the same applies for nickel with 2000 ppm. The variation of parameters is illustrated in Table 1.

Table 1: Planned chemical compositions of the cast anodes [ppm]

Bi	Sb	As	O
0	0	0	Each anode was cast with 1000 ppm, 2000 ppm and 4000 ppm O
250	0	0	
500	0	0	
0	500	0	
250	500	0	
500	500	0	
0	1000	0	
250	1000	0	
500	1000	0	
0	0	1500	
250	0	1500	
500	0	1500	
0	500	1500	
250	500	1500	
0	1000	1500	
500	500	1500	
250	1000	1500	
500	1000	1500	
0	0	3000	
250	0	3000	
500	0	3000	
0	500	3000	
250	500	3000	
0	1000	3000	
500	500	3000	
250	1000	3000	
500	1000	3000	

Each anode is run in three trials at current densities varying between 191 A/m², 300 A/m² and 409 A/m². All together 261 individual electrolysis tests have been conducted.

The initial composition of the synthetic electrolyte is kept constant for all trials with the concentrations shown in Table 2. As inhibitors a combination of lime and thiourea is used, which is added to the initial electrolyte as well as continuously to the process during electrolysis.

Table 2: Starting composition of the electrolyte

Element	Content [g/l]	Added as compound
Cu	45	$CuSO_4 \cdot 5H_2O$
Ni	10	$NiSO_4 \cdot 6H_2O$
Sb	0.5	Sb_2O_3
$As^{(3+/5+)}$	10 (1:9)	As_2O_3
Bi	0.2	Bi_2O_3
H_2SO_4	170	H_2SO_4
Cl	0.05	HCl

3 Prearrangements and setup for electrolysis trials

3.1 Preparation of the anodes

The anodes used in the electrolysis process were made in the various compositions using an induction furnace (Balzers) with a melting power of 10 to 15 kW. After reaching a temperature of 1300 °C the alloying elements are added. Graphite sticks are used for the reduction of oxygen in the melt, which was measured and adjusted before casting using an ElectroNite Oxygen measurement system. The melt is cast at approx. 1300 °C in an air cooled steel mould (H × L × W = 540 mm × 107 mm × 25 mm) with a gating (H × L × W = 540 mm × 30 mm × 30 mm). The mould temperature is maintained at about 260 °C at the top and 240 °C at the bottom. After casting the casting was sawn, holes were drilled for holder and electric contact, the anodes were milled (removal of 2 mm surface), cleaned, marked and ready for electrolytic treatment. Each anode had a weight of approximately 7500 g and a size of 430 mm × 100 mm × 25 mm.

Figure 1 shows the induction furnace, the crucible and the mould used in the process of anode casting, as well as the cast and milled anode.

The homogeneity of anodes was preliminary tested by taking samples at six positions (Figure 2) using two cast anodes. The deviation within the electrodes was only in a range of some ppm for As, Sb, Bi, less than 4 % for Ag and less than 6.5 % for O_2. The deviation was in all cases independent from the position of sample taking.

According to literature the impurities occur either in solid solution in the copper matrix or as discrete compounds concentrated along the copper grain boundaries. Silver and nickel shall exist in solid solution in the anode copper up to 85 % for silver resp. 100 % for Ni depending on the content of oxygen and other impurities in anode copper. If the nickel content exceeds 0.3 % and the oxygen content is 0.25 to 0.3 % nickel forms oxide phases like $3Cu_2O \cdot 4NiO \cdot Sb_2O_5$

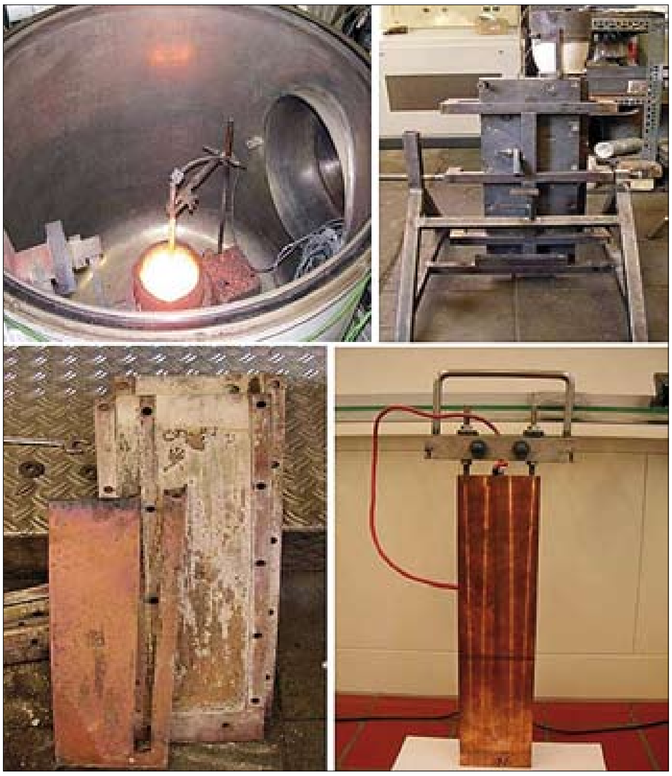

Fig. 1: Induction furnace, casting arrangement, cast and milled/assembled anode

with other impurities [1-3]. So it can be expected in the case of the present cast anodes that Ni exists in solid solution (Ni = 2000 ppm). As, Sb and Bi occur both in solid solution with Cu and as grain-boundary inclusions in the anodes in form of oxide phases. About one third of the As and Sb has previously been determined to be in solid solution in secondary copper anodes [4, 5].

To confirm the homogeneity of the anode surface and structure, one of the casted anodes was analyzed via scanning electron microscopy (SEM). Samples were taken at two different spots, close to the sample taking locations one and two (see Figure 2). The impurity concentration of this anode is: 320 ppm Bi, 450 ppm Sb and 2251 ppm O. As can be seen from Figure 3 the structure of both samples is quite homogenous. Analysis of the inclusions shows that the black phases mainly consist of oxygen and copper and the white phases close to some of them mainly consist of oxygen, antimony and bismuth. This corresponds to the anode structure reported in literature.

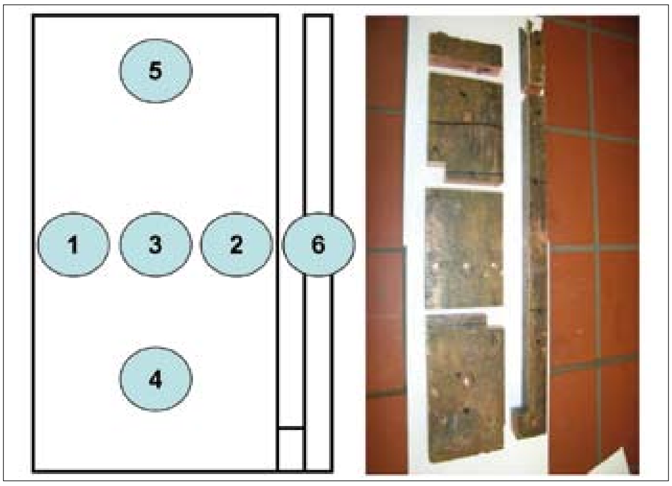

Fig. 2: Investigation of anode homogeneity locations for sample taking

3.2 Preparation of the cathodes

The permanent cathodes used are made from stainless steel with welded copper bar contacts, provided by Outotec Oyj Research Center, Finland. The cathodes were polished and subsequently cleaned with ethanol. The backside was insulated by Macroline plates and bonded to the cathodes by silicone. The edges and corners were protected by plastic bars. The active cathode surface was 405 mm × 110 mm. After electrolysis each sheet was coated with a copper deposition of a thickness of about 3 mm (~ 1000 g). The copper was stripped from the cathode sheet, dried and weighed. As preparation of the cathode sheets for the next experimental tests the plastic bars, the old Macroline plates and the silicone bonds were removed and cleaned.

Fig. 4: Cathode sheets before (front side) and after electrolysis (front with approx. 1000 g Cu deposition and back)

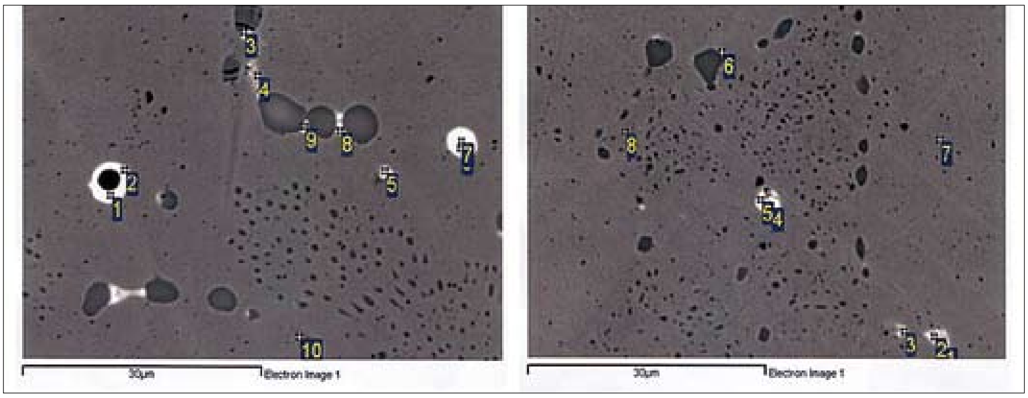

Fig. 3: Microstructure investigation (SEM) of a selected anode at two areas (320 ppm Bi, 450 ppm Sb, 2251 ppm O)

Figure 4 shows the cathode sheets before and after the electrolysis process together with the deposited copper.

3.3 Cell design

The complete electrolysis test rig consists of six electrolysis cells each with one anode and two cathodes connected to a holder shown in Figure 5. The distance between anode and cathodes was chosen to be 20 mm, thus assuring a regular natural convection between the electrodes. An inert gas airlift system (see Figure 5) is placed inside each cell to ensure electrolyte homogeneity during electrolysis trials replacing the typically used maintenance intensive and interference-prone mechanical pump systems.

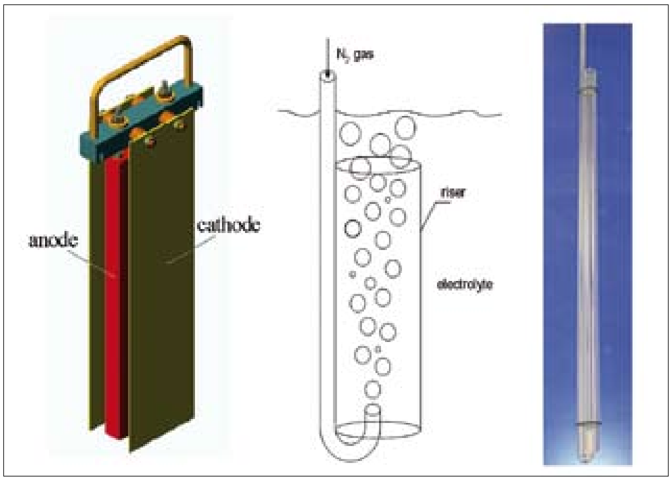

Fig. 5: Anode and cathode holder (left), inert gas airlift system (middle, right)

The cells are placed into a heating vat holding hot circulated water to guarantee a constant temperature of 65 °C in all cells. (L × W × H: 440 mm × 400 mm × 500 mm) (Figure 6). The water is pumped from a thermostat to the bottom of the vat and to each cell row. An equal flow of water from the bottom to the top of each cell is provided. All cells are made of PVC, their sides are welded together. The water vat is insulated by a styropore/aluminium compound material.

Fig. 6: The cell assembly

All cells get connected in series and 13 shunts are provided in the electric circuit for data logging. A cold inhibitor solution is fed from a 24 h storage tank continuously into each cell after previous 24 h maturation. Homogenisation of the electrolyte is assured by using an airlift system in each cell. Size, place and gas flow of this airlift systems were determined by preliminary test in a potassium-iodide solution and the results were converted with dimensionless numbers to the system nitrogen–electrolyte. Main function of this system is a mixing of the electrolyte avoiding turbulences and such the transport of anode sludge towards the cathode. The gas used is nitrogen, to avoid uncontrolled oxidation of the electrolyte, with a flow rate of 2 l/h. To assure the homogeneity of the electrolyte, electrolyte samples were taken during some electrolysis trials at fixed positions and analyzed. The resulting average deviation inside the cells was determined to be lower than 2.7 % for the Cu content and lower than 3.3 % for the Ni content.

A data logging system DA100 from Yokogawa is used. It can detect DC voltages within ranges from +/- 20 mV to +/- 50 mV, temperatures up to 2315 °C with thermocouples (depending upon type), temperatures up to 600 °C with temperature-dependent resistances and digital switching status. All entrances can be configured independently. The scanning rate can be appointed device-sided to values between 0.5 s and 60 s. For the data acquisition the software MCPS 5.0 (CAD computer GmbH) is used.

4 Electrolysis Procedure

Before starting the electrolysis, copper electrolyte was prepared individually and analysed for each test series with a volume of 36 l. Especially the As^{3+}/As^{5+}-ratio required special know-how. To prepare the solution of As^{5+}, As_2O_3 was dissolved at 90 °C in deionised water and sulphuric acid and then oxidized with H_2O_2. After two to three days of preparation time the electrolyte with a temperature of 65 °C was pumped into the cells to a level of 405 mm active cathode height. The vat was filled with hot circulating water to keep the temperature of the electrolyte constant. Depending on the current densities used in the tests, different amounts of inhibitor concentrations have been added to the electrolyte and subsequently fed continuously to each cell during the trials. Before placing the airlift systems into the cell the gas flow was set to 2 l/h for each device. It is important to open the gas flow before placing the tubes into the cells to assure that the correct flow rate is set and accordingly the correct rate of stirring inside the electrolyte. It also ensures that the electrolyte does not enter the gas tube and crystallizes inside.

When all cells were prepared, the process is started with the required currents for an equal distribution between the two cathodes at each cell. As the currents have to be adjusted regarding the required current density, the shrinked dimensions of the anodes after each trial and such the smaller surface area has to be taken into account. The shrinking of the anodes was determined in pre-tests and leads to the following process parameters summarized in Table 3. At first the electrodes were "loaded" with industrial standard current densities of 330 A/m^2 (cathode) and 300 A/m^2 (anode). After this a significant reduced load was selected and at last a final ultra high load was tested.

Figure 7 shows the entire connected electrolysis setup.

During the trials the values of cell and electrode currents, polarization of each anode via a simple copper wire "reference electrode" and all cell voltages were measured.

Table 3: Electrolysis process parameters of the three test series for each anode

i_{anode} [A/m^2]	300	191	409
A_{anode} [m^2]	0.098	0.089	0.077
I [A]	29.4	19.9	31.6
$A_{cathode}$ [m^2]	0.089	0.089	0.089
$i_{cathode}$ [A/m^2]	330	190	355

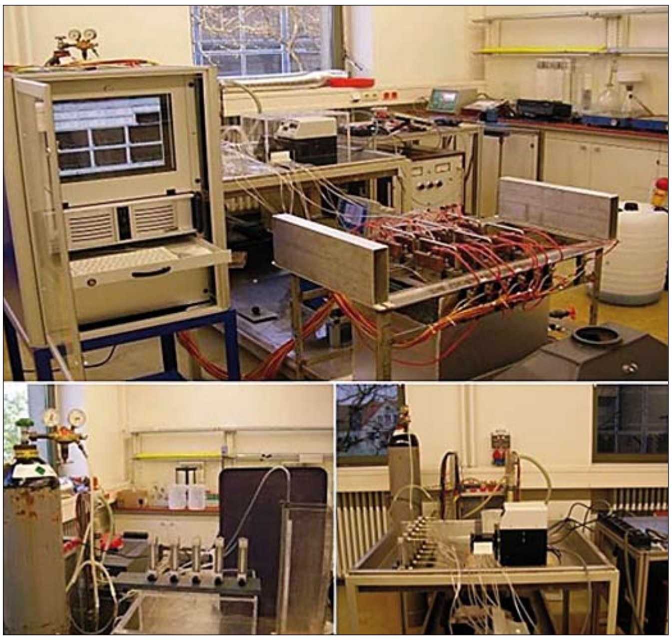

Fig. 7: The complete system of the electrolysis process with six cell system, data logger, air lift electrolyte mixing system and inhibitor pumps

Deionised hot water had to be added to each cell every 12 hours due to vaporization. All cells were switched off after 1700 Ah, since this value is suitable for obtaining considerable amounts of copper at the cathodes and anode sludge at all three current densities and to ensure a reasonable final anode surface area. The value itself was selected after experimental pre-tests. This leads to an electrolysis duration of 100 h 32 min for an anodic current density of 191 A/m^2, 57 h 49 min for 300 A/m^2 and 53 h 48 min for 409 A/m^2. After every trial each cell is dismantled and the electrodes are removed (cathodes first), washed with hot deionised water and brushed, to remove remaining anode sludge from the surface of the electrdes. In the next step, the electrolyte from each cell is filtered and the collected anode sludge is immediately washed and dried. After that it is weighted and analysed by ICP as well as the electrolyte.

5 Passivation

Anode passivation easily occurs at high current densities. The rapid dissolution of the anodes leads to an excessive ion concentration in front of the anode surface and to the precipitation of a solid layer on the anode due to an exceedance of solubility products inside the electrolyte. This film inhibits further dissolution of the anodes. Important factors are the current density, electrolyte temperature, copper- (and other ion-) concentration in the electrolyte and electrolyte circulation. Its occurrence is often associated with poor copper deposits caused by high current densities and an uneven current distribution.

This phenomenon can be induced either by the electrorefining conditions themselves or by the presence of some impurities in the anode. It is well known, for example, that higher current densities, lower electrolyte temperatures or high concentrations of total sulphate ions in the electrolyte may cause anode passivation [6].

The passivation behaviour of 261 anodes with varying impurity contents at three current densities using always the same starting electrolyte is given in the following. The reported trials investigated the effect of anode impurities (As, Sb, Bi and O) on the passivation behaviour at constant electrolyte temperature, copper concentration and electrolyte circulation. According to literature the fraction of As, Sb and Bi present in solid solution with copper

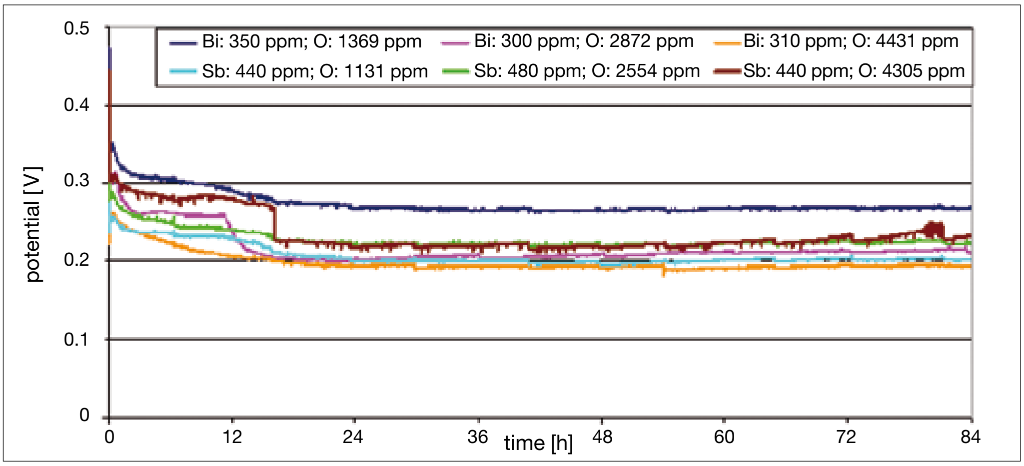

Fig. 8: Potentials of six anodes during an electrolysis series without anode passivation at 191 A/m^2

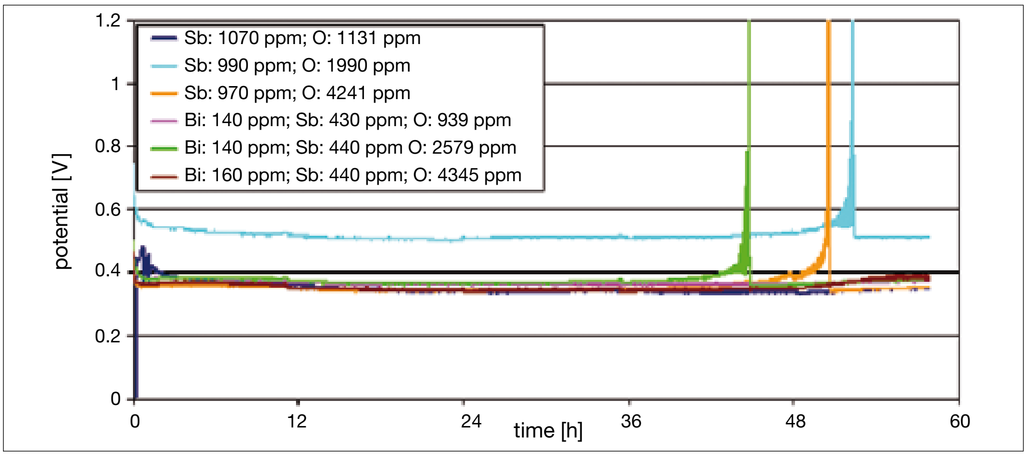

Fig. 9:
Potentials of six anodes during an electrolysis trial with anode passivation at 300 A/m^2

shall dissolve completely into the electrolyte. Their oxide phases precipitated in the copper anode matrix also dissolve chemically. Both effects result in a gradual increase of their concentration in the electrolyte [7]. When they enter the electrolyte, they can undergo a number of different reactions depending on their respective concentration in the electrolyte, as well as on the presence and concentration of other elements. During electrolysis the anode potential of each anode was measured every ten seconds. An example for the monitored potentials can be seen in Figure 8. As a criterion for a beginning passivation an increase in cell voltage of 40 mV during an eight hour period was defined. An example for passivating anodes is shown in Figure 9.

Table 4 shows the results of the electrolysis trials regarding their passivation behaviour. According to [8] passivation shall not occur at current densities below 240 A/cm^2, which was proved in almost all our trials at 191 A/cm^2 except for one anode containing high amounts of oxygen (4200 ppm) and antimony (910 ppm). This special trial was repeated twice but passivation did not occur again. So it can be assumed that the reason for this single passivation was not due to the chemical composition and therefore negligible for the interpretation. At anodic current densities of 300 A/m^2 nine anodes have shown passivation effects, at 409 A/m^2 it have been 16.

The total impurity content without distinguishing individual element concentrations shows no significant effect in the investigated range on the passivation behaviour of the anodes as can be seen from Figure 10. Important is the nature of these impurities and their combination among each other. The only clear but also expectable tendency noticed from Figure 10 is that anodes run at 409 A/m^2 generally passivate faster (many between 350 and 650 Ah after start) than anodes run at 300 A/m^2 (some between 850 and 1500 Ah after start).

The limiting values for electrolysis tests without passivation for an electrolysis duration of 1700 Ah are detected and summarized in Table 5 and Table 6. The values depend on the current density and are valid for anodes with approx. 2000 ppm Ni and 1000 ppm Ag.

At 300 A/m^2 no passivation occurs if:

- only oxygen is present in the anodes (analysed up to 3721 ppm O),

Table 4: Anode passivation behaviour (all concentrations in ppm)

O content	Bi content	Sb content	As content	Time to first passivation [h]		
				191 A/m^2	300 A/m^2	409 A/m^2
1509	0	0		-	-	-
2584	0	0		-	-	-
3721	0	0		-	-	-
1317	150	0		-	-	-
2402	150	0		-	-	-
4825	140	0		-	-	-
1369	350	0		-	-	-
2666	300	0		-	-	-
4413	310	0		-	-	-
1524	0	440		-	-	35
2425	0	480		-	35	17
4305	0	440		-	36	16
1131	0	1070		-	-	31
1990	0	990		-	51	42
4241	0	970	0	-	47	18
939	140	430		-	-	-
2408	140	440		-	33	19
4345	160	440		-	-	31
1013	340	480		-	-	-
2251	320	467		-	-	17
4378	330	460		-	-	38
925	170	920		-	-	-
2050	190	1060		-	-	20
4122	140	890		-	34	12
1099	340	856		-	-	-
2521	670	1840		-	29	11
1980	450	930		-	-	20
3500	330	1100		-	32	8
4200	360	910		66	42	12
1000-4000	0-500	0-1000	1500-3000	No passivation		

Table 5: Chemical composition [ppm] of anodes processed without passivation at 300 A/m^2

O concentration	Bi concentration	Sb concentration	As concentration
≤ 3721	0	0	0
≤ 4400	≤ 310	0	0
≤ 1100	≤ 340	≤ 1050	0
≤ 4300	Sb/Bi ≤ 2.1		0
≤ 4400	≤ 450	≤ 1100	1400 - 3300

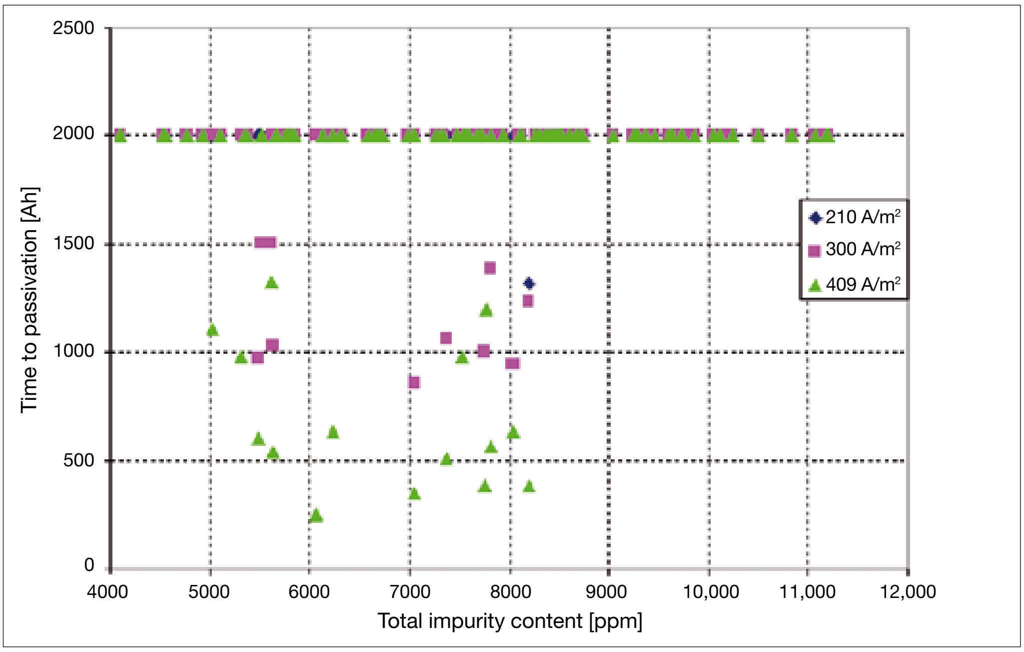

Fig. 10:
Time to passivation vs. total impurity content (not passivating anodes were set to 2000 Ah)

Table 6: Chemical composition [ppm] of anodes processed without passivation at 409 A/m²

O concentration	Bi concentration	Sb concentration	As concentration
≤ 3721	0	0	0
≤ 4400	≤ 310	0	0
≤ 1100	≤ 340	≤ 920	0
≤ 4400	≤ 450	≤ 1100	1400 - 3300

- only oxygen and bismuth up to 310 ppm are present in the anodes (analysed up to 4400 ppm O),
- if antimony up to 1050 ppm is present the oxygen content needs to be below 1100 ppm and the bismuth content below 340 ppm,
- the Sb/Bi ratio is equal or less 2.1 and oxygen content is below 4300 ppm,
- arsenic is present.

At 409 A/m² no passivation occurs if:

- only oxygen is present in the anodes (analysed up to 3721 ppm O),
- only oxygen and bismuth up to 310 ppm are present in the anodes (analysed up to 4400 ppm O),
- if antimony up to 920 ppm is present the oxygen content needs to be below 1100 ppm and the bismuth content below 340 ppm,
- arsenic is present.

From these tables it can be seen that arsenic is avoiding passivation whereas antimony has a strong effect on causing passivation. The influence of bismuth seems to be nearly neutral with a small trend to lower the passivation tendency.

Mathematical analysis of the passivation behaviour was done using the Umetrics software Modde 5.0, a MS-Windows®-based software, providing design of experiments, analysis and optimisation. The program processes measureable and metrical data respectively and is aiming at an optimal explanation of experimental results by means of linear and interaction regression models. For the present study it was used to mathematical assess and display the results of the experiments in order to detect the effects of several factors and factor combinations on the passivation behaviour. All fits were done using partial least square regression which leads to better fits than multiple linear regression.

Two sets of analysis were made, one taking into account all trials to achieve a reliable prediction if anodes passivate or not and the other one taking into account only the passivating anodes trying to predict the time (Ah) to passivation. The first analysis results in a fit of 64 % to the regression model. The fit is not optimal as the non passiving anodes received a fictive passivation probability of 0 and the passivating ones that of 100 %. Mathematical this would lead to a saltus function as a result, but Modde is not able to model this kind of function.

To visualize the quality of the designed model the experimentally observed passivation behaviour is plotted versus the predicted probability of passivation (Figure 11) (all anodes containing As or processed at 191 A/m² have a passivation probability of 0). As already discussed the investigated anodes received a probability of 100 % if they passivated and a value 0 % if they did not. The plot shows clearly that anodes with a predicted passivation probability ≤ 30 % do not passivate whereas anodes with a predicted passivation probability ≥ 50 % do passivate. Only the transition area from 30 % to 50 % gives no clear indication for the passivation behaviour. Here 50 % of the anodes passivated and the others not.

Figure 12 displays the effect of different factors and factor combinations on the passivation tendency taking into account all processed anodes. Positive effects stand for heightening and negative effects for lowering the passivation tendency. The black bars show the confidence interval. If they cross the zero line, the effect has to be defined as not significant, the smaller they are in comparison to the effect, the more accurate is the significance value.

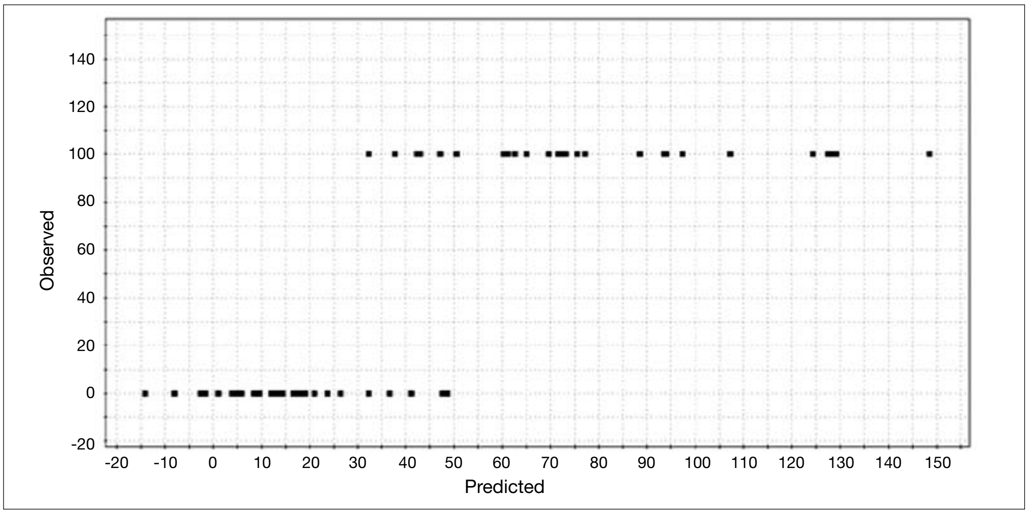

Fig. 11:
Observed versus predicted passivation behaviour (for more clearness without As containing anodes and anodes processed at 191 A/m^2)

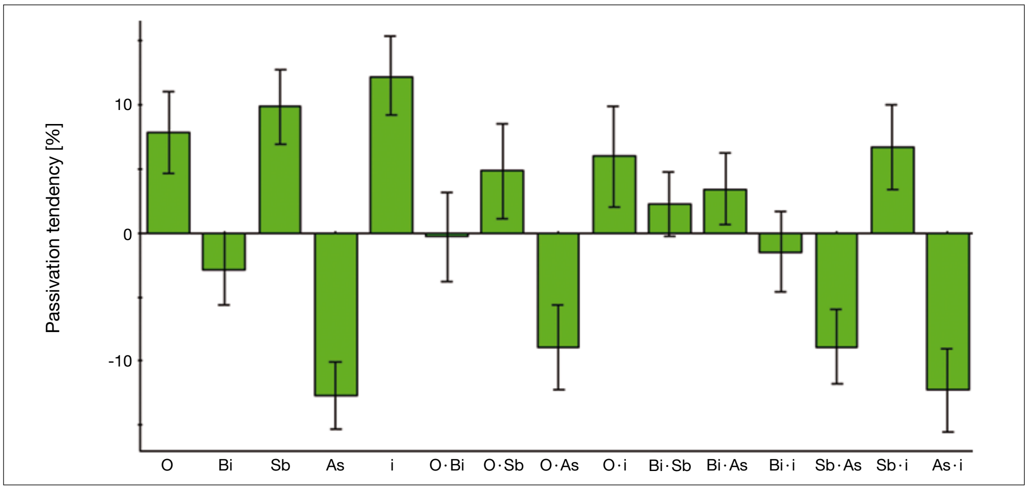

Fig. 12:
Effects on anode passivation: Scaled and centred coefficients

As can be seen from Figure 12 the current density (i) and the antimony content have the strongest heightening effect on the passivation behaviour followed by the oxygen content. The factor combinations also heightening the passivation tendency are the oxygen concentration multiplied with the antimony concentration or the oxygen/antimony concentration multiplied with the current density. All three effects show mainly the same influence which is lower than that of their single components. Arsenic has a huge influence lowering the passivation tendency whereas bismuth seems to have no or only significant effect. Except for the factor As · Bi which seems to have a small heightening effect all other factor combinations containing As also have a quite strong tendency to lower the passivation tendency, partly annulling the negative effect of these single components. This explains why no anodes containing arsenic passivated independent from their chemical composition, not only did the arsenic itself lower the passivation tendency but it also partly annulles the effect of the other components. All other factor combinations have no significance towards the passivation behaviour of the anodes. The general effects of the single components displayed in this diagram are the same already observed from Table 5 and Table 6 and the reasons for the effects of the single components were explained in the following paragraph taking into account already published literature.

The influence of the current density is straightforward and needs no further explanation. Explanation of the other effects of can be done by taking into account various publications. It was already examined by various authors [9-12] that antimony primary dissolves into the electrolyte in the trivalent form (equation 1). It has an extremely high tendency to cause passivation especially combined with high oxygen contents and/or high current densities. Caused is this effect by the oxidation of Sb^{3+} to Sb^{5+} in presence of oxygen and with catalytic actions of cuprous ions (Cu^{2+}) close to the anode interface (equation 2) and the easy exceeding of the Sb^{5+} saturation limit (0.15 g/l contrary to 0.6 g/l for Sb^{3+}) in front of the anode [13]. The result is the formation of a solid layer at the anode surface or compaction of the already formed sludge by pore precipitation.

$$Sb + 2H_2O \rightarrow SbO_2^- + 4H^+ + 3e^- \qquad (1)$$

$$SbO_2^- + 0.5O_2 + H_2O \rightarrow SbO_4^{3-} + 2H^+ + H_2O \qquad (2)$$

Bismuth on the contrary also gets dissolved in the trivalent form like antimony, but is not oxidized in the presence of oxygen under these conditions, so no solubility product is undercut and therefore no solid layer is forming at the anode.

The most obvious effect of arsenic and arsenic containing factors on the passivation tendency is because of a couple of factors. Arsenic as well as antimony and bismuth is dissolved as three valence ions into the electrolyte (equation 3) and is as well as antimony oxidized to As^{5+} in the presence of oxygen (equation 4) and with catalytic actions of cuprous ions. The oxidation of As^{3+} is reported to be more preferable and faster than that of Sb^{3+}. Therefore, the oxidation of Sb^{3+} to Sb^{5+} will not preferentially occur as long as a sufficient amount of As^{3+} is dissolved in the electrolyte [13]. The second reason for the lowered passivation tendency of anodes containing arsenic is the precipitation of antimony and bismuth as hardly soluble $2As_2O_5 \cdot 3Sb_2O_3$, $SbAsO_4$ and $BiAsO_4$ in the anode sludge [14]. The formation of $2As_2O_5 \cdot 3Sb_2O_3$ and $SbAsO_4$ does not cause passivation because with rising As concentration the pH value in front of the anode gets lower according to equation 3 and therefore the solubility of the forming components is higher in front of the anode and the components primary precipitate inside the electrolyte [15]. Furthermore the sludge adhesion gets lower during this processes [16]. A third interpretation is based on the fact that antimony and bismuth concentration is decreased to less than 100 ppm in the electrolyte, when the concentration of As^{5+} reaches 15 to 20 g/l inside the electrolyte [14, 17 - 20].

$$As + 2H_2O = AsO_2^- + 4H^+ + 3e^- \qquad (3)$$

$$AsO_2^- + 0.5O_2 + H_2O = AsO_4^{3-} + 2H^+ + H_2O \qquad (4)$$

It is common knowledge that anodes passivate due to the formation of Cu_2O according to equation 5, but this reaction only takes place if the pH value in front of the anode is > 2 and/or the oxygen content of the anode and therefore inside the electrolyte is low and the reaction according to equation 6 is hindered [16, 21, 22].

$$2Cu^+ + H_2O \rightarrow Cu_2O + 2H^+ \qquad (5)$$

$$Cu^+ + H^+ + 0.25O_2 \rightarrow Cu^{2+} + 0.5\,H_2O \qquad (6)$$

During this investigation the oxygen content was always above 900 ppm, so this reason for anode passivation did not occur. On the contrary, it was ascertained that rising oxygen contents promote anode passivation. This has also been reported by some previous investigations [13, 23]. DEMAEREL [23] showed that the oxygen content plays a significant role in influencing passivation behaviour, by influencing the slime structure and porosity. For high oxygen containing anodes (3300 ppm within the cited investigation) the slime settling rate is approx. 36 % of that for the same anode with only 1800 ppm oxygen.

Based on the effects presented in Figure 12 the passivation probability was investigated in more detail in respect to the chemical composition and the anode current density, shown in Figure 13. The passivation probability within 1700 Ah electrolysis "time" of As-free anodes processed at 300 A/m² and 409 A/m² (all anodes containing As or processed at 191 A/m² have a passivation probability of 0) in respect to the Sb- and Bi-content in ppm is displayed. This charts can be used to predict the passivation probability of anodes within the analysed parameters.

According to Figure 11 anodes with a passivation probability below 30 % will not passivate during the first 1700 Ah of processing. Therefore it is assured that anodes with low arsenic contents and industrial typical oxygen concentrations of max. 2000 ppm will not passivate within the first 1700 Ah of processing at 300 A/m² if the antimony content is below 400 ppm for anodes not containing bismuth. This value can be raised up to 1000 ppm for bismuth concentrations close to 350 ppm. Increasing the current density leads to a significant drop of the antimony limit to less than 200 ppm for anodes not containing bismuth and 400 ppm for bismuth concentrations close to 350 ppm. Processing higher amounts of antimony is only possible at arsenic con-

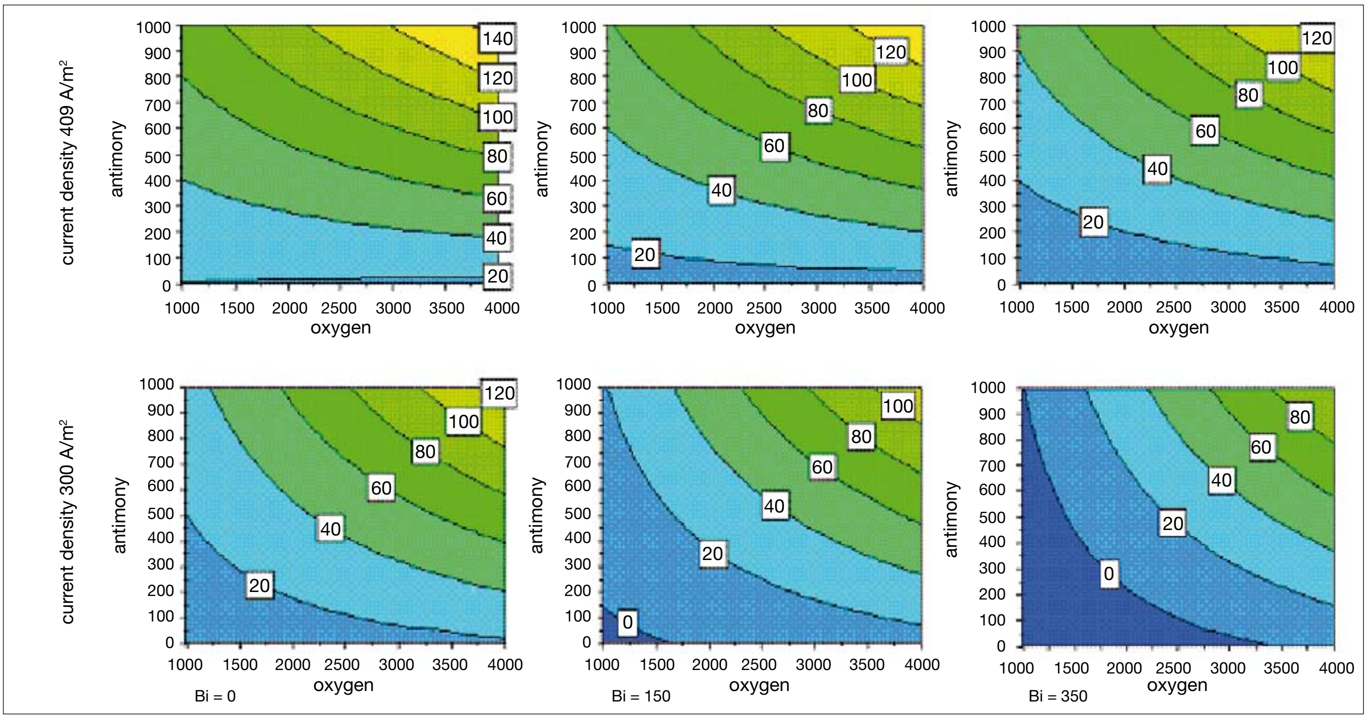

Fig. 13: Passivation probability within 1700 Ah electrolysis "time" of As-free anodes in respect to the Sb- and Bi-content [ppm] and the anode current density (anodes at 190 A/m² and As-containing anodes did not passivate at all)

centrations between 1500 to 3000 ppm, or at anodic current densities below 300 A/m².

An attempt to further improve the model to predict the "time" (Ah) to passivation was made. This time only the passivating anodes were taken into account, which were nine anodes at 300 A/m² and 16 at 409 A/m² trying to model the time until passivation occurs in respect to the Sb- and Bi-content in ppm and the anode current density. The result leads to a fit of 82 % to the regression model.

Even though the fit to the regression model is 82 % for the predicted time to passivation compared to 64 % for the passivation probability the significance of the probability model is larger. The reason for this is that the design region of this model covers all necessary vertices for the analysed range of parameters. Whereas the model predicting the passivation time only takes some points within a small part of the original design region into account extrapolating the vertices for the given parameter range. The effect is that it was not possible to model a chart to predict the time until passivation occurs similar to Figure 13.

6 Summary

In this work a new design of a copper electrolysis experimental setup is presented using synthetic anodes with linear independent target compositions of As, Sb, Bi and O making it possible to separate the effects of different elements by statistical methods. The preparation, setup and run of the electrolysis trials are described in detail as well as the casting of anodes. In the first paper of this publication series all experiments were assessed regarding their passivation behaviour. As result it can be stated that increasing Sb and/or O contents and higher current densities significantly raise the passivation tendency whereas an increased As content significantly lowers the passivation tendency. Bismuth turned out to have only a slight influence to lower the passivation tendency. The reasons for this kind of influences are:

- Sb is forming a solid layer on the anode surface, due to exceeding the Sb^{5+} saturation limit in the presence of oxygen;
- O is negatively affecting the slime structure and porosity;
- The kinetically favoured oxidation of As^{3+} to As^{5+} instead of the Sb^{3+} oxidation (As^{5+} has a much higher solubility) and the precipitation of Sb and Bi by formation of $SbAsO_4$ and $BiSbO_4$ inside the electrolyte.

Using partial least square regression it was possible to develop a prediction model for the passivation tendency. This is based on the assignment of passivation probabilities of an anode in respect to its chemical composition and a given anodic current density. Anodes with a predicted passivation probability ≤ 30 % did not passivate whereas anodes with a predicted passivation probability ≥ 50 % generally passivated. Only within a transition interval of 30 % to 50 % no clear indication for the passivation behaviour can be seen.

Unfortunately it was not possible to securely calculate/identify the dependencies of impurity content and current density on the time (Ah) to first passivation by multiple regression which would allow a better forecast. This is due to the fact that despite 261 run tests only a few anodes (25) passivated during the tests. To determine a more precise correlation further trials are necessary to develop a suitable formula.

Nevertheless it is assured that anodes with low arsenic contents and industrial typical oxygen concentrations of max. 2000 ppm will not passivate within the first 1700 Ah of processing at 300 A/m² if the antimony content is below 400 ppm for anodes not containing bismuth. This value can be raised up to 1000 ppm for bismuth concentrations close to 350 ppm. Increasing the current density leads to a significant drop of the antimony limit to less than 200 ppm for anodes not containing bismuth and 400 ppm for bismuth concentrations close to 350 ppm. Processing higher amounts of antimony is only possible at arsenic concentrations between 1500 to 3000 ppm, or at anodic current densities below 300 A/m².

The second part of this publication series will have a close look into the interdependencies between impurity content in the anode on the copper anode dissolution behaviour and the amount of anode sludge forming.

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