MEMBRANE ELECTROCHEMICAL PREPARATION OF THREE-POLYPHOSPHATE NON-CYANIDE ELECTROLYTE FOR COPPERING

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ABSTRACT

The membrane electrochemical technology for obtainment of three-polyphosphate non-cyanide electrolyte for coppering is developed and optimized. For the purpose of characterizing the selectivity of the ionic membranes used, the processes of mass transfer are examined through determining the transmission numbers of the ions in the three-chamber electrolyzer. Detailed balance of the voltage between the electrodes and quantitative evaluation of the anodic output on current during the membrane preparation of the electrolyte are made. It is found that Cu is actively solved without passivation up to current density \( i_a = 8 \, \text{A} \, \text{dm}^{-2} \). The anodic polarization during the operation of the electrolyzer is insignificant and the current efficiency is close to 100 %. It is found that the optimal environment for the membrane preparation of the electrolyte is anolyte of \( 140 \, \text{g dm}^{-3} \, \text{Na}_5\text{P}_3\text{O}_{10} \) and citric acid \( \text{C}_6\text{H}_8\text{O}_7 \) up to \( \text{pH} = 5.3 \), and catholyte solution of \( 380 \, \text{g dm}^{-3} \, \text{Na}_2\text{CO}_3 \).

Keywords: membrane technology, ionic membrane, non-cyanide electrolyte, coppering, balance of voltage.

INTRODUCTION

Electrochemistry of membranes is considered one of the most advanced tendencies in the field of electrolysis processes [1 - 3]. This technology allows processing solutions and electrolytes with concentrations varying in wide range. In addition to the dynamic growth of research worldwide, there has been an ever-lasting implementation of various membrane technologies in various fields of industry in the last 5-10 years [1 - 7]. These technologies show their advantages for the effective solution of environmental issues. The leading companies offer a variety of ionic membranes (cation- or anion-active). In some cases the ionic membranes may be highly selective, letting only one type of ions pass through [5 - 7].

There are a number of electrolytes developed for the electrochemical preparation of copper coatings that are generally classified in two groups: simple (acidic) and complex (mostly alkaline). In the first group, the sulphuric-acidic electrolyte finds the widest application [8 - 11], which has some very important advantages compared to the alkaline ones [12 - 14]: simple composition, stability, and possibility for high-speed deposition of copper. However, it has some important disadvantages: lower dissolution ability and inability for direct copper coating of steel, zinc, aluminum, magnesium and their alloys. These disadvantages are absent in the complex alkaline electrolytes for copper coating [14], the most widely used for direct galvanizing of the above metals being the cyanide electrolyte [13, 14]. It is characterized by a high dissolution ability, resulting in a fine-grain structure coatings, with a good adhesion to the substrate. As alternatives to the cyanide-electrolytes, a number of others are suggested: pyrophosphate [15 - 17], ammonia [18], ethylenediamine, ferrocyanide, glycercate [19], perchlorate [20], polyligand [21], and others.

The alternative of cyanide electrolytes, which is the
most often used in practice, is the pyrophosphate electrolyte. It is simple in composition, stable, easy to maintain and harmless. Another advantage of the pyrophosphate electrolyte is the high dissipation ability, which is close to that of cyanide ones. The three-polyphosphate electrolytes in which Na$_5$P$_3$O$_10$ is replaced with Na$_5$P$_3$O$_12$ with the same concentration are considered entirely alternative and innovative. The three-polyphosphate electrolyte show very good performance characteristics that retain during continuous electrolysis. To improve the stability and some other properties of the three-polyphosphate electrolyte, as well as the properties of the coatings, often a minor amount of a second ligand, ethylenediamine, is added. The real problem with the pyrophosphate electrolyte and the three-polyphosphate electrolytes is their chemical preparation by mixing of reagents due to the fact that in this case the electrolytes always contain a large amount of co-anions, e.g. SO$_4^{2-}$, Cl$^-$, NO$_3^-$, that may impair the quality of the coatings or to reduce the output on current. Their removal is related with processes of sedimentation and multiple washing. These disadvantages are fully avoided in the so called membrane electrolytic preparation of three-polyphosphate electrolyte.

In our previous studies [23] we have found and proved the abilities of the membrane electrochemical obtaining of rodanide silver concentrate for the purposes of galvanotechnics. The present effort is related with investigation of the appropriateness of the application of membrane electrochemical technology for preparation of three-polyphosphate non-cyanide electrolyte for coppering.

**EXPERIMENTAL**

**Examination of mass transfer anode current output and weight output in solution of Na$_5$P$_3$O$_10$**

**Determination of the ion transference numbers:**
The average ion transference numbers $t_\pm$ was used to quantify the transfer of cations and anions in the membrane preparation of three-polyphosphate electrolyte for coppering. The three-chamber electrolyzer shown in Fig. 1 was used for the purpose. Its principle of operation is shown in Fig. 2.

The two membranes used were MA-4 and MC-4 (Fig. 2), as MA-4 is anion-exchange and is designated with (-), and MC-4 is cation-exchange and is designated with (+). The middle compartment works as desalination chamber. The two electrodes are made of platinum-coated titanium. Upon realization of the above scheme the process of electrodialysis is carried out and the concentration of Na$_5$P$_3$O$_10$ in the middle chamber decreases with time. Ideally $t_+$ and $t_-$ are supposed to be equal to 1, since the membranes are defined as anion- and cation-active. This means that upon flowing of 1F amount of electricity, the middle chamber will be depleted of 1 g-ion Na$^+$ and the same quantity of P$_3$O$_10^{4-}$, i.e. the initial concentration of Na$_5$P$_3$O$_10$ is going to decrease with 1g-eq.

The average value of the ion transference number was calculated based on the following relation:

$$t_\pm = \frac{(N_1 - N_2) V}{Q_F}, \quad (1)$$

where: $N_1$ - initial concentration of Na$_5$P$_3$O$_10$ g-eq dm$^{-3}$; $N_2$ - concentration at a certain moment during electrolysis, g-eq.dm$^{-3}$; $V$ - volume of the middle chamber, [dm$^3$]; $Q_F$ - amount of electricity, [F]. For its part, $Q_F = Q/F$, where $F = 26.8$ [Ah]. The amount of the real flow of electricity was calculated on the base of the product $Q = I \tau$, as the time $\tau$ was measured precisely and the
experiment was carried out in galvanostatic mode. Both the initial and the final concentration of Na$_5$P$_3$O$_{10}$ after a definite amount of electricity was determined through analytical titration.

**Calculation of anode current efficiency**: The anode current efficiency (Wa) was calculated using the relation:

$$W_a = \frac{m_d}{m_F} \times 100, \%$$  \hspace{1cm} (2)

where: $m_d$, [g] is the actual mass of copper dissolved for a definite time of electrolysis; $m_F$, [g] is the calculated theoretical mass under the Faraday’s law. The value of $m_d$ is determined gravimetrically observing all the requirements to this method for control. After each experiment the sludge is removed from the working copper electrode. The theoretical mass is determined under Faraday’s law:

$$m_F = q_{\text{Cu}^{2+}/\text{Cu}} I \tau$$  \hspace{1cm} (3)

where: $q_{\text{Cu}^{2+}/\text{Cu}}$ is electrochemical equivalent ($q_{\text{Cu}^{2+}/\text{Cu}} = 1,186$ [g Ah$^{-1}$]); $I$ is current, [A]; $\tau$ is time for dissolution, [h].

**Determining the specific electric consumption and the balance of voltages between the electrodes in two-chamber membrane electrolyzer**

The specific electric consumption in [kWh] is calculated upon the relation:

$$J = U \times 10^3 \times W_a \times q \times \tau$$  \hspace{1cm} (4)

where: $U$ is the voltage between the electrodes, [V]; $W_a$ – anode current efficiency, [%]; $q$ - electrochemical equivalent of copper (Cu$^{2+}$/Cu), [g Ah$^{-1}$].

The experimental setting shown in Fig. 3 was used to assess the components of the voltage between the electrodes. Two-component low acidic electrolyte with composition 140 g dm$^{-3}$ Na$_5$P$_3$O$_{10}$ and citric acid C$_6$H$_8$O$_7$ up to initial pH = 4,3 was used as anolyte and catholyte correspondingly. The initial temperature was $17^\circ$C and no stirring was applied. The copper anode and the cathode made of permalloy (Ni-Fe alloy) are insulated from behind. The two compartments with volumes 100 ml each are separated with horizontal cation-active membrane $\text{MC}_{-4}$ fitted in plastic frame as a holder. The distance between the membrane and both electrodes was 5,5 cm and the current was constant 0,5 A. Besides $i_s = i_c = 2,5$ A dm$^{-2}$. There were four salt bridges arranged in the laboratory membrane cell by which the reference calomel electrode was repositioned after washing.

The experiment was carried out through successive measurement of the components of the voltage between the electrodes and its value $U$ by means of high impedance millivoltmeter.

With the present design of the two-chamber membrane electrolyzer and ignoring the ohmic drop in the first order conductors, the following equation is valid:

$$U = E_{i,a} - E_{i,c} + U_{\text{anolyte}} + U_{\text{catholyte}} + U_{\text{membr.}}$$  \hspace{1cm} (5)

where: $U$ - the measured voltage between anode and cathode, [V]; $E_{i,a}$ – the measured working potential of the copper anode, [V] with Lugin’s capillary tightly resting against it. Saturated calomel electrode (SCE) was used as reference electrode; $E_{i,c}$ – cathode potential measured using the Lugin’s capillary tightly resting against it. The ohmic drops of voltage in the anolyte and the catholyte are calculated using the relations:

$$U_{\text{el.,anolyte}} = |E_{i,a,\tau} - E_{i,a}|$$  \hspace{1cm} (6)

and

$$U_{\text{el.,catholyte}} = |E_{i,c,\tau} - E_{i,c}|$$  \hspace{1cm} (7)
where $E_{i,a}$ and $E_{i,c}$ are correspondingly the anodic and cathodic potentials measured through repositioning of SCE in the capillary, which rests tightly against the membrane wall.

Finally, using the measured components $E_{i,a}$, $E_{i,c}$, $U_{el,anolyte}$, $U_{el,catholyte}$, and the value of $U$, we can calculate the ohmic drop in the membrane $U_{membr}$.

Using the measured values of $U_{el,anolyte}$ and $U_{el,catholyte}$ and the relation $U_{el} = \rho_{el} \cdot i \cdot l$, where $i$ is density of current, A.dm$^{-2}$, and $l$ is distance between the electrodes and the membrane we can determine the specific resistance $\rho_{el}$, and subsequently the specific conductivity:

$$\sigma_{el} = \frac{1}{\rho_{el}} \Omega^{-1} \cdot \text{cm}^{-1}.$$

### RESULTS AND DISCUSSION

**Determination of the ion transference numbers**

The ion transference numbers are determined using electrolyte containing $\text{Na}_2\text{P}_3\text{O}_{10}$ with concentration 177 g dm$^{-3}$ (2.4 g-eq dm$^{-3}$) with current 2 A, volumetric current load 10 A dm$^{-3}$, membrane current density $i_{membr} = I/S_{membr} = 6$ A dm$^{-2}$ and volume of the middle chamber 0.2 dm$^3$. The values of the ion transference numbers obtained using equation (1) are presented in Table 1.

The value of $t_{i} = 0.9867$ obtained is the weight output on Cu$^{2+}$ in the membrane obtained of this non-cyanide copper electrolyte ($W_{a} = 0.9876 \cdot 100 = 98.67 \%$). This means that when an amount of electricity of 1 F flows, then 0.9867 g-jon of Cu$^{2+}$ will accumulate in the anolyte due to the active anodic dissolution ($W_{a} = 100 \%$), and 0.0133 g-jon of Cu$^{2+}$ will shift in the cathode space.

The insignificant reduction in the weight output (from 100 % to 98.67 %) characterizes the high degree of permeability of the two types of membranes towards cations and anions, that does not change and remains constant with the time of saturation.

**Determination of the critical densities of current for passivation of the copper anodes and the anode current output**

Initially, the critical values of current density for passivation of the copper anodes are determined through galvanodynamic construction of the anodic polarization dependencies at different rates of potential scanning (Fig. 4). As is seen, in stationary galvanostatic mode in the working electrolyte up to anode current densities of 6 A dm$^{-2}$ the copper anodes actively dissolve without passivation as the anodic polarization is insignificant and reaches maximum 200 mV. The potential-time dependencies, $E-t$ (Fig. 5) are taken in electrolyte of the same composition at anode current densities, corresponding to the area of active dissolution of copper. Simultaneously, the mass of dissolved copper was determined gravimetrically and the anode current efficiency $W_{a} [%]$ was calculated based on the data taken (Table 2).

The course of $E-t$ dependencies suggests that the active dissolution of copper, i.e. such without passiva-

![Fig. 4. Anodic polarization dependencies of Cu in electrolyte containing 15.3 g dm$^{-3}$ Cu; 140 g dm$^{-3}$ Na$_2$P$_3$O$_{10}$ and C$_6$H$_5$O$_2$, up to initial pH = 4.3 at rates of potential scanning, v [mA min$^{-1}$]: (1) – 3; (2) - 15; (3) – 30; (4) – 60 (t = 20°C).](image-url)

<table>
<thead>
<tr>
<th>$\tau$, h</th>
<th>$Q$, Ah</th>
<th>$Q_{r}$</th>
<th>$N_2$, g-eq dm$^{-3}$</th>
<th>$\Delta N \cdot V_{1}$, g-eqv</th>
<th>$t_{a}$</th>
</tr>
</thead>
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<tr>
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<td>0.075</td>
<td>2.03</td>
<td>0.074</td>
<td>0.9867</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.150</td>
<td>1.66</td>
<td>0.148</td>
<td>0.9867</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.300</td>
<td>0.92</td>
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</tr>
<tr>
<td>8</td>
<td>12</td>
<td>0.450</td>
<td>0.18</td>
<td>0.444</td>
<td>0.9867</td>
</tr>
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Table 2. Data for the anode current efficiency determined in dissolution of Cu in low acidic pyrophosphate electrolyte at anode surface $S_a = 50 \text{ cm}^2$.

<table>
<thead>
<tr>
<th>№</th>
<th>$i_a$, A.dm$^{-2}$</th>
<th>I, A</th>
<th>$\tau_{\text{dissol}}$, min</th>
<th>$m_F$, g</th>
<th>$m_d$, g</th>
<th>$W_a$, %</th>
</tr>
</thead>
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<td>0,1008</td>
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<td>100</td>
</tr>
<tr>
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<td>10</td>
<td>0,2016</td>
<td>0,2016</td>
<td>100</td>
</tr>
<tr>
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<td>0,4032</td>
<td>100</td>
</tr>
<tr>
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<td>3,0</td>
<td>10</td>
<td>0,6048</td>
<td>0,6047</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
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<td>4,0</td>
<td>10</td>
<td>0,8064</td>
<td>0,7798</td>
<td>96,7</td>
</tr>
<tr>
<td>6</td>
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<td>5,0</td>
<td>10</td>
<td>1,0080</td>
<td>0,9073</td>
<td>90,0</td>
</tr>
<tr>
<td>7</td>
<td>12,0</td>
<td>6,0</td>
<td>10</td>
<td>1,2096</td>
<td>1,0225</td>
<td>84,5</td>
</tr>
</tbody>
</table>

The ascertained anode behavior of copper is supported by the data for the influence of the anode current density on the anode current efficiency (Table 2).

**Specific electric consumption, voltage balance and optimization of the working conditions**

The main parameter in the calculation of the specific electric consumption, which is susceptible to electrochemical influences is the voltage $U$ between the electrodes. It is taken into account that the electrochemical equivalent of the redox system $\text{Cu}^2+/\text{Cu}$ is equal to 1,186 g Ah$^{-1}$, and the anode current efficiency related to the dissolution of Cu is close to 100 % as it was proved above. The detailed balance of the voltage $U$ between the electrodes was composed and the shares of the participating components were estimated. For anolyte and catholyte we used the two-component low-acidic electrolyte containing 140 g dm$^{-3}$ $\text{Na}_5\text{P}_3\text{O}_{10}$ and $\text{C}_6\text{H}_8\text{O}_7$ up to initial pH = 4,3 at $t = 20^\circ\text{C}$. The values for the components of $U$ in the cell with vertical membrane MC- 4 are shown in Table 3.

Moreover, it should be emphasized that the values of the potentials are measured against SCE and the ohmic voltage drop in the first-order conductors is assumed 5 % of the sum of $E_{i,a}$, $E_{i,c}$, $U_{\text{anolyte}}$, and $U_{\text{catholyte}}$. The temperature $20^\circ\text{C}$ is maintained equal both in the anolyte and the catholyte by means of a thermostat.

The data from the last row are taken after the electrolyzer has worked for time $t = 2,5$ h when the desired concentration of copper in the anolyte 1,6 g.dm$^{-3}$ is achieved. This data is analyzed more particularly for the influence of the shares of components on the value of $U$. This analysis suggests some major conclusions. With the time for saturation the voltage between the electrodes $U$ decreases from 9,34 V to 7,66 V, mainly by the reason of the significant decrease of the ohmic drop of the catholyte $U_{i,c}$, catholyte from 3,45 to 2,66 V. This can be explained with the increase of temperature with almost 15°C in both spaces.

The detailed analysis for the influence of the components on the voltage between electrodes measures by the end of saturation, i.e. after 2,5 h also indicates that:

- The lowest share is that of $E_{i,a}$ (2,35 %) confirming...
achieving the optimal conditions for active dissolution of copper with low polarization;

- The ohmic voltage drop in the membrane 0,4 V (4,4 %) is also insignificant, which is indicative for the appropriateness of using this type of membrane;

- The shares of the rest three components $E_{i,c}$, $U_{\Omega,anolyte}$ and $U_{\Omega,catholyte}$ of the voltage between electrodes are commensurable but the share of $U_{\Omega,catholyte} = 2,66$ V (34,7 %) is the largest.

In our research we have turned a special attention to the environment and the processes in the anolyte, in which the high-speed active dissolution of copper with anode output close to 100 % is achieved.

The same two-component low-acidic electrolyte with content 140 g dm$^{-3}$ Na$_5$P$_3$O$_{10}$ and C$_6$H$_5$O$_7$ complement up to initial pH = 4.3 was the environment to examine the variation of pH of the anolyte and the catholyte, as well as the concentrations of copper ions and free sodium three-polyphosphate in both spaces. The results are presented in Fig. 6. The data obtained enable making the following conclusions:

- The high weight efficiency $W_a = 98.7$ %) obtained through determination of the transference numbers is confirmed. It is important to notify that it is constant and does not change with the time of membrane electrolysis since the concentration of the copper ions increasing linearly and the concentration of sodium three-polyphosphate decreases linearly too, as the ratio $\frac{m_{PO_4^{3-}}}{m_{Cu^{2+}}}$ remains constant;

- pH in the two chambers changes unexpectedly but significantly, the more significant being the change in the catholyte, from 4,3 too 5,3. This increase of pH results in increase of the overvoltage of hydrogen evolution, as $E_{i,c}$ being shifted in negative direction with almost 0,5 V (from $E_{i,c} = 1,44$ V to $E_{i,c} = 1,91$ V), which follows from Table 2. On the other hand, the specific conductivity of catholyte=0,052 $\Omega^{-1}$ cm$^{-1}$ is lower than anolyte=0,062 $\Omega^{-1}$ cm$^{-1}$. These two effects established for the catholyte result in the relatively high voltage between electrodes achieving about 7.7 V by the end of the electrolysis. This is the reason why during the examinations for optimization the two-component low acidic catholyte with pH = 4,3 was replaced with K$_3$CO$_3$ with high initial concentration of 380 g dm$^{-3}$. As the most appropriate one, the cathode shaped as grid with large surface made of mild steel 3 i$_3$ suggested.

The variation of the voltage between the electrodes in the catholyte during this last version of optimization is shown in Table 4.

The comparison between the data in Table 4 and Table 3 indicates that there were substantial differences after the catholyte had been replaced, and namely: $E_{i,c}$

<table>
<thead>
<tr>
<th>$\tau$, h</th>
<th>$t$, $^\circ$C</th>
<th>$U$, V</th>
<th>$E_{i,a}$, V</th>
<th>$E_{i,c}$, V</th>
<th>$U_{\Omega,anolyte}$, V</th>
<th>$U_{\Omega,catholyte}$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>25</td>
<td>9,34</td>
<td>0,09</td>
<td>-1,44</td>
<td>2,34</td>
<td>3,45</td>
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<td>0,09</td>
<td>-1,89</td>
<td>2,18</td>
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<td>1.5</td>
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<td>0,18</td>
<td>-1,91</td>
<td>2,22</td>
<td>2,66</td>
</tr>
</tbody>
</table>

Table 3. Values of the components participating in the voltage balance of electrolytic cell with vertical membrane for three-polyphosphate copper electrolyte.

Fig. 6. Variation of pH$_{\text{catholyte}}$ (1), pH$_{\text{anolyte}}$ (2), $C_{\text{Cu}^{2+}}$ (3) and concentration of free Na$_5$P$_3$O$_{10}$ (4) in the electrolyte with the time for saturation.
decreases with almost 400 mV (from -1.91 to -1.54 V), and the specific conductivity \( \sigma_s \) increases about 3.5 times. The changes identified are highly beneficial for the reduction of \( U \) with about 30% from 7.66 to 5.3 V. In the final version of the optimization the specific electric consumption decreases also with 30% from 95 Wh kg\(^{-1}\) to 66.5 Wh kg\(^{-1}\).

**CONCLUSIONS**

The high efficiency of the membrane electrochemical technology for preparation of non-toxic three-polyphosphate copper electrolyte is proven. This technology has a pronounced environmental and economic effect and innovative character. The transfer numbers (\( t_s = 0.9867 \)) determined proved that the selectivity is stable and close to 100% thus confirming the effectiveness of the selected membranes. The detail voltage balance confirms the appropriate usage of this particular type of membranes.

**REFERENCES**


