Recent Developments in Trivalent Chromium Plating Process

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A major disadvantage of a trivalent chromium plating process operating with an insoluble anode placed into an auxiliary membrane cell is a continuous build-up of sulfuric acid in this cell resulting in changing transport numbers and all other parameters of the process (pH, current efficiency, etc.) An improved version of the process was developed. It includes simultaneous operation of two anodic cell and allows complete automation of the process control.

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Trivalent chromium plating process is very sensitive to the solution pH. However, pH value is changing quite rapidly due to the formation of free acid in the amounts equivalent to the amount of chromium metal deposited at the cathode:

- cathodic reaction

$$2Cr_2(SO_4)_3 + 12\ e^- \rightarrow 4\ Cr + 6SO_4^{2-} \qquad (1)$$

- anodic reaction

$$6H_2O \rightarrow 3O_2 + 12H^+ + 12\ e^- \qquad (2)$$

- overall reaction:

$$2Cr_2(SO_4)_3 + 6H_2O \rightarrow 3O_2 + 4\ Cr + 6H_2SO_4 \qquad (3)$$

The use of a divided cell with an anion-exchange membrane and the accumulation of sulfuric acid formed in the anodic compartment was recently proposed for the stabilization of solution pH and for removal of excessive sulfate ions introduced periodically into the solution in the form of chromium sulfate[1]. Since constant pH in the plating solution is reached only, if the transport of hydrogen ions from the anodic compartment corresponds strictly to their consumption in the reaction:

$$2H^+ + 2e^- \rightarrow H_2, \qquad (4)$$

the control of these two processes requires certain means. It was shown recently[1] that the transport of ions between the chromium plating solution and the auxiliary anolyte depends on the type of the membrane and the compositions of both solutions. With cationic membrane acidification of stage the plating solution took place in all cases. With the anionic membrane the results were determined by the concentration of hydrogen ions in the anolyte. Constant pH was preserved only at certain concentration of sulfuric acid in the anolyte. It should be noted that any variations in the cathodic current efficiency will inevitably change this balance. On the other hand, the transport of sulfate ions into the anolyte and resulting bult-up of sulfuric acid will effect the transport numbers and, consequently, will change the pH value in the plating solution. Simultaneous operation of two anodic compartments with different membranes or/and different anolytes will probably allow to use automatic control of transport process and the maintenance of pH in the plating solution.

Experimental Procedure

Electrolytic cell consisted of cathodic chamber (300 ml) and one or two anodic chambers. Cathodic chamber contained chromium plating solution (Table 1) of the following composition[2]:

Table 1

$Cr_2(SO_4)_3 \bullet 6H_2O$	250 g/l
$Al_2(SO_4)_3 \bullet 18H_2O$	120 g/l
Na_2SO_4	40 g/l
HCOONa (sodium formiate)	27 g/l
$CO(NH_2)_2$ (urea)	45 g/l
pH	1.3 to 1.7
Room temperature	~25 °C
Cathode current density	25 A/dm^2

Sulfuric acid solutions of different concentrations were used as the anolyte. Anodic chambers had cationic and anionic membranes and platinized titanium anodes with individual current controls. A new copper cathode 2 × 2 cm was used in each plating experiment.

Results and Discussion

Stable and reproducible values of current efficiency (at constant temperature, pH and current density) have been observed only after preelectrolysis with either cationic or anionic

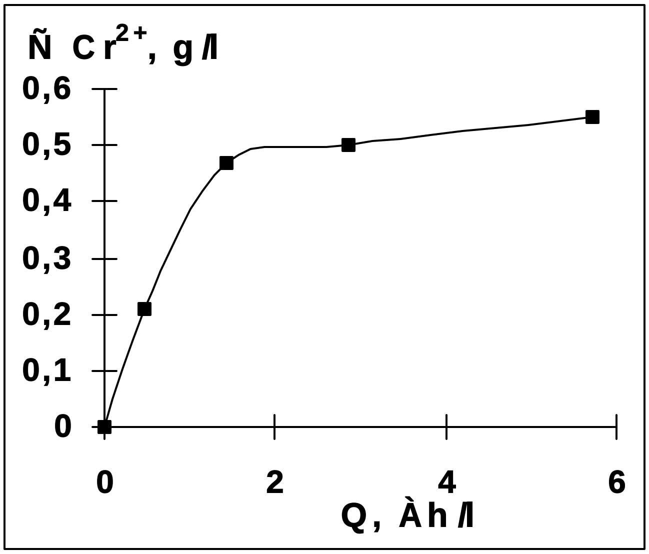

Fig. 1 - Concentration of Cr^{2+} *in the catholyte (plating solution) vs. electric charge passed through the catholyte.*

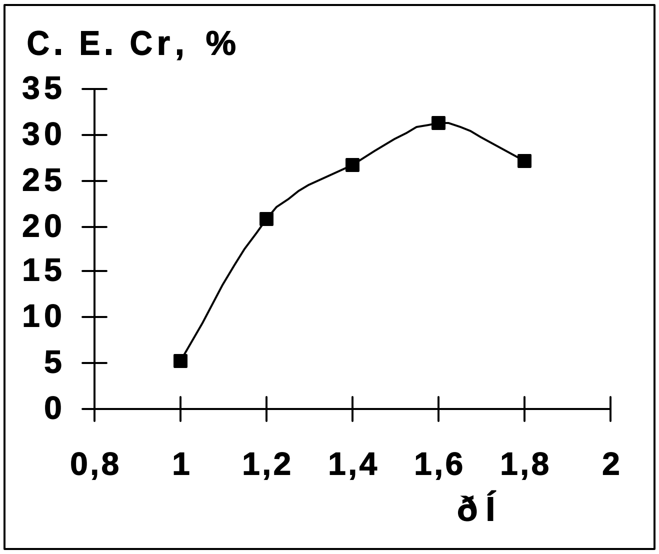

Fig. 2 - Current efficiency of chromium vs. catholyte pH.

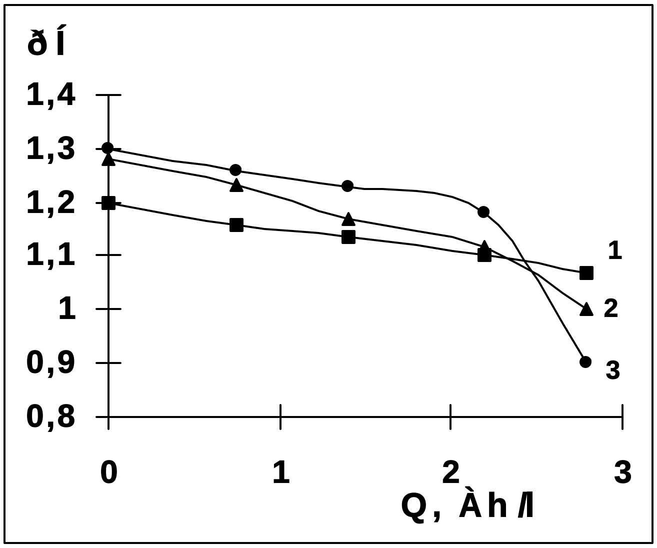

Fig. 3 - Changing pH of the catholyte (plating solution) in the course of electrolysis. Initial concentration of sulfuric acid in the anolyte: 1, 0.5 M; 2, 1 M; 3, 2 M. Anodic chamber has the cationic membrane.

membrane. During this stage the concentration of Cr^{2+} was rising from its initial value (close to zero for a fresh solution) up to its steady-state value (Fig. 1). Another parameter determining current efficiency (at constant temperature and current density) is solution pH (Fig. 2).

Individual operation of a single anodic chamber with the cationic membrane leads to gradual lowering of pH in the catholyte (Fig. 3), since irrespectively of the concentration of sulfuric acid in the anolyte the transport number of hydrogen ions is close to 0.9 (Fig. 4). In the case

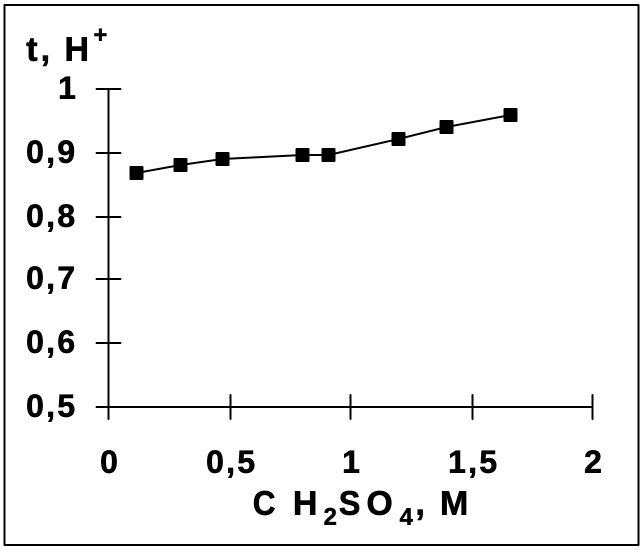

Fig. 4 - Transport number of H^+ ions vs. the concentration of sulfuric acid in the anolyte. Anodic chamber with the cationic membrane.

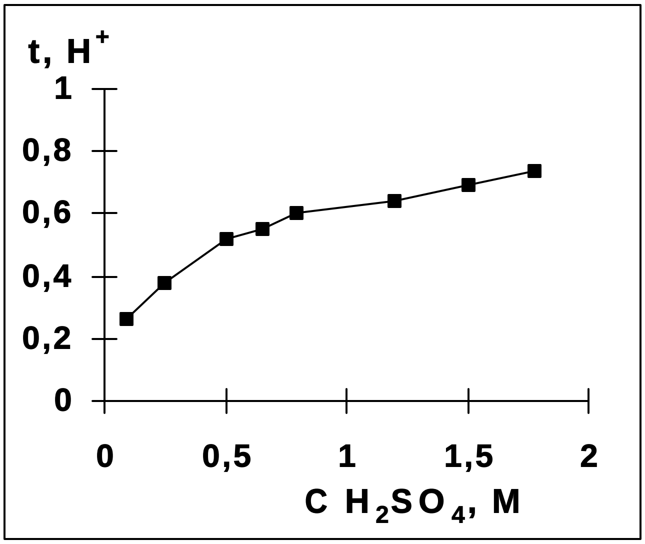

Fig. 5 - Transport number of H^+ ions vs. the concentration of sulfuric acid in the anolyte. Anodic chamber with the anionic membrane.

of the anionic membrane the transport number is varying between 0.8 (2M H_2SO_4) and ~0.3 (0.1 M H_2SO_4) (Fig. 5). Therefore, with the anionic membrane pH in the plating solution (i.e. in the catholyte) may rise or decrease (Fig. 6) depending on the concentration of sulfuric acid in the anolyte. An appropriate concentration of sulfuric acid in the anolyte allows obviously to keep the balance of the consumption of hydrogen ions at the cathode and their input from the anolyte. However, in any actual chromium plating process this balance cannot be maintained, since current efficiency will never be constant because of

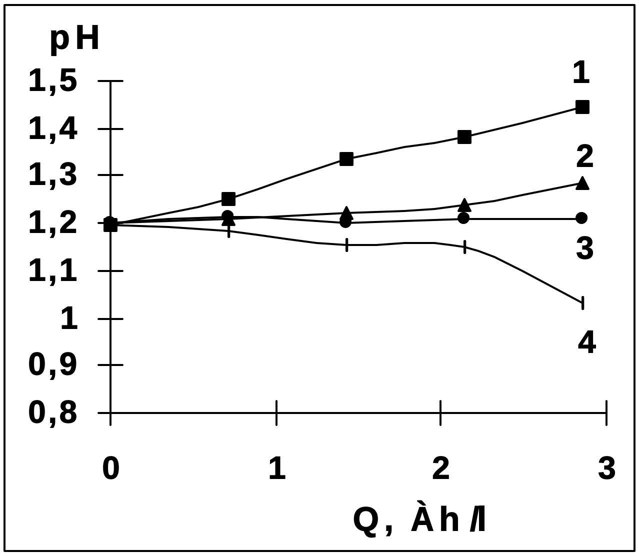

Fig. 6 - Changing pH of the catholyte (plating solutions) in the course of electrolysis. Concentration of sulfuric acid in the anodic chamber with the anionic membrane: 1, 0.1 M; 2, 0.3 M; 3, 1.4 M; 4, 2 M.

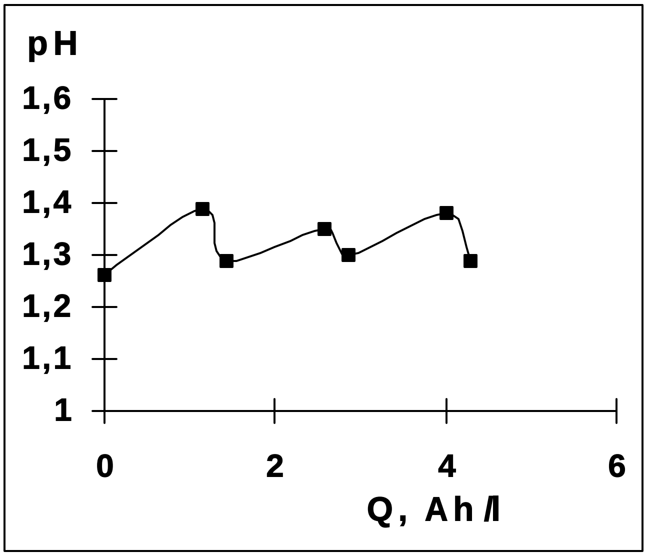

Fig. 7 - Operation of the cell with two anodic chambers (combination of cationic and anionic membranes). Concentration of sulfuric acid in the anodic chamber 1 M. Periodic operation of the anodes: full cycle 30 min = 24 min with the anionic membrane + 6 min with the cationic membrane.

inevitable changes in the geometry of chromium plated parts and nonuniform distribution of current density (and current efficiency) over their surface.

Apart from all these considerations, gradual built-up of sulfuric acid in the anolyte should be taken into amount. Therefore, a combination of two anodic chambers has been proposed. The first chamber has the cationic

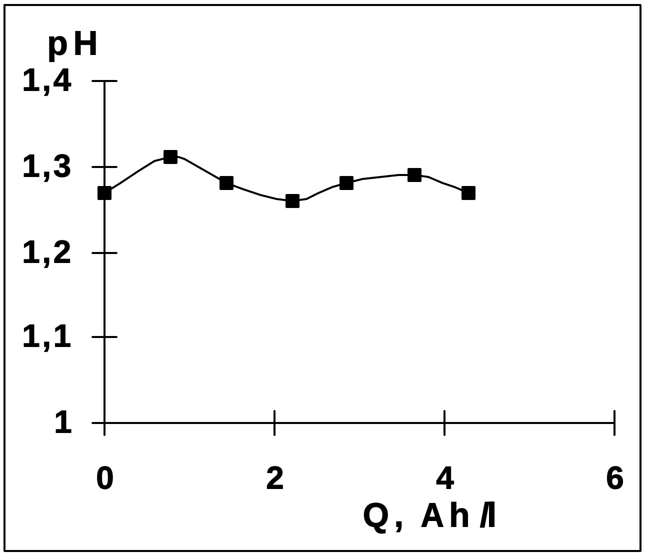

Fig. 8 - Operation of the cell with two anodic chambers (combination of cationic and anionic membranes). Concentration of sulfuric acid in the anodic chamber 0,5 M. Periodic operation of the anodes: full cycle 30 min = 16,5 min with the anionic membrane + 13,5 min with the cationic membrane.

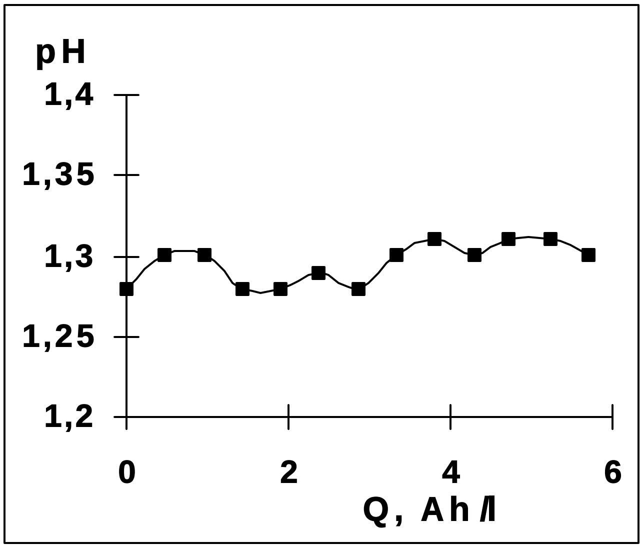

Fig. 9 - Operation of the cell with two anodic chambers (combination of cationic and anionic membranes). Concentration of sulfuric acid in the anolyte 1 M. Simultaneous operation of two anodes: 80 % of total current passed through the anionic membrane and 20 % of that passed through the cationic membrane.

membrane and is used for the acidification of the plating solution. The second one has the anionic membrane and contains sulfuric acid solution with moderate concentration (e.g. 0.5 to 1 M). A ratio of electric charges passed through the first and second anodic chambers is the only parameter which determines the behavior of pH in the catholyte. Figs. 3, 7 and 8 show changes in the catholyte pH in the course of electrolysis. The two anodic chambers were operating alternatively. Same current passed through the first or second chamber. Another way of regulating the above ratio was based on continuous operation of the two anodic chambers with appropriate control of the two currents (Fig. 9).

Any devices based on pH measurements may be used for the automatic control of the operation of two anodic chambers in chromium plating tanks. As soon as pH reaches upper limit the chamber with the anionic membrane is switched off and the chamber with the cationic membrane starts its operation. When the pH value reaches the lower limit, the operation of the cationic membrane chamber is stopped and the operation of the anionic membrane chamber starts again.

Conclusions

1. Two-chamber plating cell with an anionic membrane can be used for adjusting pH in a trivalent chromium plating solution only in laboratory-scale plating experiments because of continuously changing concentration of sulfuric acid in the anolyte.
2. Two anodic chambers with one cationic and one anionic membranes allow to shift pH up- and downwards by changing the percent of electric charge passed through the anodic chamber with the certain membrane.
3. The system can operate both at constant or varying concentration of sulfuric acid in anodic chambers.

References

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2. V. N. Kudryavtsev, S. R. Schachameyer, O. E. Azarko, E. G. Vinokurov, Proc. AESF SUR/FIN' 95, 503 (1995)