Automatic Control of Process Solutions: the Use of Insoluble Anodes and Ion-exchange Membranes

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Stable composition of various process solutions is maintained by adding those components which are consumed in the course of the operation and by continuous or periodic removal of reaction products and impurities. A combination of soluble and insoluble anodes connected to separate rectifiers allows to prevent excessive built-up of metal ions. A half-cell with a cationic membrane and a cathode inside immersed into the process tank with an insoluble anode is used for the regeneration of passivating, etching and stripping plating solutions. A combination of two half-cells with insoluble anodes, cationic and anionic membranes allows maintaining constant pH of trivalent chromium plating bath and to remove from it access of sulfate ions.

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Introduction

Stable operation of a process in plating and surface treatment industry becomes possible, provided the composition of the process solution is maintained within certain limits. There are three types of the components of process solutions: (a) reactants, which are continuously consumed; (b) reaction products, which are built up in the course of normal operation, and (c) impurities, which may be contained in the chemicals or soluble anodes or get access to a process solution either by dragging into it from previous treatment stage, or may appear due to dissolution of a metal from the surface of parts.

The ions of a metal deposited at the cathode are a typical example of (a) component, and same ions represent (b) component for the anodic reaction. Typical cases of (c) type are ferric ions in chromium plating solutions.

Concentrations of hydrogen ions in acid solutions or hydroxyl ions in alkaline solutions are usually critical parameters. These ions take part in numerous chemical and electrochemical reactions: cathodic hydrogen and anodic oxygen evolution, etc. A disbalance between the cathodic deposition and the anodic dissolution of a metal, chemical reaction between metals and different solutions change the concentrations of hydrogen, hydroxyl and metal ions. Periodic replenishment, “bleed-and-feed” method allow to extend the life time of process solutions. An alternative approach is based on the use of ion-exchange membranes and auxiliary membrane electrolytic cells which allow to add or to remove certain ions and to convert reaction products back to the initial state. Few examples are discussed below.

Compensation of Difference between Cathodic and Anodic Current Efficiencies in the Electroplating Processes

If anodic dissolution of a metal proceeds with current efficiency close to 100% and cathodic deposition with lower current efficiency, a combination of soluble and insoluble anodes allows to prevent undesirable changes both in the concentrations of metal and hydrogen (hydroxyl) ions (Fig. 1).

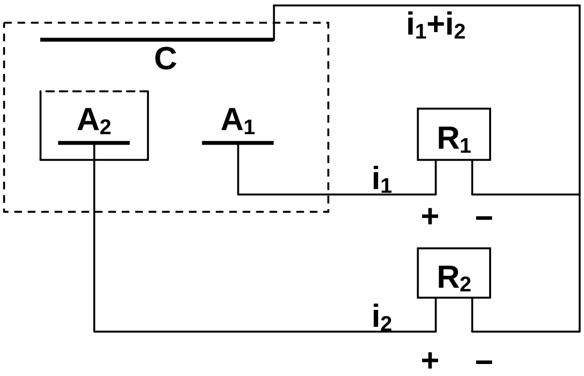

Fig. 1. Simultaneous operation of soluble (A_1) and insoluble (A_2) anodes;
C, Cathode;
R1 and R2, Rectifiers.

Constant composition of the plating solution will be maintained, if the amount the metal deposited at the cathode is equal to the amount dissolved from the soluble anode:

$$\Delta m_C = \frac{M}{z} \frac{i_1 + i_2}{F} \frac{CE_C}{100} \quad (1)$$

$$\Delta m_a = \frac{M}{z} \frac{i_1}{F} \frac{CE_A}{100} \quad (2)$$

Here Δm_A and Δm_C are amounts of deposited and dissolved metal per unit time; M – is an atomic mass; z is metal valency; F is Faraday's number; CE_C and CE_A are cathodic and anodic current efficiencies.

For example, anodic dissolution of zinc in an acid chloride-based solution proceeds with CE_A>100% and cathodic deposition with CE_C<100%. An additional insoluble anode in a combination with a cationic membrane prevents liberation of toxic chlorine gas, maintains constant pH and concentration of zinc ions.

Regeneration of chromate-based solutions

Various types of chromate-based solutions are used for passivation, stripping, removal of sludge, etc. A reaction between a divalent metal M and chromate is the ionization of the former and the reduction of the latter:

$$3M + 2CrO_4^{2-} + 16H^+ \rightarrow 3M^{2+} + 2Cr^{3+} + 8H_2O \quad (3)$$

The regeneration of the solution must include (a) removal of accumulated metal ions M^{2+}, (b) oxidation of Cr^{3+} into CrO_4^{2-}, which is also accompanied by (c) the liberation of hydrogen ions, consumed in the reaction (3). A cell shown in Fig. 2 is able to remove dissolved metal ions, regenerate chromate and restore the acidity of the solution.

Trivalent chromium is oxidized into chromate at the insoluble anode. Hydrogen ions are also formed in the course of this reaction:

$$Cr^{3+} + 4H_2O \rightarrow CrO_4^{2-} + 8H^+ + 3e^- \quad (4)$$

There is another anodic reaction – oxidation of water molecules:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (5)$$

In addition to reactions (4) and (5) the transport of metal ions M^{2+} together with some part of hydrogen ions through the cationic membrane also takes place.

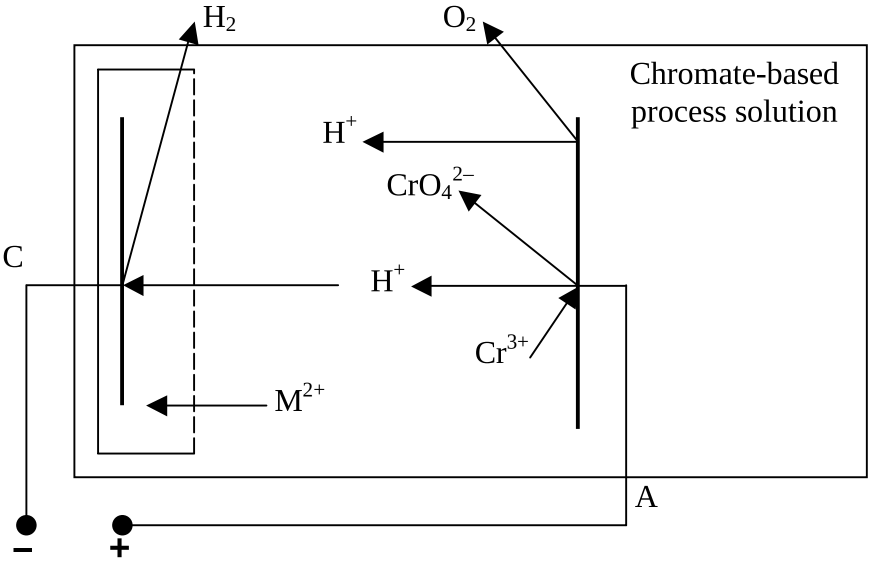

Fig. 2. Regeneration of chromate-based process solutions.

Maintenance of required pH is reached by increasing and decreasing electric current (the higher current the lower is steady-state pH value). Of course, this problem does not appear in chromate-based solutions, containing appreciable concentrations of free acid (e.g. mixtures of chromic and sulfuric acids used for the treatment of copper).

Simultaneous Operation of Two Membrane Cells

Various combinations of cathodic and anodic membrane half-cells can be used for the solution of particular problems. For example, removal of sulfate ions and pH adjustment of a trivalent chromium plating solution is made by simultaneous operation of two insoluble anodes placed in two anodic half-cells (Fig. 3).

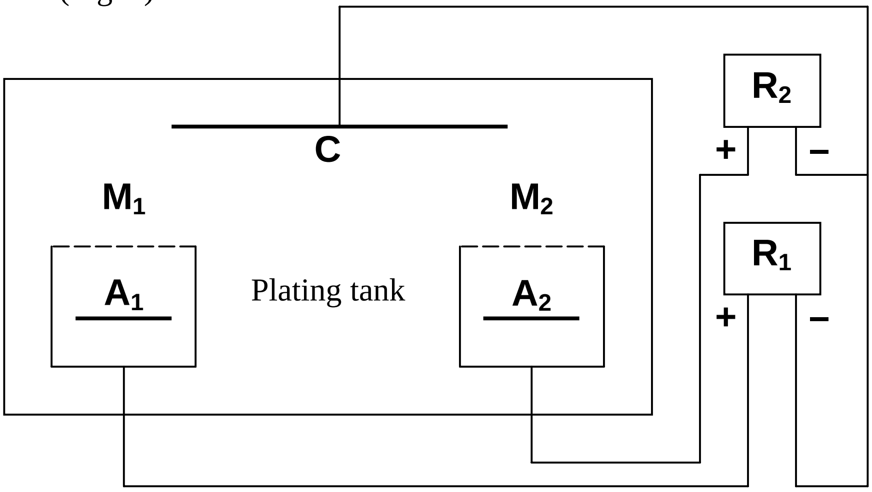

Fig. 3. Chromium plating tank with two anodic half-cells with insoluble anodes; M_1, cationic membrane;

M_2, anionic membrane;
A_1 and A_2, insoluble anodes;
C, the cathode;
R_1 and R_2, the rectifiers.

Sulfate ions pass through the membrane M_2 and are accumulated in this half-cell. Hydrogen ions pass through the membrane M_1 with the rate equal to that of their consumption at the cathode.

Removal of Metal Ions from Process Solutions

Other examples are different combinations of a cathodic cell and an anodic one installed in a tank with certain process solution (Fig. 4).

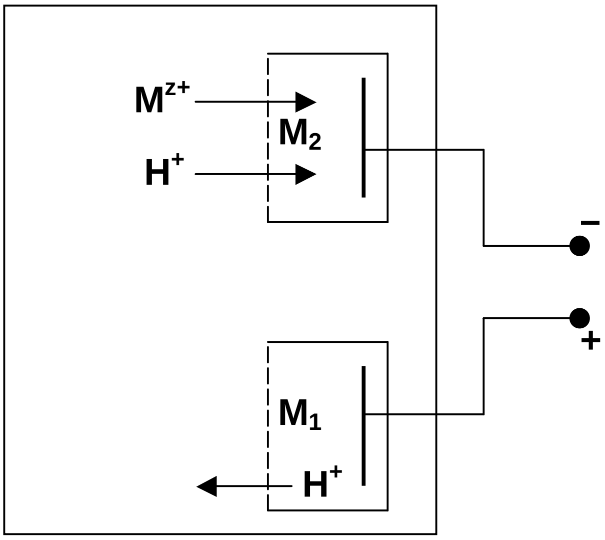

Fig. 4. A combination of a cathodic cell and an anodic cell with two cationic membranes;
M_1 and M_2 are cationic membranes.

Such a combination is used for the removal of M^{z+} cations from a process solution. Operation of the cells in Fig. 4 may lead to acidification of the process solution. If it is undesirable, an additional anodic half-cell with an anionic membrane is installed, which is connected to a second rectifier (see Fig. 1).

The system shown in Fig. 4 can be used for the removal of metal cations from chromate-based solutions containing chlorides (passivation of Zn-Ni coatings) or fluorides (solutions used in the treatment of Al).

Summary

The use of various types of membrane half-cells with cationic and anionic membranes and insoluble anodes allows developing reagent-free technologies for automatic control of process solutions in plating shops and to extend the life-time of solutions which are periodically dumped.