The Use of Immersed Electrochemical Modules (IEMs) in Plating Industry

Dr. Sergey S. Kruglikov
S.S. Kruglikov Consultants, Moscow, Russia

IEM is a half-cell with an ion-exchange membrane and an internal cathode or anode. IEM is installed directly in plating tanks with process solutions in order to keep them in operation without periodic dumping (etchants, passivating, stripping solutions, etc.). Proper choice of combinations of cathodic or anodic reactions and ionic transport through the membranes allows to remove impurities, reaction products, regenerate reactants and maintain desirable pH value. Another application of IEM is the removal of ions from reclaim tanks either by cathodic deposition (copper, zinc, nickel, etc.) or by migration through membranes (chromic acid). Over 100 IEMs are now in operation in Russia.

For more information contact:
Prof. Sergey S.Kruglikov
Bolshaya Spasskaya, 33, apt. 107
Moscow, 129090, Russia
Phone/Fax: +7-495-680-02-81
Cell phone: +7-916-616-96-99
E-mail: gtech@muctr.edu.ru

Introduction

Membrane electrolysis is a combination of an electrolytic transfer of ions through ion-exchange membranes and electrochemical reactions taking place at the electrodes. Proper choice of such combination allows to change the composition of a particular solution in a desirable direction or to keep it constant. Regeneration of various process solutions and removal of the components of process solutions from rinse water in reclaim tanks are major fields of application of membrane electrolysis.

The membrane electrolysis may be carried out in a separate unit – an electrolytic cell usually with one or two membranes. In such a case the process solution or rinse water is circulating continuously between an appropriate compartment in the membrane cell and the tank in the plating line. This version of the process seems reasonable, if a required overall surface area of membranes is quite large (> 1 m^2). For smaller area the membrane cell (i.e. IEM) can be installed in the reclaim tank or in the tank with a process solution directly in the plating line. In such a case the tank itself represents one of the compartments of the whole membrane electrolytic cell and there is no need in the circulation system, pumps, etc. Therefore IEM is more popular in plating industry rather than separate membrane electrolytic cells.

Regeneration of process solutions

Various types of chromate-based etchants, passivating and stripping solutions are continuously regenerated in order to eliminate periodic dumping and to reduce consumption of chromate for replenishment.

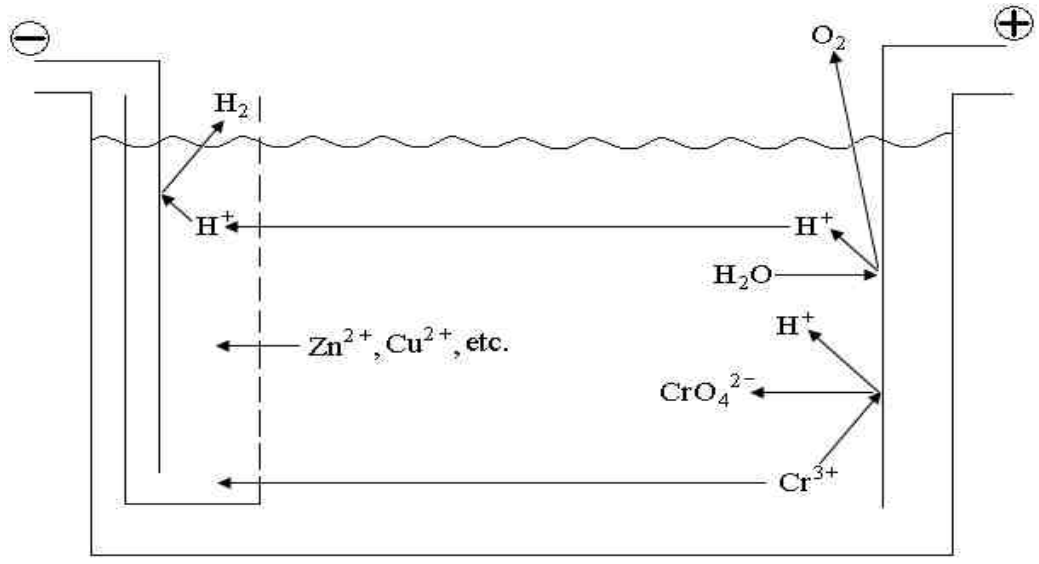

Fig. 1. Regeneration of chromate-based solutions.

The reaction between a metal and a chromate-based solution is an oxidation of this metal and reduction of chromate:

$$3Zn(Cu, etc.) + 2CrO_4^{2-} + 16H^+ \rightarrow 3Zn^{2+}(Cu^{2+}, etc.) + 2Cr^{3+} + 8H_2O \quad (1)$$

The regeneration means anodic oxidation of Cr^{3+} into CrO_4^{2-} accompanied by the formation of an acid (H^+):

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

and the removal of Zn^{2+} (Cu^{2+}, etc.) by an electrolytic migration through a cationic membrane. Some part of Cr^{3+} passes into the catholyte together with hydrogen ions and other metal cations. These ions are built up in the catholyte, while others (Zn^{2+}, Cu^{2+}, etc.) are discharged at the cathode to a metal state. Therefore the catholyte may be added periodically to the process solution in order to convert all Cr^{3+} ions into chromate.

Another type of process solution regenerated by means of IEM is copper etchant containing persulfate and used in the manufacture PCBs. Copper ions migrate through the cationic membrane into the catholyte (i.e. IEM) and form metal deposit at the cathode. Cathodic reduction of persulfate ions is completely excluded since no anions can pass through the cationic membrane. Unfortunately persulfate is not regenerated by anodic oxidation of sulfate due to too low concentration of the latter in the etchant.

IEM in reclaim tanks

Practically all toxic inorganic components of process solutions can be recycled from reclaim tanks into process tanks using IEM for their removal from rinse water. The steady-state concentrations of heavy metal ions, chromates, etc. in the reclaim tanks under the conditions of continuous operation may be as low as 0.1 to 5 per cent of those in the process tanks. This means that the input of these ions into following rinses and waste water is reduced by 20-1000 times.

IEM can reduce energy consumption in evaporation units in chromium plating lines by maintaining tenfold difference between CrO_3 concentrations inside the module and in the reclaim tank (e.g. 30 g/L in the IEM and 3 g/L in the tank). Fig. 2 illustrates the operation of IEM in the chromium plating line.

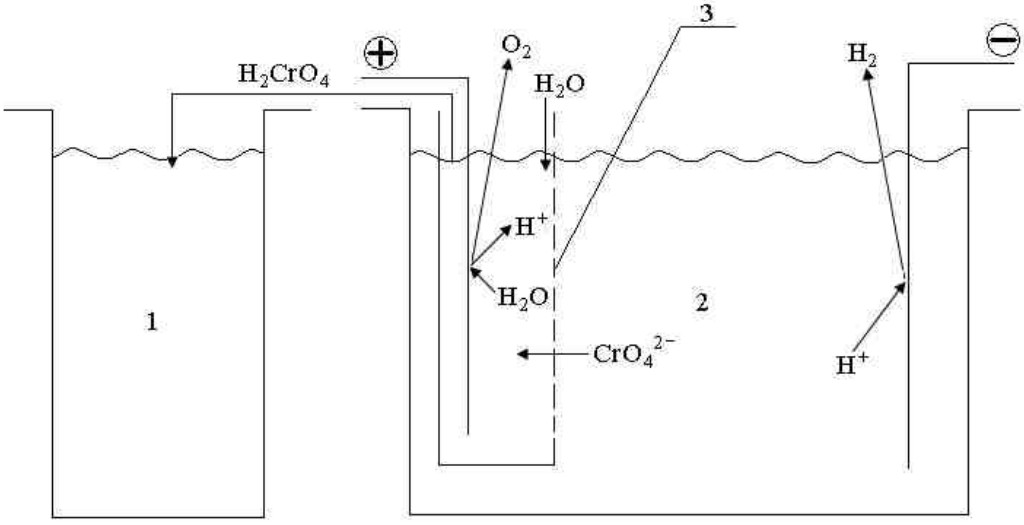

Fig. 2. Operation of the IEM in the reclaim tank in chromium plating line.
1, Chromium plating tank;
2, Reclaim tank;
3, Anionic membrane.

The solution of chromic acid formed in the IEM is added periodically to the plating solution.

Another example is copper plating from sulfate solutions (Fig. 3).

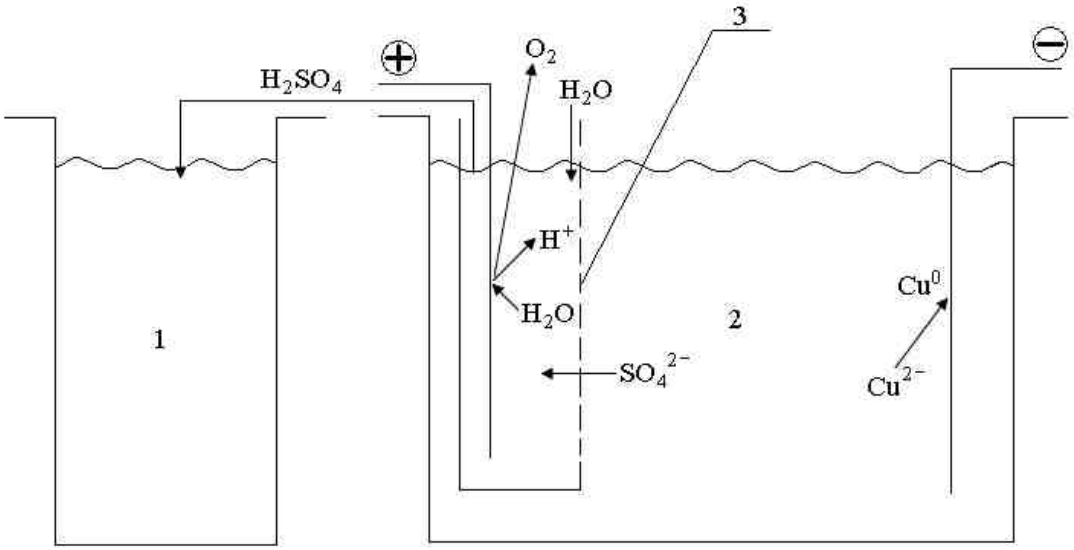

Fig. 3. Operation of the IEM in the reclaim tank in copper plating line.
1, Copper plating tank;
2, Reclaim tank;
3, Anionic membrane.

In addition to the recycling of sulfuric acid the copper-plated cathode is periodically placed at the anode bar and copper deposit is then dissolved. The input of copper ions into waste water is usually reduced by 100 to 500 times and the input of sulfuric acid – 10 to 50 times.

Summary

Industrial applications of IEM include the regeneration of chromate-based solutions used for different purposes: passivating, stripping, descaling, polishing of zinc, cadmium, ferrous metals, copper and its alloys. Conventional operation of these solutions always includes periodic dumping and now dumping is completely eliminated.

Still more modules are installed in reclaim tanks after plating zinc (from alkaline, acid and cyanide baths), chromium, nickel, cadmium (all types of baths), copper (sulfate, pyrophosphate and cyanide), tin and its alloys, as well as reclaim tanks after the treatment in chromate-based solutions.

