Purification of Hard Chromium Plating Baths—Options & Challenges

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Electrolytic purification is a likely option for purifying contaminated hard chromium plating solutions. This article presents a comparison between two principal electrochemical processes used to treat hard chromium plating baths: (a) the porous ceramic membrane (PCM) cell and (b) the fuel cell membrane process (FCMP) cell. The latter process was developed at the Illinois Institute of Technology. Both cells are controlled by transport phenomena, diffusion, migration and convection, governed by the basic Navier-Stokes equation. The results obtained from laboratory scale experiments are promising and indicate that the removal rates are marginally better with the PCM cell, while the energy (current times potential) is lower in the FCMP. A major drawback to the PCM process is sludge formation resulting from an increase in catholyte pH and consequent precipitation. Accordingly, this process does involve interruption and sludge removal. Sludge formation presents a major challenge in the operation of a PCM cell. On the other hand, sludge formation is an unlikely event in a FCMP cell. However, the metal removal rates in a FCMP cell are lower than those in the PCM cell. Improvements in metal removal rates in a FCMP cell might be possible by modifying the membrane electrode assemblies, cell design, and operating conditions.

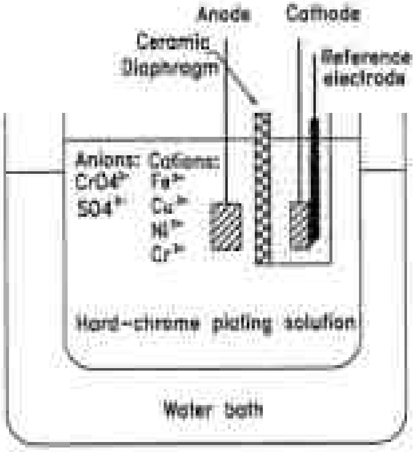

Fig. 1—Schematic diagram of porous ceramic pot (PCM).[4]

Safe handling of hexavalent-type hard chromium solutions, while avoiding the release of carcinogenic hexavalent chromium, is a big challenge in the hard chromium electroplating industry. As an alternative, trivalent chromium solutions are available, but the technology is not mature. That being said, purification of contaminated hard chromium plating solutions presents an altogether different problem. Chromium plating solutions are subject to contamination by the bivalent cations of copper, iron and nickel, as well as by trivalent chromium ion resulting from incomplete reduction of hexavalent chromium during chromium plating. The sources of these contaminants are:

1. Corroding metal accessories;
2. Drag-in from other plating baths, particularly from nickel plating baths.[1-5]

Production of deposits of unacceptable quality (*e.g.*, roughness) is the primary reason for purification. When needed, purification needs to be accomplished in the shortest possible time during shutdown for maintenance. It is much easier to dispose of the plating solution by precipitation in an environmentally acceptable manner than expending efforts and resources for solution purification. This could be quite an expensive approach, however, particularly when the intervals between plating solution disposal become shorter and shorter in situations where increased production leads to a more rapid build-up of impurities. Increasingly stringent environmental regulations are a strong incentive to search for novel processes that regenerate hard chrome plating baths *in situ*, by continuously removing metallic contaminants.

An alternative option is to purify the plating solution in place, such as is done commercially with ion exchange and electrodialysis, concurrent with the plating process or during the shutdown. Such a purification process entails the use of a suitably designed electrolytic cell, in tandem with an actual chromium plating tank.[5,6]

Ion exchange is a well-established technology with great potential for metals pollution control. Its application, however, is limited. Basically, for pollution control, ion exchange serves one of two functions. One is tertiary, or polishing treatment of an effluent before discharge. The ion exchange resins cannot be heavily loaded if ion leakage into the effluent is to be prevented, and the consequent resin regenerant will not be sufficiently concentrated in

Nuts & Bolts: What This Paper Means to You

An easy way of purifying hard chromium baths has been sought for years. The folks at IIT have studied two potential methods, one based on a porous ceramic membrane and the other a spin-off from fuel cells. The authors are refreshingly candid in noting that neither process is perfect. The porous ceramic creates sludge. The fuel cell system has a lower metal removal rate. However, they do offer hope for the fuel cell system and plans are afoot to refine the fuel cell design.

Fig. 2—Schematic view of fuel cell membrane process (FCMP).[7]

metal to warrant recovery. Recovery is further hampered by the relatively non-selective nature of most commercially available resins, resulting in the accumulation in the regenerant of secondary and undesired contaminating ions. For many wastewaters, irreversible resin fouling and associated loss of exchange capacity are also problems. The second type of application of ion exchange is for direct recovery. Examples include recovery of chromate in plating rinsewater. This latter application involves a complicated three-column ion exchange sequence. In addition, if the chromic acid produced in the regeneration step is too concentrated, resin matrix oxidative damage occurs. Therefore, the concentration of chromic acid recovered through regeneration is governed by the chemical instability of the resin used.

Membrane separation has been widely touted for pollution control and resource recovery. Excluding ultrafiltration, which is more precisely a physical separation process, the principal commercially available membrane processes are electrodialysis and reverse osmosis. The perceived advantages and established disadvantages of both processes have been widely reported. Disadvantages primarily involve:

1. High capital and/or operating costs;
2. The non-selective nature of the separation process;
3. Membrane fouling and biological, chemical, or physical deterioration of the membrane; and
4. Inability to economically achieve sufficient brine concentration to justify application for recovery.[2,4]

There have been ongoing investigations on the use of porous ceramic membrane (PCM) cells. Earlier research in this laboratory has shown that impurities such as Ni, Fe, and Cu ions present in hard chromium plating solutions can be removed and concentrated as a metal hydroxide sludge using a porous ceramic membrane (PCM) cell.[2,4] A small PCM electrolysis cell was operated in the chromium plating bath, either in parallel with the main operation or during downtime. One of the drawbacks to this process was the need for frequent cleaning of the cell and disposal of the sludge. Although contaminant removal is continuous during operation, the operation of the porous pot is, for all practical purposes, a batch process because of the need for frequent cleaning of the cell. Moreover, the process is difficult to optimize, because the voltage rise accompanying the sludge build-up is not consistent and, therefore, is unsuitable for accurate process control.

In recent years, this laboratory has been developing a new process known as the fuel cell membrane process (FCMP),[7] which utilizes the oxygen reduction reaction from fuel cell technology. The process principles, along with the process advantages, capabilities and drawbacks, are discussed in this article, and are compared to corresponding laboratory data obtained for the PCM process.

Process Description

Common Principles

Both PCM and FCMP are electrolytic processes. In both processes, the passage of electrolytic current causes oxidation of trivalent chromium ions to the hexavalent state at the anode. In PCM, however, the divalent cations are deposited as metals at the cathode, and are also precipitated as hydroxides within the solution and in the pores of the PCM. In FCMP, the oxygen electrode is used as a cathode. Because the standard electrode potential for the oxygen reduction is 1.2 V_H, it can be hypothesized that the energy consumption in an FCMP process can be lower than that for PCM. The effectiveness of contaminant removal in these processes is controlled by a combination of convection, diffusion and migration, as described by Navier-Stokes equation below:

$$\mathbf{N}_i = -z_i u_i F c_i — f - D_i — c_i + c_i n \qquad (1)$$

Where $\mathbf{N}_i$ is the flux, z_i is the charge on the ion, u_i is the mobility, c_i is concentration of species, F is Faraday's constant, —f is the potential gradient, D_i is the diffusivity, and n is the bulk fluid velocity.

This equation is based on the assumptions that: (1) the concentrations of electroactive species are small and (2) solute-solute interactions can be neglected. Only the interactions between the solute and solvent are considered. The three terms on the right side of the equation represent fluxes resulting from migration (the first term), diffusion (the second term), and convection (the third term). The equation is valid for infinitely dilute solutions, yet it is rather common to extend this equation to concentrated solutions.[8]

PCM Cell

The PCM cell is either a closed-end cylinder or a rectangular trough of a suitable porous ceramic material, having a lead cathode inside the pot and a perforated oxide-coated lead anode surrounding the porous pot on the outside. A schematic view of the laboratory cell is shown in Fig. 1. This assembly is suspended inside the chromium plating bath. During operation, contaminant metal ions are preferentially drawn into the cell, where they accumulate as a hydroxide sludge. Concurrently, trivalent chromium is reoxidized to the hexavalent state at the outer lead cathode. A drawback of the PCM pot is that frequent cleaning and sludge disposal are required. Part of the cathodic reaction involves hydrogen evolution. As hydrogen evolves, the pH increases and metal hydroxides start to form. Depending on the current density and pH, a

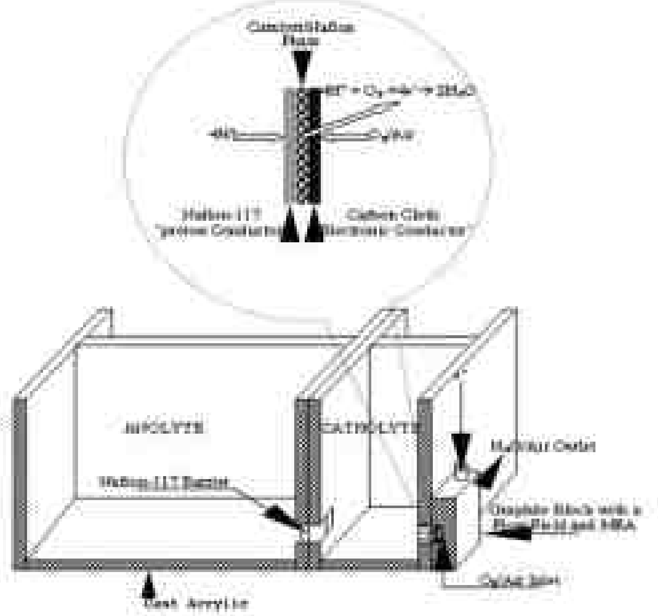

Fig. 3—Longitudinal cross sectional view of FCMP cell and membrane electrode assembly (MEA).[7]

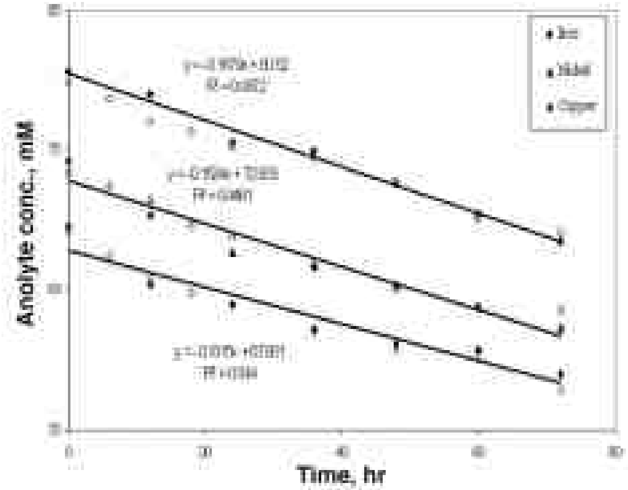

Fig. 4—Changes in anolyte concentration with time.[7]

hydroxide slime may also form inside the pores of the PCM and clog the diaphragm.

FCMP Cell

A laboratory scale FCMP electrolytic cell utilizing a high-surface-area oxygen fuel cell cathode is shown in Fig. 2. A longitudinal view of the same cell is shown in Fig. 3. The cell is an open parallelepiped-shaped acrylic tank, divided into two compartments using a Nafion®-117 membrane. The fuel cell cathode also uses a Nafion® membrane and consists of a non-noble metal catalytic layer contacted to the Nafion® surface.

Experimental Procedure

Initially, cathode fabrication was based on the methods of Wilson, *et al*.[9,10] A platinum black catalyst was incorporated into an ink consisting of solubilized Nafion® in alcohol. The ink was painted onto a Teflon® blank, which was then baked in an oven at 120°C (248°F). The catalyst was decal-transferred by hot-pressing onto the Nafion®. The catalytic surface of this membrane electrode assembly (MEA) was exposed to the atmosphere (oxygen electrode), while the other side of the Nafion®, having no catalyst surface, was exposed to the chromium plating solution in the cathodic compartment. A carbon paper sheet was used as the current collector. A graphite block with flow fields milled into the surface served both as a current collector and a distributor of air over the surface of the electrode. As air flowed through the platinum cathode, electrons derived from the external circuit, along with the protons migrating through the Nafion®, combined with oxygen in the air to form water. The exhaust was humidified air, somewhat enriched in nitrogen. Either oxidation of water or oxidation of Cr(III) at the lead anode in the plating solution produced electrons from the external circuit. Electroneutrality was maintained by migration of protons and the trace metal impurities through the Nafion® into the auxiliary chamber. The cathode interface was characterized by the double-layer capacity of the solution in the catalyst (Pt-C) pores. The electric current was then carried from the cathode to the anode by the migration of anions.

Using this cell configuration, the electrolysis experiments were conducted[7] in simulated hard chromium plating solutions [Cr(VI): 250 g/L] containing iron, copper, and nickel (at 80 mM, 72 mM and 72 mM, respectively). The electrolysis experiments were conducted at room temperature and at applied currents of 0.2 A, 0.4 A and 0.6 A.

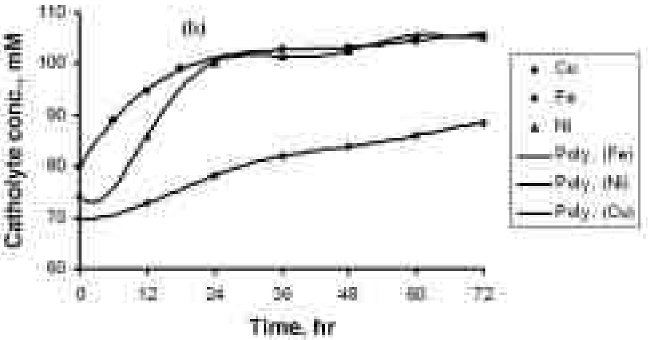

Fig. 5—Changes in catholyte concentration with time.[7]

Results & Discussion

Tables 1 and 2 provide a summary of the removal rates obtained in stirred solutions, and cell potentials for the FCMP and PCM systems. The observed removal rates at 0.2 A using a FCMP cell[7] are presented in Figs. 4 and 5, which show the changes in the catholyte metal concentrations with time. The removal rates of iron, nickel, and copper were estimated from the analysis of anolyte, cathode deposit, and membrane layers. The deposits on the cathode and membrane were dissolved in hot nitric acid and analyzed using atomic adsorption analysis. As shown, removal rates in the FCMP system increased with increasing current.[7] The removal rates were the same for iron, copper, and nickel at the lowest two currents. However, at 0.6A, the removal rates were highest for nickel and lowest for iron. This was likely the result of precipitation of iron hydroxide in the catholyte chamber.

The results in Table 1 and Fig. 4 show that the FCMP removal rates were extremely low, corresponding to low current efficiencies for the removal process. This suggested that the cell potentials had within themselves additional components of overvoltage from the anodic and cathodic reactions (the total cell voltage, V, comprised of cathodic polarization, anodic polarization, potential across the membrane, and the product of current and cell resistance).

Because the cathode configuration is a porous electrocatalytic electrode, consisting of Pt-C catalyst in contact with a low pH chromic acid solution, a complex environment exists for the cathodic reactions. The poor cell performance, low removal rates, and increase in cell potentials during each experiment suggest the occurrence of a mixed potential in the cathode and a significant loss in the expected extent of oxygen reduction.

Theoretically, FCMP system cell thermodynamics should favor oxygen reduction at the cathode, rather than hydrogen evolution or metal deposition. However, as experimental data indicate, the kinetic limitations and appreciable decrease in the cathode potential occur in the cell, possibly because of metal deposition on the catalyst, deactivation and/or dissolution/deposition of the platinum particles of the electrode.

By comparison, as shown in Table 2 and Fig. 6, higher removal rates for nickel and iron and lower removal rates for copper are reported for the laboratory PCM experiments,[4] despite the disadvantages observed for PCM systems described earlier. It should be noted that the electrolyte volume is less in a PCM experiment than in the FCMP experiment. The catholyte-to-anolyte volume ratio, therefore, was higher for the PCM than for the FCMP cell configuration. These differences might account for the observed differences in the metal removal rates. Future experiments should be conducted under identical conditions for a reasonable comparison of the metal removal rates. On the other hand, even the initial cell potentials are higher in the PCM cell than for the FCMP cell, thereby signaling energy savings with the FCMP cell operation.

Table 1
Removal Rates* & Final Cell Potentials, FCMP System[7]

Current	Removal Rates, mM/hr			Cell potential during 72-hr test, V
	Ni	Fe	Cu	
0.2A	0.168	0.158	0.132	2.0 - 3.5
0.4A	0.264	0.235	0.248	2.6 - 5.0
0.6A	0.306	0.259	0.288	3.0 - 7.9
$1.5xC_o$ at 0.4A	0.336	0.296	0.283	2.5 - 4.5

**In stirred solutions: temperature: 23°C (73°F), catholyte volume: 300 mL, anolyte volume: 900 mL.*

Table 2
Removal Rates* & Final Cell Potentials, PCM System[4]

Current	Removal Rates (mM/hr)			Initial Cell Potential
	Ni	Fe	Cu	
0.25A	0.28	0.50	0.110	3.6
0.25A	0.34	0.52	0.110	3.6
0.34A	0.26	0.29	0.055	4.3
0.66A	0.58	0.93	0.160	5.1

**In stirred solutions; temperature: 23°C (73°F); total electrolyte volume: 250 mL; catholyte:anolyte ratio: 1:1.*

Summary

Laboratory research with the porous ceramic membrane (PCM) cell showed that there were serious limitations with that process. In the absence of any published results on industrial experiences with this cell, successful industrial use requires improvement of the initial cell design. As with the fuel cell membrane process (FCMP), the promising results indicate that the process is feasible, but considerable improvements are necessary. These improvements include the following:

1. Development of membrane electrode assemblies with improved performance characteristics, including reduced overvoltage, high tolerance to chromium plating solutions, and increased electrocatalytic activity.
2. Development of membranes that are tolerant to chromium plating solutions.
3. Improvements in cell design to guarantee constant supply of oxygen on the cathode side.

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References

1. N.V. Mandich, *Proc. AESF Chromium Colloquium*, AESF, Orlando, FL, 1994; p. 51.
2. C.C. Li, Masters Thesis, Illinois Institute of Technology, Chicago, IL (1995).
3. G. Cushnie & W. Anderson, *Proc. AESF Hard Chromium Plating Workshop*, AESF, Orlando, FL, 1989; p. 21.
4. S.L. Guddati, T.M. Holsen, C.C. Li, J.R. Selman & N.V. Mandich, *J. Appl. Electrochem.* **29**, 1129-1132 (1998).
5. N.V. Mandich, C.C. Li & J.R. Selman, *Plating & Surface Finishing*, **84**, 82 (December 1997).
6. K.N.G. Patrick, D.S. Dexter, *J. Mem. Sci.*, **13**, 327 (1983).
7. M.E.I. Ahmed, PhD Thesis, Illinois Institute of Technology, Chicago, IL (2000).
8. J. Newman, *Electrochemical Systems*, 2nd Edition, Prentice Hall, N.J. (1991).
9. M.S. Wilson, J.A. Valerio & S. Gottesfeld, *Electrochim. Acta*, **40**, 355 (1995).
10. M.S. Wilson, & S. Gottesfeld, *J. Appl. Electrochem*, **22**, 1 (1992).

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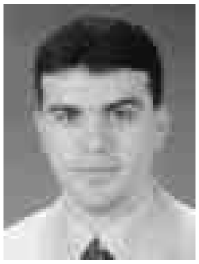

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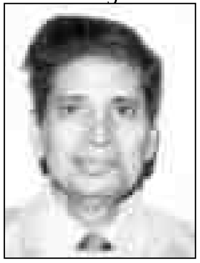
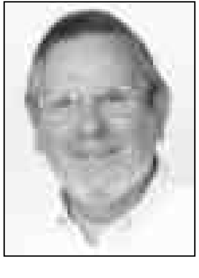


Dr. V. S. Donepudi received his PhD (1966) degree in electrodeposition of metals and alloys from the Indian Institute of Science, Bangalore, India. He held various research and academic positions in government, industry and universities within Canada, and retired as project manager in 1995 from the Electrochemical Science and Technology Center, University of Ottawa, Ontario, Canada. In 1997, Dr. Donepudi immigrated to the U.S. and is now working at the Illinois Institute of Technology as a research associate professor. His research interests are in batteries, electrodeposition and corrosion. Dr. Donepudi has published 70 papers in the above and related topics.



Dr. Robert Selman, after completing chemical engineering studies at T.U. Delft, Netherlands, Madison, WI, and Berkeley, CA, has been active in electrodeposition, corrosion, and battery/fuel cell research at Illinois Institute of Technology. He is a professor of chemical engineering and director of the Center for Electrochemical Science and Engineering.