

DEVELOPMENT OF A PROCESS FOR CHROMIUM DISPOSAL PREVENTION FROM THE HARD CHROMIUM PLATING INDUSTRY

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ABSTRACT

An electro dialysis process utilizing fuel cell cathode / ion exchange membrane, which removes contaminants continuously from hard chrome plating baths while effecting energy savings, has been designed conceptually and verified experimentally on laboratory scale. The process is designed to extend the lives of hard chromium plating baths and therefore resulting in chromium source reduction and prevention of its disposal into the environment. This paper reports initial cell design methodology and testing for contaminant removal. Laboratory studies conducted at room temperature (25°C) and at constant current indicate the feasibility of the process and its potential benefits when integrated into industrial-scale plating operations. The principal benefits of the FCMP process are continuous regeneration of the plating bath, energy savings in the separation of contaminant metals, and ease of application in-process (in-situ). Further experimental studies to optimize the fuel cell cathode structure and field-work to achieve integration with industrial-scale operations are needed.

Keywords: Pollution Prevention, Environmental Engineering Technology Development, Electrodialysis, Ion-Exchange, Fuel Cell Electrodes, Nafion-117

INTRODUCTION

Spent plating solutions are generated when the chromic acid baths become contaminated by the buildup of trivalent chromium and an increase in the concentration of heavy metals. In the hard-chrome plating industry, acid chromate ($\text{Cr}_2\text{O}_7^{2-}$) plating-baths become contaminated by Cu^{2+} , Fe^{2+} , and Ni^{2+} ions as well as Cr^{3+} ions. The former ions accumulate in the bath as a result of corrosion of metal accessories and drag-in from adjacent nickel baths. Cr^{3+} ions are generated by partial $\text{Cr}_2\text{O}_7^{2-}$ reduction at the cathode. A portion of the bath must then be discarded even though it contains large amounts of chromic acid. These contaminants, though present at low levels, accumulate during successive plating operations using the same bath, and degrade the quality of hard-chrome deposit by causing roughness [1]. It is, therefore, desirable to remove them continuously from the plating bath to avoid the expense and legal liability associated with frequent bath disposal and treatment of

effluents. 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 such as the aforementioned metals.

Previous work using a porous ceramic membrane (PCM) cell [2], has confirmed that impurities such as Ni, Fe and Cu ions present in hard-chromium plating solution can be removed and concentrated as a metal hydroxide sludge. This is the basis of the "porous pot process" known since 1840 and classified as an "electrolytic" contaminant removal process [3]. In this process a small PCM electrolysis cell is operated in the chrome plating bath, in parallel with the main operation, or during the latter's downtime. The "porous pot", i.e., a closed-end cylinder or rectangular trough of a suitable porous ceramic material, is suspended in the plating bath to form a diaphragm cell. The diaphragm cell consists of a lead cathode hung inside the ceramic pot, and a perforated oxide-coated lead anode surrounding the porous pot on the outside. During the operation of this PCM cell, contaminant metal ions are preferentially drawn into the cell, where they accumulate as a hydroxide sludge, while trivalent chromium in the bath is re-oxidized to hexavalent chromium at the outer lead anode.

Although the "porous pot" process is used in some, mostly smaller, hard-chrome plating operations, it has not found general acceptance for several reasons. One of the drawbacks of this PCM process, in its present form, is the need for frequent cleaning of the PCM and disposal of the sludge. Although contaminant removal is continuous during operation, the operation of the porous pot is inherently a batch process. Moreover, the process is difficult to optimize, because the voltage rise due to sludge build-up is poorly reproducible and therefore unsuitable for accurate process control. As found in laboratory investigation of the PCM process [2,4,5], a rather complicated series of reactions takes place inside the diaphragm cell. Initially, the metal ions transported into the ceramic pot deposit on the cathode. However, the main reaction at the cathode is proton reduction under hydrogen evolution. Due to consequent pH rise, metal hydroxides start forming which initially cover part of the cathode as a (non-conducting) slime, but ultimately form a suspension at the bottom of the pot. Depending on current density and pH, hydroxide slime may also form inside the pores of the PCM and clog the diaphragm. Therefore, a gradual or accelerating voltage rise occurs toward the end of an operational cycle, and this can be used to some extent for process control. Nevertheless, the "porous pot" process requires close personal control and laborious cleaning. Most of all, however, it is energy-inefficient because the cathode process serves essentially to produce hydroxyl ions in quantities that far exceed the sludge-forming requirement. Energy requirements, therefore, expressed as kWh/g of contaminant removed, are fairly high, and it is desirable to explore improvements of the PCM process, or alternative processes. In this work, we address one such alternative, using an ion-exchange membrane but combining it with an energy-efficient fuel cell cathode to remove contaminants.

A process recently described by GM, which uses a Nafion separator and lead electrodes, showed good efficiency for trivalent chrome re-oxidation [6]. In 1980 the U.S. Bureau of Mines [7] demonstrated a flow-through system for regeneration of

chromic acid using a cell composed of a copper cathode, a lead anode, and a Nafion separator. These processes, however, are basically consisting of water electrolysis. This implies that most of the current at the anode is used not for trivalent chromium oxidation but for oxygen evolution, and most of the current at the cathode serves to develop hydrogen at the cathode. Therefore, these processes require a relatively high cell voltage.

PROCESS DESIGN

To avoid high voltage in the regeneration cell, we used, in the investigation reported here, fuel cell cathodes of the PEMFC (proton exchange membrane fuel cell) type, in combination with a Nafion separator between the anolyte (plating bath electrolyte) and catholyte (contaminant-enriched electrolyte) compartments. At a fuel cell cathode, oxygen (from air) is reduced by combination with protons (from the electrolyte, in this case chromic acid), to form water. Since this electrode process takes place at a much higher electrode potential than hydrogen evolution (at thermodynamic equilibrium under standard conditions, 1.23 V higher), there is a good probability that the overall cell voltage for the contaminant removal cell will be much lower than that required for a cell based on water electrolysis.

1. Experimental Cell

The laboratory-scale cell container (schematic in Fig.1) was a lucite trough designed to contain 1.2 L electrolyte, which had a Nafion-117 separator across the cell cross-section, with a projected area of 40 cm². The anode was a lead plate of 100 cm² projected area, and the cathode assembly, of 5 cm² projected area, was embedded centrally in the lucite wall facing the Nafion separator. The cathode assembly (schematic in Fig.2) consisted of a modified membrane-electrode-assembly (MMEA), which on one side (the membrane side) was in direct contact with the catholyte, and on the other side (the reaction layer side) with a gas-diffusion backing layer of carbon cloth (non-catalytic). The latter was in direct contact with a flow distributor plate of graphite, which served to feed air supplied by a blower uniformly to the pores in the gas diffusion backing plate. The graphite plate was thick enough to serve also as a pressure-bearing end plate in the compression of the cathode assembly against the lucite cell wall.

The MMEA of this cell was similar in structure to the state-of-the-art MEA of PEMFC cells, but without the anode reaction layer and anode gas diffusion backing plate. It consisted of a cathode reaction layer made up of electrocatalyst particles (finely divided platinum metal) supported on carbon particles, intimately mixed with Nafion in a very thin "reaction layer". On one side this reaction layer is adjacent to, and partially embedded in, a very thin Nafion layer, and this Nafion layer is exposed to the catholyte. On the other side, the reaction layer is adjacent to the cathode gas diffusion layer as discussed above.

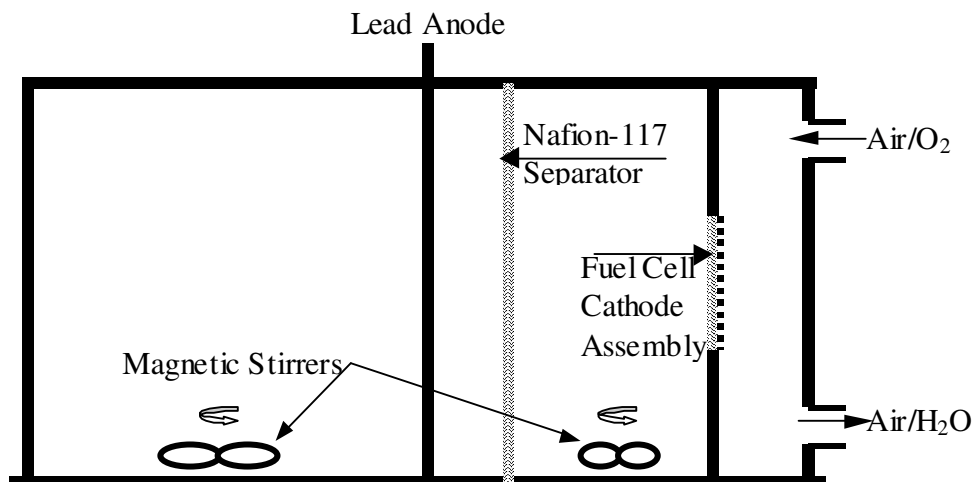


Figure 1. Schematic of Experimental Cell. Anode Projected Area 100 cm², Cathode Projected Area 5 cm², with 5mg/cm² Pt-black Loading, Separator 7.5x12.5 cm (40 cm² used), and the Utilized Volume of Cell 1.2-L. Hg/HgSO₄ Reference Electrode

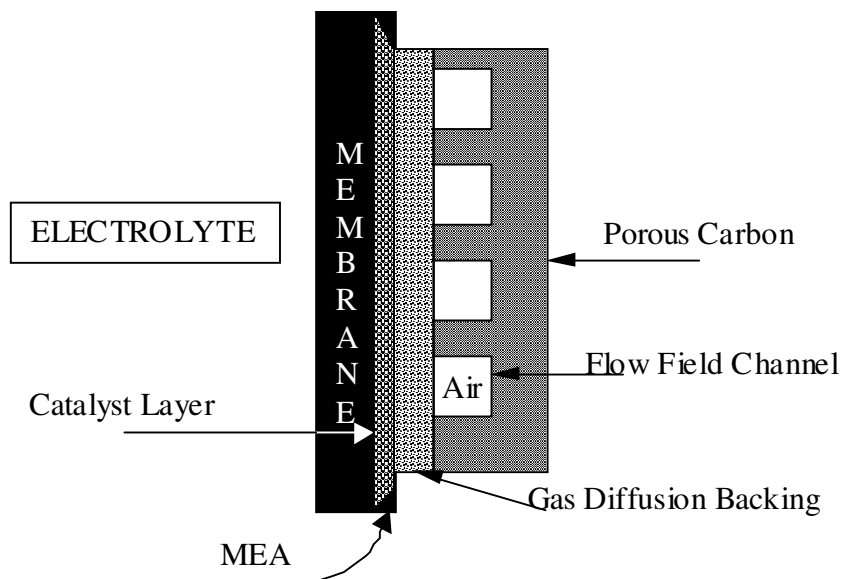


Figure 2. Details of the Fuel Cell Cathode Assembly, Including Membrane Electrode Assembly (MEA), Gas Diffusion Backing Layer, and Flow Distribution Plate

A new MMEA was used in each experiment. These assemblies were manufactured based on the method developed by Wilson et al. [8,9].

In these initial experiments to prove the concept of FCMP process we used the

materials and construction known from PEMFC technology. These are not necessarily the optimal materials. Cost effectiveness is, of course, an important goal in developing a new process for continuous decontamination of hard-chrome plating baths at reduced cost. The highly corrosive environment may require very stable and hence expensive materials. As an example, in preliminary experiments overheating of the cathode assembly led to its disintegration, and damage to the cathode membrane. Therefore, we tried different materials and configurations of the cathode assembly to improve electronic conduction and water removal, without, however, adopting new materials. These changes were successful in preventing overheating. As shown below, the PEMFC state-of-the-art materials show reasonably good stability, so that the FCMP concept could be demonstrated satisfactorily.

In all experiments the anolyte and catholyte were stirred independently by Teflon-clad magnetic stirrer bars. This stirring was vigorous (at 350 RPM of the stirrer bars, of 3.75 and 2.0 cm length for the anolyte and catholyte, respectively) to eliminate as much as possible any mass transfer limitations to and from the anolyte/catholyte separator, as well as at the cathode.

2. Procedure

All experiments were carried out in typical simulated spent chrome plating solution, containing 2.5M (250 g/L) chromic acid and 2.5g/L sulfate concentration. Nickel, iron, copper and trivalent chrome impurities were added to the solution to establish a concentration of each averaging approximately 0.1M (5-6 g/L) [3,10], unless stated differently. The impurities were added to the 250 g/L chromic acid solution in the form of their sulfates, i.e., $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, CuSO_4 , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{Cr}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$. Barium carbonate (BaCO_3) was used to eliminate excess sulfate anion by precipitation of water-insoluble BaSO_4 , which was then filtrated from the plating solution.

The performance of the process with respect to separation was assessed by operating the cell under three constant current conditions (0.2, 0.4, 0.6 A), while maintaining the same stirring rate in anolyte as well as catholyte. These constant current conditions were also used to assess the effect of using different initial concentrations and catholyte-to-anolyte-volume ratios. Samples were taken to determine composition of the anolyte and catholyte. Chromic acid concentration was determined by iodometric titration. Cu, Ni, and Fe concentrations were determined by Flame Atomic Adsorption Spectrometry (AAS).

RESULTS AND DISCUSSION

1 Process Components Stability and Performance

Nafion-117 Stability

Nafion-117[®] ion-exchange membrane stability and behavior during use in the experimental cell is investigated and assessed using various experimental techniques. Nafion was found to withstand the highly acidic environment of such solutions (pH \approx 1) with only minor rotations in the fluorocarbon backbone due to accommodation of anionic chromic acid species within its clusters. This conclusion is evident from the small angle x-ray diffraction (SAX) pattern of Nafion-117 before and after use in the experimental cell (Fig. 3). The ion-exchange selective behavior was found to suffer minor reduction and the transport resistance to metallic cations was found to be solely due to reduction in the volume of ion clusters of fixed charge sites which result from reduced water uptake (10%) and reduced ion solvation energies inside the membrane pores [11]. The reduced pore size of Nafion-117 (3.2 nm, originally > 5 nm) is the major cause of increased transport resistance [12]

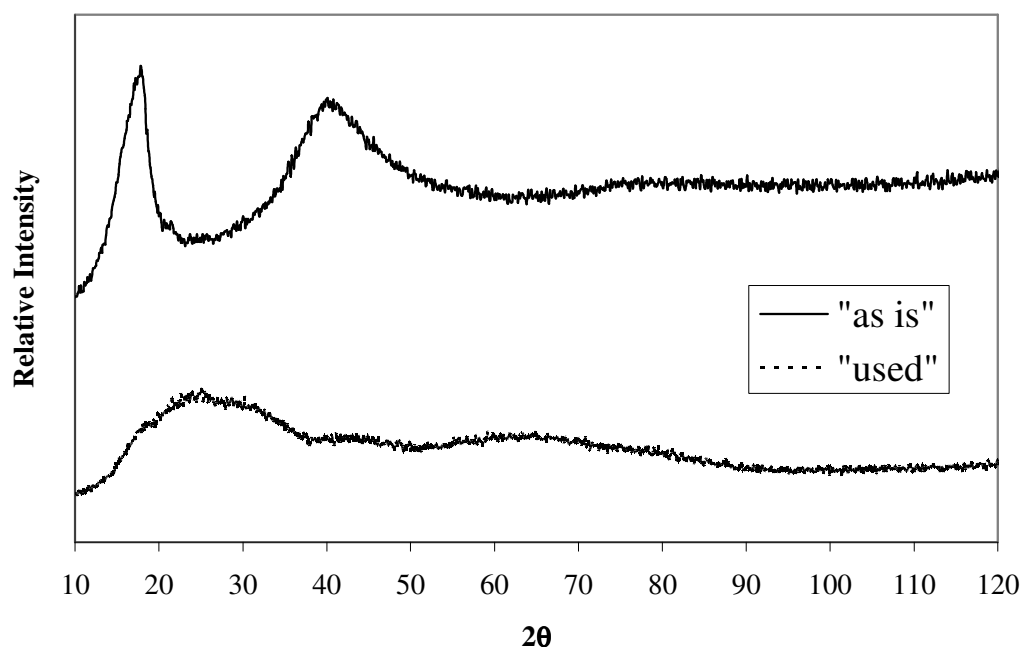


Figure 3. Nafion-117 X-ray Diffraction Before and After Use

Fuel Cell Electrode Performance

Electrochemical Impedance Spectroscopy (EIS) and stationary polarization curves were used to characterize the performance of a fuel cell cathode in the regeneration cell. The configuration of the MEA, current collector, and flow distributing backing plate may, during long-term operation, lead to excessive ohmic resistance (Fig. 4), which necessitates a special design of the cathode assembly. This was achieved by using a platinum gauze current collector inside the default carbon paper backing material and the resulting EIS is shown in Fig. 5. resulting and a negligible electronic resistance. X-ray diffraction indicated that Cu, Fe, Ni, and Cr were deposited on the

electrode matrix, leading to deactivation of the Pt-catalyst (Fig. 6). The deactivation causes a rising cell voltage during electrolysis. Nevertheless, the energy consumption of the regeneration cell is at least one volt less than that of a comparable cell with hydrogen evolving cathode (Fig. 7).

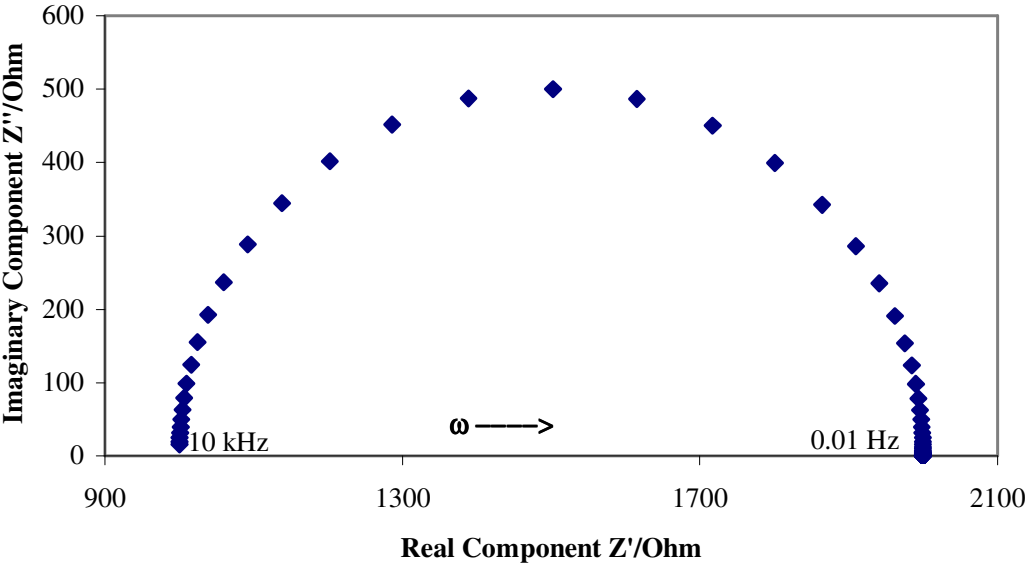


Figure 4. A.C Impedance Diagram (Cole-Cole plot) of the Fuel Cell Cathode (Old Configuration) in Contaminated Chromic Acid.

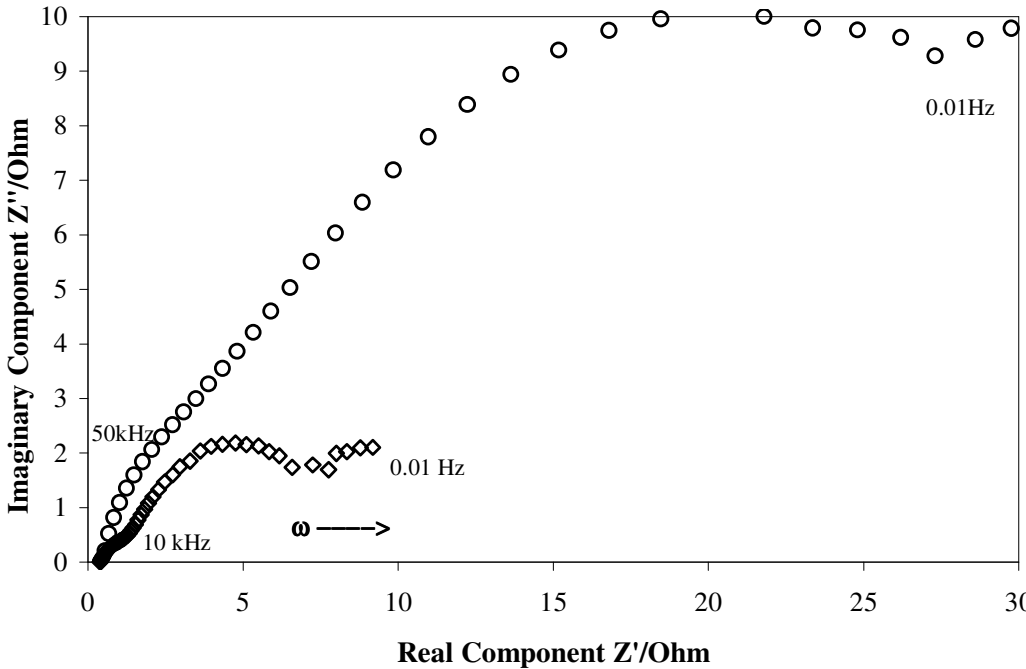


Figure 5. A.C Impedance Diagram (Cole-Cole plot) of the Fuel Cell Cathode with the New Configuration in Contaminated Chromic Acid

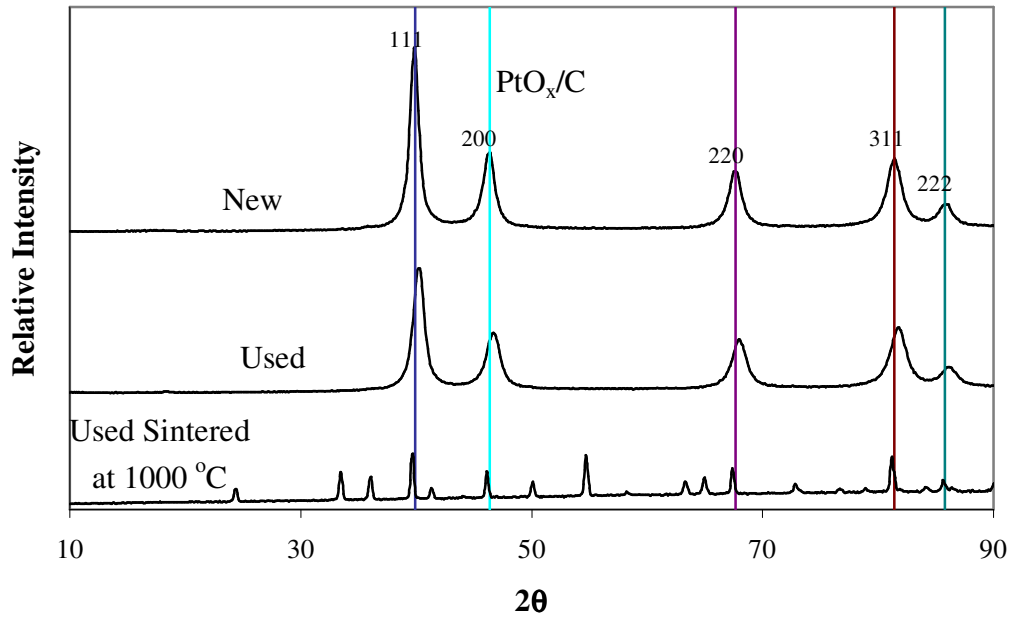


Figure 6. X-ray Diffraction of Oxygen Fuel Cell Electrode (4.1 mg cm^{-2} Pt-black on Carbon) Before and After Use in a Removal Experiment. (—) O.C.V, (—■—) operating at 0.2 A

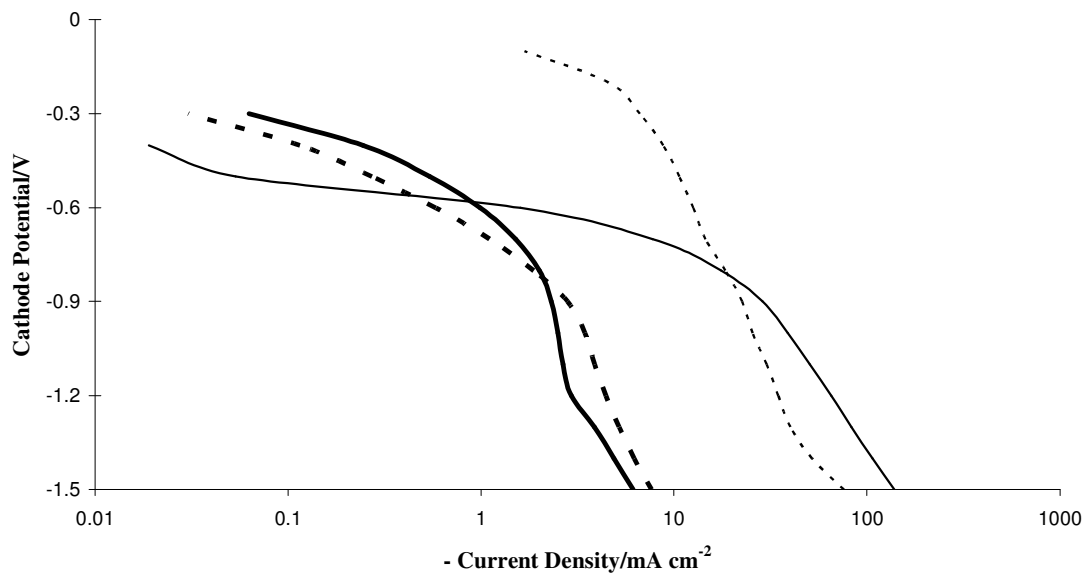


Figure 7. Cathode Polarization Curves in Contaminated Chromic Acid and Sulfuric Acid, while Air or Argon is Supplied. The Catalyst Loading is 4.9 mg cm^{-2} Pt-black on carbon. (—) chromic-Ar, (—) chromic-O, (- -) sulfuric-Ar, (- · -) sulfuric-O

2- Chromic Acid Regeneration and Metal Impurity Removal

The following operating parameters were systematically varied:

- (1) applied current (0.2, 0.4, 0.6 A);
- (2) initial contaminant concentrations (high, low);
- (3) catholyte-to-anolyte-volume ratio (1/3, 1/6).

In addition, the cathode gas environment was changed from air to argon, to assess the effect of the change in cathode reaction on contaminant removal efficiency.

The variation of Cr(VI) and Cr(III) concentrations in the anolyte as a function of time are shown in Fig.8a for various levels of operating current (0.2, 0.4, 0.6 A), initial contaminant concentration (low, high), and cathode gas composition (air, argon). The corresponding catholyte concentrations are shown in Figure 8b. Rather conspicuous are the oscillations of hexavalent chromium concentration in both anolyte and in catholyte (of 5-10% amplitude). These may be explained by variations of the liquid level, caused by intermittent H₂O additions to keep the total electrolyte volume constant. These additions lead to bulk flow, as charge is always balanced during the movement of Cr(VI) and Cr(III) species, by the movement of H⁺ as well as SO₄²⁻ and HSO₄⁻ ions. However, compared to these oscillations, the fluctuations of Cr(III) concentration in the catholyte are negligible, and in the anolyte, zero.

The most interesting conclusion from the data in Fig. 8a and 8b is that the change of cathode gas from air (oxygen consumption) to argon (hydrogen evolution) does not affect the contaminant removal rate drastically. This was confirmed by further systematic experiments, which showed that, in contrast, the cell voltage at identical cell currents was much lower when using air than when using argon as cathode gas.

All experiments in Fig. 8 were carried out with a catholyte-to-anolyte volume ratio of 1/3. Lowering this volume ratio (at constant total cell volume, therefore, decreasing the catholyte volume and increasing the anolyte volume) decreased the metal removal rate from the anolyte. The reasons are not completely understood, but this may indicate that mass transfer limitations in the anolyte were not completely eliminated by vigorous stirring.

For the experiment carried at 0.2 A, the decrease of metallic impurity (Fe, Ni, Cu) concentrations in the anolyte, and their increase in the catholyte, are shown separately in Figures 9.a and 9.b. Linear regression correlations of the type shown in Fig. 9.a for each species have also been established for each metallic species under various current, concentration and volume-ratio conditions. These are shown in Table 1 as impurity removal rates normalized with respect to the initial impurity concentration, i.e., in units of inverse time (h⁻¹ in Table 1).

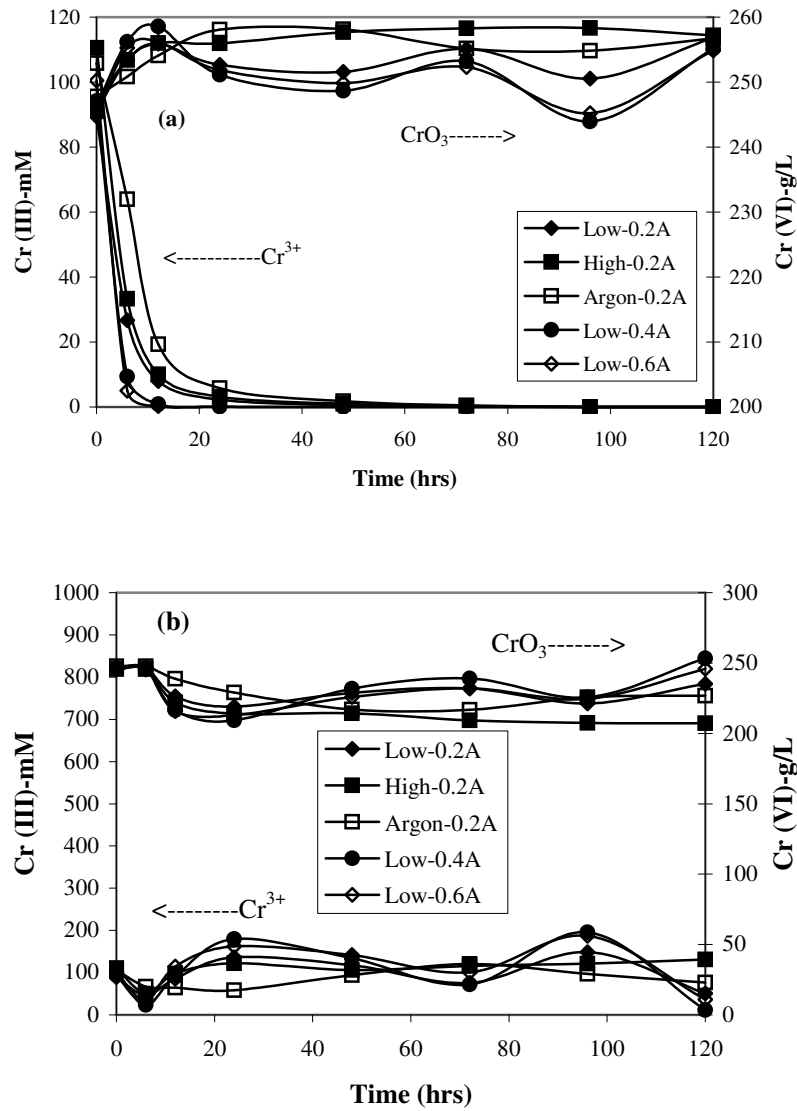


Figure 8. Trivalent (Cr^{3+}) and Hexavalent (as CrO_3) Chromium Concentrations in the Anolyte (a) and Catholyte (b)

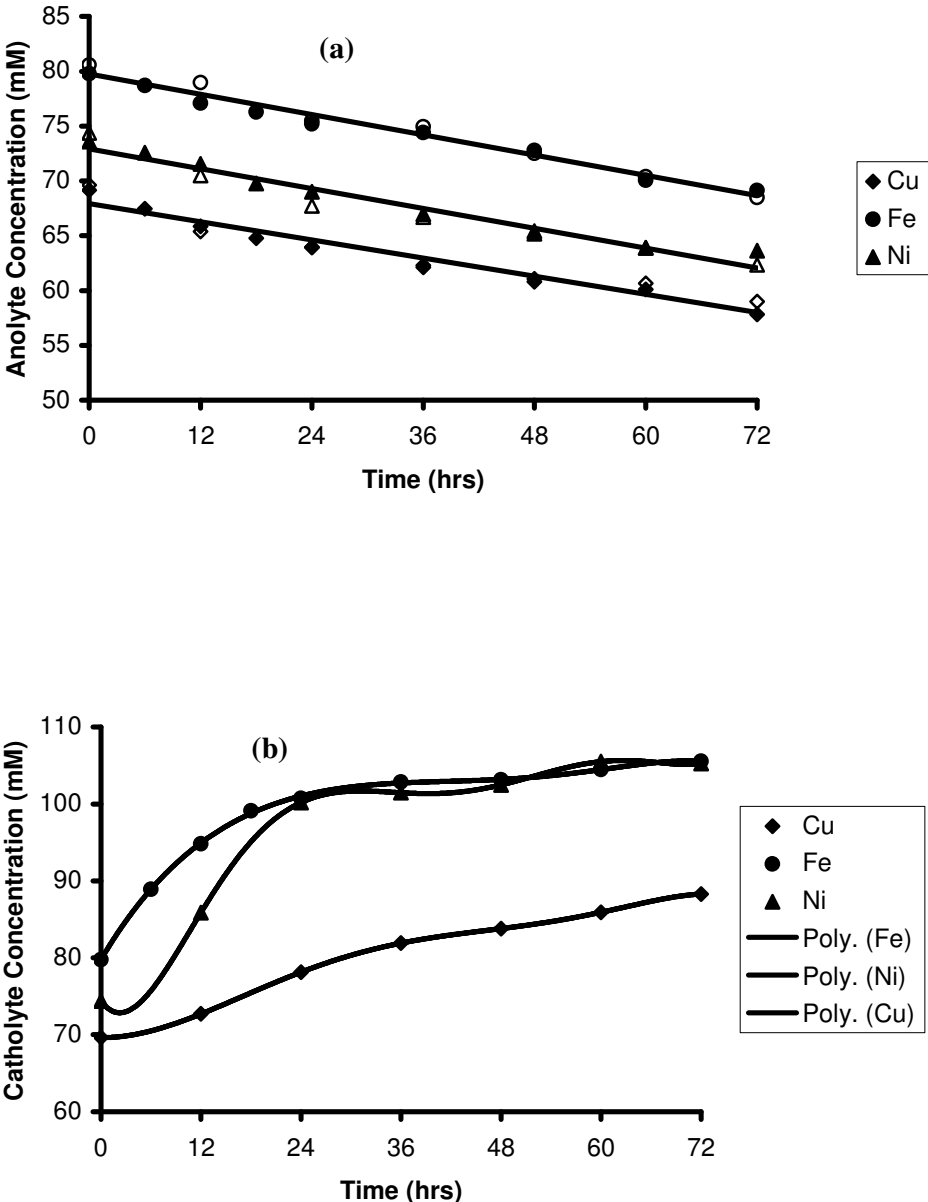


Figure 9. Impurity Concentrations in the Anolyte and Catholyte Operating at 0.2 A

Table 1. Impurity removal rates from the anolyte based on a linear fit and normalized with respect to initial anolyte concentration.

Experiment	Metal removal rate (h ⁻¹)			
	Duration-h	Cu	Fe	Ni
0.2 A	72	0.047	0.053	0.050
0.4 A	120	0.060	0.055	0.053
0.6 A	120	0.071	0.065	0.069
0.4 A-High	120	0.053	0.049	0.051
0.2 A-1/6 Vc/Va	120	0.023	0.044	0.032

It can be seen that these normalized removal rates tend to be somewhat higher for Cu than for Fe and Ni, which have similar values. However, taking into account the experimental error, the normalized removal rates seem to be of the same order for all three species. This is in agreement with a mechanism by which migration of the contaminant ions through the Nafion membrane is the rate determining mechanism for their removal from the anolyte.

It is noteworthy that the process of metallic impurity removal is slow compared to trivalent chrome reoxidation at the anode, which disappeared completely in about two days.

The amount of metal impurity plated onto the cathode during each experiment was calculated from the mass balance. These amounts are shown in Table 2, as a fraction of the total current passed, and as a fraction of the amount removed from the anolyte.

Taking into account the rather large standard error in the measurements (typically 10%), the results in Table 2 do not show any consistent trends. However, they do show that the current efficiency of electrodeposition is low (the total for the three species varying from 2 to 10%), and that the amount deposited relative to catholyte concentration does not follow the order of the standard electrode potentials at all. The latter conclusion seems contrary to what Fig. 9 suggests, at first sight. This shows that a complete data analysis is essential to avoid incorrect conclusions about the mechanism of the metal removal within the catholyte and metal deposition at the cathode.

Table 2. Amount of impurity plated onto the cathode during operation at various current densities, as a fraction of the total amount of current and as a fraction of the amount removed from the anolyte

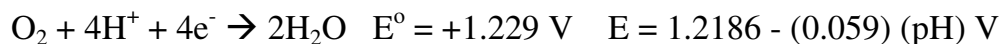
Current	Metal plated out (m-moles)			
	Duration (h)	Cu	Fe	Ni
0.2 A	72	0.0159	0.00326	0.00532
		0.43	0.17	0.14
0.4 A	120	0.0301	0.0211	0.0263
		0.95	0.72	0.91
0.6 A	120	0.0182	0.0177	0.0211
		0.78	0.80	0.82
0.4 A [High Conc.]	120	0.0329	0.0312	0.0422
		0.91	0.84	0.93
0.2 A-1/6 [Vc/Va]	120	0.00541	0.0192	0.00996
		0.40	0.62	0.44

3. Energy consumption and efficiency

The potential for energy savings by using a fuel cell cathode (consuming oxygen) over a lead cathode (evolving hydrogen) can easily be appreciated when the different values of the thermodynamic potentials of hydrogen evolution and oxygen reduction are taken into account. The hydrogen evolution reaction and its thermodynamic potential at 25°C is



The oxygen reduction reaction and its equilibrium potential in air is



where E° is the standard potential of the electrode reaction, which is valid for 1 atm H_2 , and 1 atm O_2 combined with $\text{pH}=0$, respectively.

Thus, replacing hydrogen evolution by oxygen reduction from air reduces the theoretical (thermodynamic) cell voltage by 1.2186 V at 25°C. The actual reduction in cell voltage will be less, depending on kinetics and mass transfer losses. Also, to

translate these voltage savings into cost savings, the price of pressurized air (at slight overpressure) must be taken into account.

Figure 10a shows the actual cell voltage required to sustain the operation at 0.2 A, under air, as compared to argon (which forces the cathode reaction to be hydrogen evolution). Figure 10b shows the actual cell voltage at 0.2, 0.4, or 0.6 A during the regeneration experiments. The cell voltage is obviously dependant on the applied current and initial concentration. The cell voltage during electrolysis at 0.4 A with a higher initial concentration is less than that at low concentration. However, in all cases, the cell voltage increases with time indicating increased cell resistance. The most important feature in Figure 10a is the potential energy savings by supplying air to the cathode, compared to purging with argon leading to hydrogen evolution. There was at least a 1-V difference in the cell potential. However, as Fig. 10 also indicates, both in air and under argon a slow increase of the cell voltage occurs (about 20 mV/h), whose mechanism cannot easily be explained on the basis of the present measurements.

To put the energy savings realized in this FCMP process into perspective, we may express the overall effectiveness of the process in several "figures of merit". One is the portion of the current that serves to remove contaminant from the anolyte, which as already discussed (Table 1) is relatively low. Another represents energy consumption per mole of contaminant removed. Table 3 shows both metrics for the various experiments. For the first metric, the flux of each of the contaminants through the separator is expressed as a partial current, and the total metal ion current is expressed as a fraction of the total current through the separator. The total energy consumption per mole of contaminant removed is obtained by multiplying total current by actual cell voltage (taken to be the initial value), and dividing by the total rate of contaminant removal from the anolyte (given in Table 1). Finally, the relative savings in energy suggested by Fig. 10a, for a current level of 0.2 A, are included in Table 3.

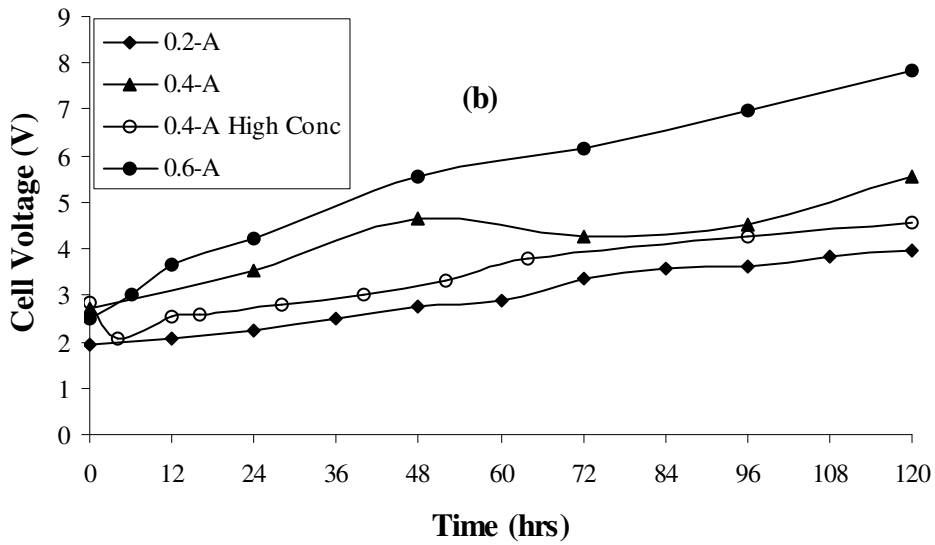
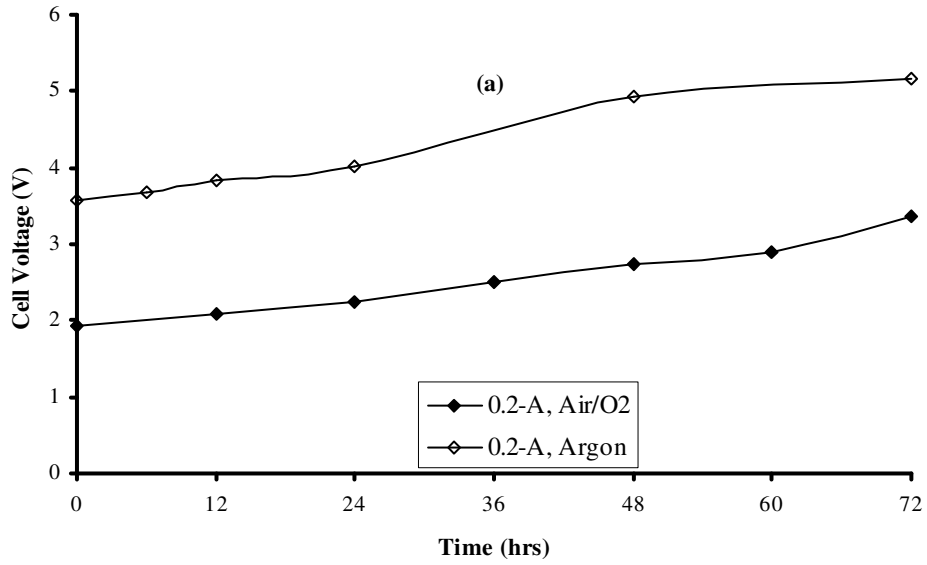


Figure 10. Cell Voltage during Operation at Various Constant Total Currents. (a) Comparison between Air/Oxygen Supplied Cathode and Argon Purged Conditions (b) during Removal Experiments at Various Currents.

Table 3. Electrical energy consumption per mole of contaminant

Experiment	Duration (hrs)	Partial currents of contaminants (mA) and metal-ion current efficiency				Energy (kJ/mol)	
		Cu	Fe	Ni	Efficiency %	Consumption	Savings
0.2 A	72	6.65	7.42	7.28	10.8	4200	3500
0.4 A	120	12.76	11.79	11.87	9.1	8000	-
0.6 A	120	13.87	13.01	15.12	7.0	14000	-
0.4 A- high c_a^0	120	13.67	14.49	16.90	11.3	5500	-
0.2 A- $V_c/V_a=1/6$	120	4.38	10.10	6.80	10.6	-	-

The contaminant removal current efficiency decreases with increasing applied current, however, increasing the initial concentration by 50% increased the efficiency by 25% in the 0.4 A case. Yet the least energy consumption was obtained at 0.2 A. Thus, operating at higher currents should be avoided, and operation at low current density (0.2 A over 40 cm² of separator, or 5 mA/cm²) and low concentration of impurity is preferred. This result, though to be confirmed by further work, which is ongoing, suggests that in the FCMP process large membrane area is preferable over high current density.

Although, as demonstrated in Fig. 10, a significant energy savings can be effected by using an oxygen-reducing rather than a hydrogen producing cathode, Table 3 shows that the process of regeneration is still relatively inefficient, in terms of energy per m-mol contaminant removed. It appears that the determining factor in this metric is the cell resistance, rather than the overpotential of the process taking place in the cathode. Thus, it is the transport resistance through the Nafion separator as well as the Nafion membrane at the cathode that plays a dominant role. This may be put in terms of co-ion rejection by Nafion. In addition, the relative mobility of minor co-ions concurrent with protons in the Nafion structure is a key factor. However, a more complete analysis and additional data are required to corroborate these preliminary conclusions about limiting rates and determinants of energy consumption

CONCLUSIONS

The feasibility of chromic acid regeneration using a FCMP process has been demonstrated on laboratory scale. The experimental data have shown that:

- a. The process of metallic impurity removal is slow compared to trivalent chrome reoxidation at the anode, and appears to be rate-controlled by migration of contaminant ions through the Nafion separator. Removal rates increase as the applied current is increased, and the higher the initial concentration the higher the removal rates, although some mass-transfer resistance in the liquid may limit the rate at high current densities.
- b. Supplying oxygen to the cathode has no significant effect on removal rates, however, a significant reduction in the cell voltage results.
- c. The contaminant removal current efficiency decreases with increasing applied current, however, the minimal energy consumption per concentration unit of contaminant removed was obtained at 0.2 A. Thus, operating at higher currents should be avoided, and operation at low current density (0.2 A over 40 cm² of separator, or 5 mA/cm²) and low concentration of impurity is preferred. This result, though it is to be confirmed ongoing work, suggests that large membrane area is preferable over high current density.

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