Chromic acid recovery by electro-electrodialysis
I. Evaluation of anion-exchange membrane

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Abstract

Electro-electrodialysis (EED) is a promising technology for economic recovery of chromic acid in plating shops. It could potentially achieve chromic acid recovery, removal of metallic impurities and purification of static rinses in one step. There are however, process limitations. These are mainly, the poor stability of the applied anion-exchange membrane (AEM) against the oxidative chromic acid solution and the increase of the AEM resistance, especially at the starting phase of the process, due to the formation of polychromates in the membrane.

In this work, various AEM are investigated for chromic acid recovery. The membrane fumasep® FAP (FuMA-Tech GmbH) seems to be the most efficient. Its current efficiency is much higher than those previously reported in the literature. Furthermore, the fumasep® FAP is used for process optimisation experiments. The process performance depends on the concentration gradient between product (anolyte) and central compartment (exhausted rinse water) and the temperature. Our results show that batch processing is recommended and the chromate transfer rates through the AEM could be significantly increased when increasing the temperature up to 50 °C. Finally, low initial current density (10–20 mA cm^{-2}), feed flow rate higher than 7 cm s^{-1} could help overcoming the process limitations attributed to high AEM resistance.
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1. Introduction

Safe handling of hexavalent-type chromium solutions is a big challenge for the chromium electroplating industry due to its toxicity and carcinogenicity [1–4]. Twenty to sixty percent of the chromic acid used in Europe is being wasted instead of re-used [5]. Since many years [6,7] there are more and more legislative restrictions forcing for changes. At chromium plating process, hexavalent chromium is reduced in a multi-stage deposition reaction to elementary chromium. In this process besides trivalent chromium other undesirable impurities are present (iron, copper, aluminium, zinc, organics, chlorides, etc.). Such impurities could accumulate during the deposition

process and create deposits of unacceptable quality. Moreover, these impurities reduce the cathode current efficiency and the bath conductivity and increase resistance. Therefore, exhausted plating solutions should be replaced.

Three-compartment electro-electrodialysis (EED) could be a promising technology for efficient chromic acid recycling. EED combines electrolysis and electrodialysis. It allows removal of chromic acid from the plating bath (together with impurities) and recovering it from static rinse solution. Fig. 1 shows the process principles. One module consists of three compartments and the outer compartments include the electrodes. The rinse water from the plating process containing chromic acid and metallic impurities such as copper, iron, zinc, aluminium, nickel and trivalent chromium, flows through the central compartment. Cationic impurities migrate towards the cathode through the cation-exchange membrane

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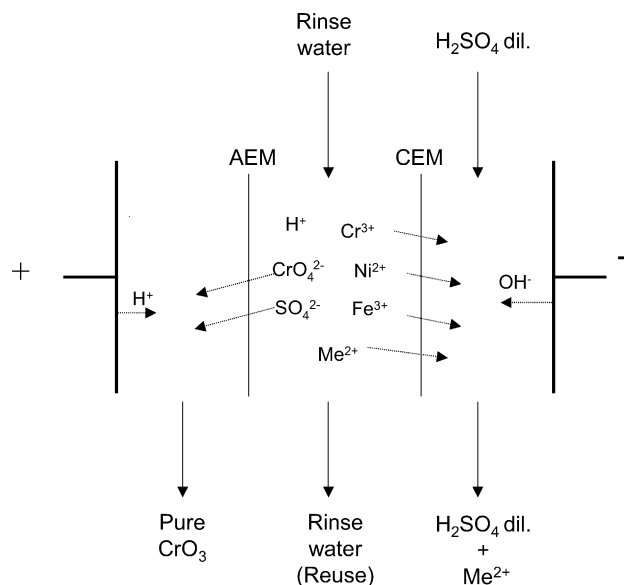E-mail address: d.stamatialis@utwente.nl (D.F. Stamatialis).

Fig. 1. Principles of electro-electrodialysis (EED) for chromic acid recovery.

(CEM). The cathode compartment is fed with diluted sulphuric acid to form dissolved metal sulphates. The acidic conditions prevent precipitation of metal hydroxides. Hexavalent chromium anions (chromates) migrate towards the anode through the AEM. There, chromic acid is formed by the chromate and dichromate anions and the protons generated at the anode. The treated rinse water is reused in the rinsing process and the pure chromic acid is returned to the plating bath. This process provides purification of chromium plating solutions and the treatment of the rinse water in a single step without need of either water or chemicals. Exhausted catholyte solutions can be treated by common physical–chemical treatment together with other effluents generated in plating shops. With respect to industrial requirements some process parameters are fixed. The concentration of the chromic acid recovered should be higher than $1 \, mol \, l^{-1} \, CrO_3$ in order to avoid strong dilution of the process bath. The average concentration of the static rinse water is $0.1 \, mol \, l^{-1} \, CrO_3$, but can strongly differ depending on the plating shop.

The EED process was described by Audinos [8] proposing a two-compartment EED with an anion-exchange membrane (AEM) for chromic acid recycling up to $280 \, g \, l^{-1}$ and energy consumptions in the range of $10–20 \, kWh \, kg_{CrO_3}^{-1}$. Frequent AEM replacement was required since the membrane worked under very severe conditions. Audran et al. [9,10] pointed out that poor AEM stability might prevent application of this technology and studied a two-compartment EED system using an AEM by the company MORGANE (France). They could reach an average current efficiency of 48% and power consumptions of $18 \, kWh \, kg_{CrO_3}^{-1}$ at $40 \, °C$ and $50 \, mA \, cm^{-2}$. The maximum anolyte (product) concentration was $310 \, g \, l^{-1} \, CrO_3$. The authors stated that the membranes have been working for 4000 h, however the performance during this long period was not reported and further com-

mercialisation is not known. Cohen and Duclert [11] also described a two-compartment EED configuration equipped with anion-exchange membranes from MORGANE (type ARA 17-10) and Sybron Co. (IONAC 3475 XL). Two applications for chromic acid recovery were briefly considered: re-concentration of chromic acid in the anode compartment from chromic acid plating solution ($250 \, g \, l^{-1}$ at $58 \, °C$) and from a solution containing $8 \, g \, l^{-1} \, CrO_3$ and $1.6 \, g \, l^{-1} \, Fe$, which was re-concentrated to $323 \, g \, l^{-1}$ in the anode compartment. Using the high concentrated plating solution, the AEM MORGANE ARA 17-10 showed better transfer rates and lower power consumption than the IONAC MA 3475 XL. However, the authors did not mention the test duration and long-term stability of the membranes.

Other studies described the transport properties of anion-exchange membranes at low chromate concentration solutions. The AEM used were SB 6407 (Gelman Science), Neosepta AFN and ACM (Tokuyama Soda Co.) at $0.01 \, M \, K_2Cr_2O_7$ [12], Raipore 1030 (RAI Research Co.) at $0.02 \, M \, Cr(VI)$ solutions [13,14] and Selemion AMT (Asahi Glass Co.) in solution containing $1.7 \, g \, l^{-1} \, Cr(VI)$ [15]. Vallejo et al. [16] found that the membrane AW 11 (Solvay Co.) was not suitable for chromic acid recovery because of rapid increase of membrane resistance. However, Vallejo et al. [17] reported more promising results with the AEM IONAC MA-3475 (Sybron Co.). They showed that the Cr(VI) concentration in the anode compartment, the pH and temperature are critical parameter influencing the process. The maximum current efficiency achieved in acid environment was ~11%. Roualdes et al. [18] tested a new AEM from plasma-grafted PVDF polymers with hexavalent chromium containing solutions obtaining Cr(VI) transport number of 0.16. Finally, it is worth noting that less membrane stability problems occur when using perfluorosulfonated CEM, which are stable in chromic acid. Nevertheless, the efficiency for the removal of cationic contaminants is low compared to the anodic electrolyse efficiency (anodic oxidation of Cr(III)–Cr(VI)) [15,19–27].

From process design point of view, the three-compartment EED technology might be better for the plating industry, because it can manage three different tasks simultaneously: (i) removal of contaminants, (ii) chromic acid recovery and (iii) purification of static rinse water. Dalla Costa et al. [15] compared a two- and three-compartment configuration at lab-scale and found maximum process efficiency in the three-compartment system in the absence of sulfate ions. A publication and patent of Bergman and Iourtchouk [28,29] describe a three-compartment cell for chromic acid recovery at bench-scale. The authors studied various electrode materials and compared a two- and three-compartment system using exhausted plating solution in the central compartment. They reported process limitations due to high voltage increase and current efficiencies between 12% (chromating solution) and 20% (hard chromium plating solution). However, the type of AEM, membrane stability and test duration was not stated. Shuster et al. [30] and Kidon et al. [31] also patented a three-compartment system,

however, they used a porous diaphragm to separate the anode compartment.

In this work, the newly developed AEM (fumasep® FAP FuMA-Tech GmbH, Germany) is compared with other commercial membranes for the recovery of chromic acid by EED showing promising results and overcoming above described obstacles. In addition, the application of this membrane under various process conditions is studied aiming to the optimisation of the process and to the successful up-scaling.

2. Experimental

2.1. Membranes, chemicals and analysis

The IONAC MA 3475 (Sybron Co.), PC 100 D (PCA GmbH) and the newly developed fumasep® FAP FuMA-Tech membranes were selected for a the membrane screening (see Table 1). The fumasep® FAP membrane could only be used at acidic environment, therefore the permselectivity, area resistance and IEC could not be determined by standard methods. As cation-exchange membrane reinforced Nafion®324 (Du Pont Polymers) was used (see Fig. 1). All solutions were prepared using deionized water. Synthetic rinsing solution was prepared from chromium(VI) oxide (Fluka Chemie GmbH, 27083, p.a.) and nickel(II) sulfate hexahydrate (VWR International, 106727, p.a.). Sulfuric acid was also from VWR International (100731, p.a.). The chromic acid was determined by iodometric–potentiometric titration with thiosulphate using a combined Pt electrode (Mettler-Toledo GmbH, DL67 automatic titrator and ST20A sample changer). The chemicals used for this determination were potassium iodide (Riedel-de Haën, 30315, p.a.), sulfuric acid (VWR International, 100731, p.a.) and 0.1N sodium thiosulfate solution (VWR International, 109950, Titrisol®). The proton concentration (acidity) was determined by acid-basic titration and the metals were analysed by ICP.

2.2. Equipment and process conditions

For the comparison of the AEM and the influence of temperature, current density and concentration, the test cell consisted of three compartments divided by the AEM and
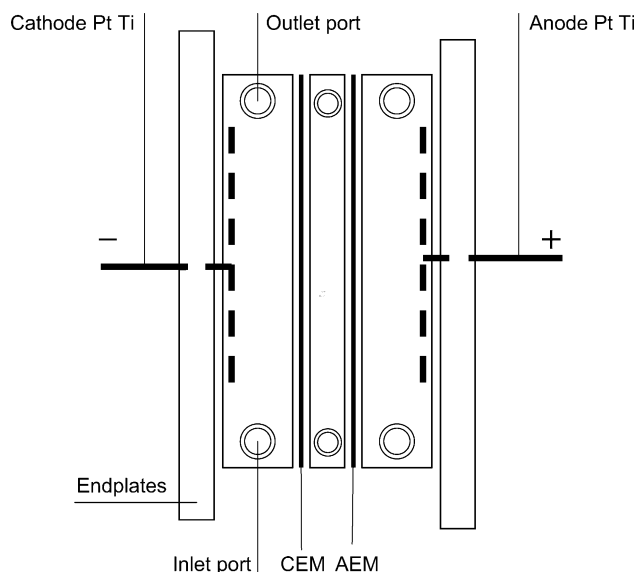

Fig. 2. Three-compartment test cell.

the CEM. The cell frames were made of polypropylene pressed together with gaskets (Viton®) between two endplates (Fig. 2). The compartment thickness was 0.7 cm for the central and 1.2 cm for the outer compartments. Polypropylene spacers (Naltex® 3604) were used for turbulence improvement and membrane support. The effective membrane area was 100 cm². Haber–Luggin capillaries were installed to measure single membrane potentials. For this, and due to the strong chromic acid solution, a resistant solid electrolyte capillary filling was developed containing sodium trisilicate, potassium chloride and hydrochloric acid. The voltage drop over the AEM was measured with Ag/AgCl/KCl (saturated) reference electrodes. As electrode material platinised titanium was used (mesh type). The test equipment was designed for minimum dead volume (approximately 0.4 l per compartment) in order to follow concentration changes within short experimental time (2 h). All solution reservoirs were kept at constant temperature using double wall glass bottles and three magnetic drive pumps supplied the cell (flow velocity in all compartments was adjusted to 10 cm s⁻¹). Power was supplied by a Voltcraft laboratory rectifier (0–2.5 A, 0–30 V).

Table 1
Characteristics of AEM used in membrane screening experiments

	PC 100 D	IONAC MA-3475	Fumasep® FAP
Manufacturer	PCA GmbH	Sybron Chemicals Inc.	FuMA-Tech GmbH
Reinforcement	Reinforced	Reinforced	Plain film
Thickness (μm)[a]	110	570	46
Swelling (%)	39.8	27.2	30.4
Area resistance ($\Omega\,cm^2$)[b]	1.87	30	n.a.[*]
Permselectivity (%)[c]	91.0	92.3	n.a.[*]
IEC (meq g⁻¹)	1.45	1.26	n.a.[*]

[*] n.a., not available (see text).

[a] Membranes left for 24 h in measuring solution.
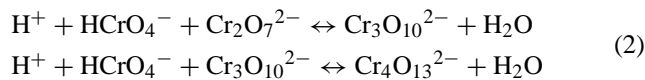
[b] 0.5N NaCl, 25 °C.

[c] 0.1N KCl/0.5N KCl, 25 °C.

The experiments for optimisation of flow velocity were performed with the commercial Micro Flow Cell® from ElectroCell A/S, Denmark and a ED pilot plant which allow the adjustment of different flow velocities. The cell was equipped with a MOX coated Ti anode (DSA® for O_2) and a stainless steel cathode. The synthetic rinsing solution for the central compartment contained 0.1 M CrO_3, 0.01 M $NiSO_4$ and 10^{-4} M H_2SO_4 except one experiment where a mixture of 0.3 M CrO_3 and 0.003 M H_2SO_4 was used. The anolyte solution ranged from 0.1 to 1 M CrO_3 (pure). The catholyte solution was basically 0.05 M H_2SO_4, except for the experiments where cell voltage was followed. There, 0.2 M H_2SO_4 solution was used (see results). The experiments were performed for up to 3.5 h at 20–50 °C. The current density was varied from 10 to 30 mA cm^{-2}. During all experiments, samples from each compartment were regularly taken and analysed for chromate and total acidity. Parallely, the current, voltage, temperature, conductivity and pH in each compartment were carefully monitored.

3. Theoretical background

The process performance could be evaluated on the basis of current efficiency (concerning formation of chromic acid in the anode compartment) and specific energy consumption (kWh kg^{-1}). The overall current efficiency for the product (chromic acid), Φ_P^e, is defined as the current carried by chromate ions relative to the total current used:

$$\Phi_P^e = \frac{m \nu_e F}{M I t} \tag{1}$$

where m is the mass of product, M the molar weight, ν_e the stoichiometric number of electrons for the reaction, F the Faraday constant, I the electric current and t is the time [32]. In chromic acid solutions, the chromium is present as different anionic species (monochromate, dichromate, trichromate, polychromate ions). The formation of large polychromate ions increases at higher chromic acid concentration and low pH, as described by Sarmaitis et al. [33,34]. In fact, the following reactions take place:

$$\begin{aligned} H^+ + HCrO_4^- + Cr_2O_7^{2-} &\leftrightarrow Cr_3O_{10}^{2-} + H_2O \\ H^+ + HCrO_4^- + Cr_3O_{10}^{2-} &\leftrightarrow Cr_4O_{13}^{2-} + H_2O \end{aligned} \tag{2}$$

This means that different chromate species may migrate through the anion-exchange membrane depending on solution composition. Rinsing effluents used in this study contained 0.1 M CrO_3 of pH around 1.2. The chromate ions are either monovalent or bivalent charged. At these conditions, the chromate is present as monochromate (mainly $HCrO_4^-$, 20%), as dichromate ($Cr_2O_7^{2-}$ and $HCr_2O_7^-$, 62%) and to a lower extent (18%) as trichromate ($Cr_3O_{10}^{2-}$). The valence regarding one mol of chromium is predominantly 1. Therefore, the stoichiometric number $\nu_e = 1$ was used in all calculations. Nevertheless, it should be considered that the
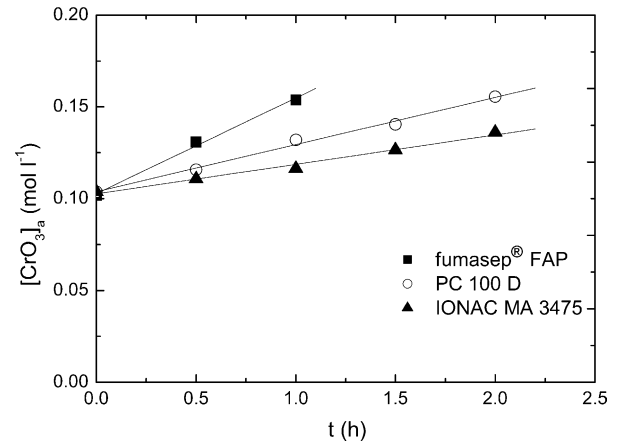

Fig. 3. Variation of CrO_3 concentration in the anode compartment. System parameters: 30 mA cm^{-2}, 30 °C, anode compartment: 0.1 M CrO_3.

interstitial pH in the membrane phase could be much lower resulting in increased polychromate formation in the membrane [16].

The specific energy consumption, $E_{S,m}$ (in kWh mol$^{-1}_{CrO_3}$) is essential for comparison of the efficiency of the EED with other recycling methods. Here, the total cell voltage, U_c, is an important influence factor:

$$E_{S,m} = \frac{U_c \nu_e F}{M \Phi_P^e} \tag{3}$$

4. Results and discussion

4.1. Membrane screening

Experiments with diluted and highly acidic solution in the anode compartment were performed. The experiments with diluted chromate solution (anode compartment: 0.1 M CrO_3, $i = 30$ mA cm^{-2}, $T = 30$ °C) were used for screening of the AEM and for comparison with recent literature results. Fig. 3 shows the increase of Cr(VI) concentration in the anode chamber for the studied membranes and Table 2 presents the overall results. The experiment with fumasep® FAP was performed for only 1 h due to the fast depletion of the rinse water in the central compartment resulting at low electrolyte conductivity. For this membrane, the current efficiency was more than two times higher than for the other membranes. Both fumasep® FAP and PC 100

Table 2
Performance of the various AEM using 0.1 M CrO_3 in the anode compartment

	IONAC MA 3475	PC 100 D	Fumasep® FAP
$\Phi_{CrO_3}^e$ [a]	0.13	0.18	0.42
$E_{S,m}$ (kWh mol$^{-1}_{CrO_3}$)	3.7	1.0	1.1

Process parameters: $i = 30$ mA cm^{-2}, $T = 30$ °C.
[a] Overall current efficiency.

Table 3
Performance of the various AEM using 1 M CrO_3 in the anode compartment

	IONAC MA 3475	PC 100 D	FT-FAP
$\Phi^e_{CrO_3}$ [a]	0.10	0.08	0.14
$E_{S,m}$ (kWh $mol^{-1}_{CrO_3}$)	1.9	1.4	1.6

Process parameters: $i = 20$ mA cm^{-2}, $T = 30\,°C$.

[a] Overall current efficiency.

D membrane show promising results having low power consumption per mol CrO_3. The IONAC MA 3475 membrane shows the lowest current efficiency and the highest power consumption due to high voltage drop. It is important to note that for this membrane our results are in excellent agreement with those reported earlier in the literature [17].

The performance of the PC 100 D, fumasep® FAP and IONAC MA 3475 membranes were then studied using 1 M CrO_3 concentration in the anode compartment. The experiments were conducted at lower current density (20 mA cm^{-2}) because high initial voltage increase was observed when using 30 mA cm^{-2}. In all cases, the current efficiency is lower compared to the previous experiments with 0.1 M CrO_3 solution (see Table 3). The fumasep® FAP shows the highest chromium transport and current efficiency and low power consumption. This membrane had the best overall performance; therefore, it was further used in process optimisation experiments.

4.2. Process optimisation

4.2.1. Use of synthetic and industrial rinse water

Industrial rinsing solution was used in the central compartment to see whether the use of synthetic solution could affect the membrane performance. Depending on the bath type, the chromic acid solution could contain organic additives acting as reaction catalysts or wetting agents [35]. Fluoride surfactants could be present, which could cause fouling of the ion-exchange membranes [36–38]. The industrial solution for the central compartment was obtained from exhausted chromic acid bath from a plating company, which produces chromium automotive accessories. The rinsing effluent was prepared by dilution. The composition of both synthetic and industrial solutions used in the central compartment is given in Table 4. The test parameters were the same as in membrane screening experiment. Table 5 presents the comparison showing that the current efficiency and the power consumption are comparable indicating the suitability of the membrane using industrial rinse solution.

Table 5
Effect of the type of rinsing solution on the performance of the fumasep® FAP membrane (1.0 M CrO_3 in the anode compartment)

	Industrial rinse water	Synthetic solution
$\Phi^e_{CrO_3}$ [a]	0.18	0.14
$E_{S,m}$ (kWh $mol^{-1}_{CrO_3}$)	1.1	1.6

Process parameters: $i = 20$ mA cm^{-2}, $T = 30\,°C$.
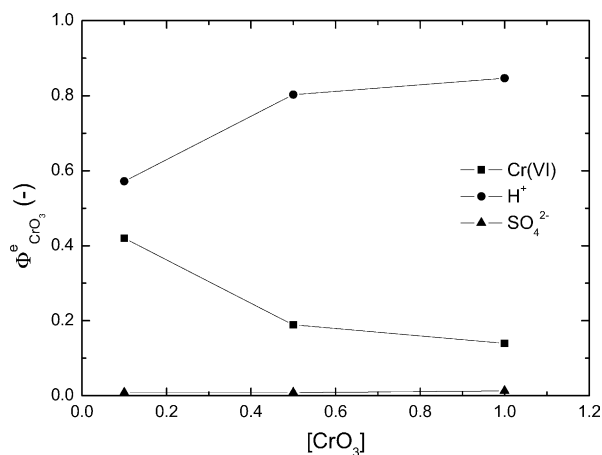
[a] Overall current efficiency.

Fig. 4. Current efficiency for CrO_3, SO_4^{2-} and H^+ vs. the initial CrO_3 concentration in the anode compartment. System parameters: 30 mA cm^{-2}, 30 °C.

4.2.2. Influence of chromic acid concentration in the anode compartment

The industrial process could be performed either in batch mode with fluctuating chromic acid concentration in the anode compartment (due to fluctuating acid recycling to the bath) or in continuous mode with permanent high acid concentration in the anode compartment (continuously acid recycling). Vallejo et al. [17] reported for the IONAC MA 3475 membrane that the current efficiency strongly depends on the anolyte concentration. In our experiments, the current efficiency for Cr(VI) transport decreases from 0.42 to 0.14 when the initial CrO_3 concentration in the anode compartment increases from 0.1 to 1 M (Fig. 4). The decrease of the current efficiency for Cr(VI) results in an increase of the current efficiency for protons from 0.57 to 0.85 whereas the sulphate transport remains generally low (Fig. 4). Besides the proton leakage, a loss of water occurs in the anode compartment. Others [39] also studied the relationship between proton leakage and water flux at high acidic conditions and found that the proton flux increases while the water transport to the anodic side decreases, in agreement with our findings. Besides, the nature of chromic acid in the AEM is
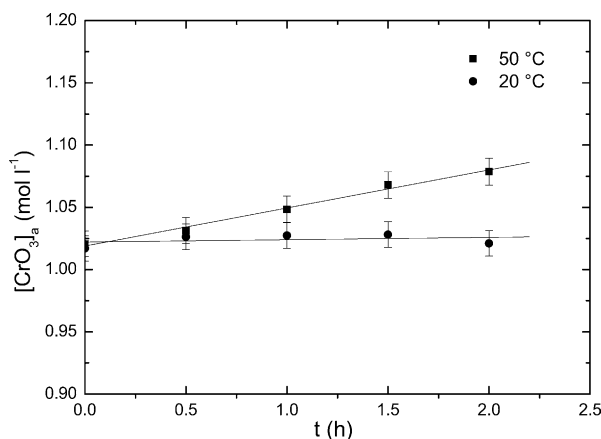
Table 4
Composition of effluents used in the central compartment (rinse solution)

	Al (ppm)	B (ppm)	Cr (ppm)	Cu (ppm)	Fe (ppm)	Mg (ppm)	Na (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	SO_4^{2-} (ppm)
Synthetic	0	0	5730	0	0	0	0	651	0	0	1090
Industrial	<3	15	5490	<1.2	2.7	<1	23	36	<2	167	99

Fig. 5. Variation of CrO_3 concentration in the anode compartment at 20 and 50 °C. System parameters: $20\,mA\,cm^{-2}$, anode compartment: $1.0\,M\,CrO_3$.

also important. Chromates could be present in many different species depending on pH and chromic acid concentration. At high acid environment, the proton leakage could be enhanced by the formation of polychromates under dehydration acting as proton conductors [33,34]. These large polychromates immobilised in the membrane could even reverse the AEM character due to their second negative charge. As a result, the membrane becomes highly permeable for protons and cations. Nevertheless, in our experiments no other cations besides proton where found in the anode compartment.

4.2.3. Influence of process temperature

Experiments with high chromic acid concentration in the anode compartment ($\sim$1 M) were performed, besides at 30 °C (see earlier results), at 20 and 50 °C too. The CrO_3 concentration in the anodic compartment during the experiments is shown in Fig. 5. Apparently, the product concentration increases much stronger at 50 °C than at 20 °C. Table 6 presents the current efficiencies and power consumptions. The current efficiency was 0.33 at 50 °C compared to 0.04 at 20 °C. The increased chromium transport at higher temperatures could be attributed to lower proton leakage at higher temperatures [40]. The decrease of proton transport is mainly associated with reduced water organization at the membrane–solution interface at the anodic side [36]. Similar behavior was also observed with the IONAC MA-3475 membrane [17] but not to this extent. For the latter, the current efficiency for hexavalent chromium was 0.16 at 50 °C and 0.11 at 30 °C using $0.1\,M\,CrO_3$ solution in the anode and central compartment. The difference in our case might be attributed to the high pro-

Table 6
Effect of temperature on the performance of fumasep® FAP membrane (1.0 M in the anode compartment)

	20 °C	30 °C	50 °C
$\Phi^e_{CrO_3}$ [a]	0.04	0.14	0.33
$E_{S,m}$ ($kWh\,mol^{-1}_{CrO_3}$)	3.7	1.6	0.5

Process parameters: $i = 20\,mA\,cm^{-2}$.

[a] Overall current efficiency.
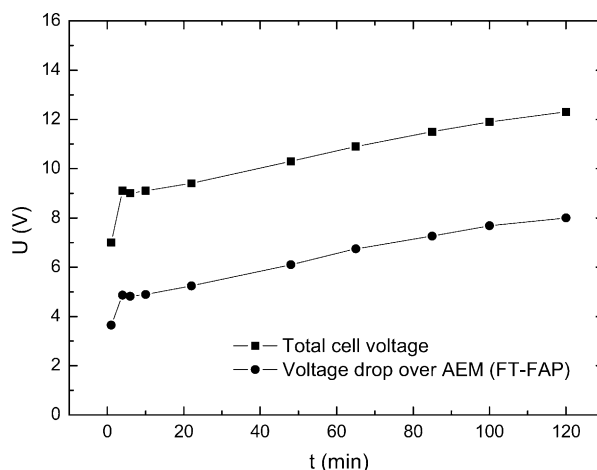
Fig. 6. The cell voltage at $30\,mA\,cm^{-2}$. Anode compartment: $1.2\,M\,CrO_3 + 0.012\,M\,H_2SO_4$; central compartment: $0.3\,M\,CrO_3 + 0.003\,M\,H_2SO_4$; cathode compartment: $0.2\,M\,H_2SO_4$ at 25 °C.

ton concentration in the anode compartment especially at the solution–membrane interface. The protons there have lower kinetic energy at higher temperatures and the entry into the membrane might be hampered.

In conclusion, the improved Cr transport at higher temperature could be exploited in the EED process. Nevertheless, the benefit from the improved transport should be weighed against long-term material stability (membranes and/or equipment) and extra heating costs of the process solutions.

4.2.4. Influence of current density–voltage drop

In all experiments, the voltage increases sharply during the first minutes. Both total voltage drop over the EED system and single voltage drop over the AEM were measured using Haber–Luggin capillaries. Fig. 6 presents the first two hours of this experiment at $30\,mA\,cm^{-2}$ showing that the increase of the cell voltage is parallel to the voltage increase over the AEM. Similar increase of resistance has been observed by Vallejo et al. [16], too. They attributed this phenomenon to the formation and accumulation of low mobility polychromate inside the membrane at high acidic conditions resulting to the deprotonation of the membrane active sides and increase of resistance. This was confirmed from the following experiments where a different AEM pre-treatment procedure is applied. A commercial test cell (Micro Flow Cell®) is used and $30\,mA\,cm^{-2}$ are applied. The first experiment is performed with $0.2\,M\,H_2SO_4$ in each compartment and the voltage stays constant at 2.7 V (Fig. 7a). A second piece of AEM is pretreated in $0.2\,M\,H_2SO_4$ and then directly overflowed with $0.1\,M\,CrO_3$ while the current starts passing. There is a strong increase in voltage observed in the beginning. The voltage reaches to 6 V in the first minute and remains at this level. Finally a piece of AEM is pretreated in $0.2\,M\,H_2SO_4$ and rinsed in $0.1\,M\,CrO_3$ for 2 h. Then, the experiment with $0.1\,M\,CrO_3$ is repeated and the voltage reaches very high level (18 V). From these results, we can conclude
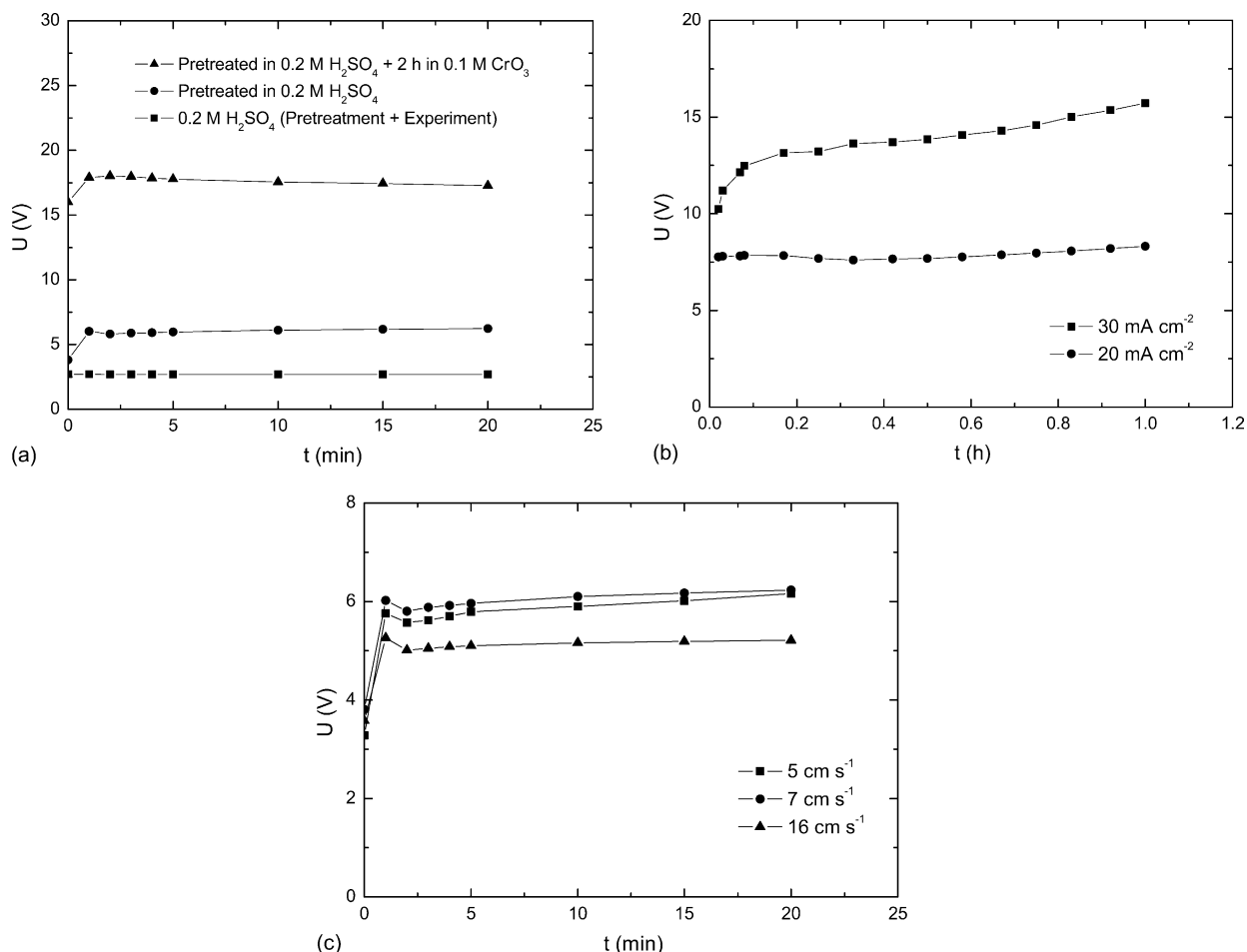
Fig. 7. (a) The cell voltage at $30\,\mathrm{mA\,cm^{-2}}$. System parameters: $20\,°C$, anode and central compartment: $0.1\,\mathrm{M\,CrO_3} + 10^{-4}\,\mathrm{M\,H_2SO_4}$ or $0.2\,\mathrm{M\,H_2SO_4}$; cathode compartment: $0.2\,\mathrm{M\,H_2SO_4}$, $v = 7\,\mathrm{cm\,s^{-1}}$. (b) The cell voltage at 20 and $30\,\mathrm{mA\,cm^{-2}}$ anode compartment $1.0\,\mathrm{M\,CrO_3}$ ($30\,°C$). (c) The cell voltage at $30\,\mathrm{mA\,cm^{-2}}$. System parameters: $20\,°C$, anode and central compartment: $0.1\,\mathrm{M\,CrO_3} + 10^{-4}\,\mathrm{M\,H_2SO_4}$, cathode compartment: $0.2\,\mathrm{M\,H_2SO_4}$.

that the initial voltage is strongly associated with the chromic acid concentration inside the membrane and the formation of polychromates discussed earlier. It is worth to note that De Körösy and co-workers [41,42] also described the increase of the membrane resistance due to presence of multivalent ions in the membrane. However, they reported simultaneous breakthroughs of ions and change in membrane permselectivity, which we have not observed. Korngold et al. [36] have also reported similar behavior for anionic membranes in the presence of insoluble acidic colloids. According to them the high initial membrane resistance could be reduced when using lower initial current densities and high flow rates. The following experiments aim to investigate this.

Fig. 7b shows the variation of voltage in time at 20 and $30\,\mathrm{mA\,cm^{-2}}$ using $1\,\mathrm{M\,CrO_3}$ anodic solution. The initial voltage increase is very rapid, especially for the higher current density. The average voltage drop is $7.7\,\mathrm{V}$ for $20\,\mathrm{mA\,cm^{-2}}$ and $13–15\,\mathrm{V}$ for $30\,\mathrm{mA\,cm^{-2}}$. The increased current density (greater than $20\,\mathrm{mA\,cm^{-2}}$) considerably improves the chromate transport (the chromate flux was around 30% higher at $30\,\mathrm{mA\,cm^{-2}}$ in accordance to Faraday's law) but also results in a steadily growing high voltage drop over the EED system. This might cause damage on membranes and/or other equipment. Additionally, processing with increased voltage leads to high power consumptions. Table 7 presents the current efficiency and power consumption for these two current densities. Practically there are no differences in current efficiency between the two experiments. The power consumption was $1.6\,\mathrm{kWh\,mol_{CrO_3}^{-1}}$ at $20\,\mathrm{mA\,cm^{-2}}$ and $2.5\,\mathrm{kWh\,mol_{CrO_3}^{-1}}$ at $30\,\mathrm{mA\,cm^{-2}}$ due to higher cell voltage. All the above results show that the process should be operated at maximum $20\,\mathrm{mA\,cm^{-2}}$.

The cell voltage was also measured in the Micro Flow Cell® at three different flow velocities. The superficial flow

Table 7
Effect of the current density on the performance of fumasep® FAP membrane ($1.0\,\mathrm{M\,CrO_3}$ in the anode compartment)

	$20\,\mathrm{mA\,cm^{-2}}$	$30\,\mathrm{mA\,cm^{-2}}$
$\Phi_{CrO_3}^e$ [a]	0.14	0.14
$E_{S,m}$ ($\mathrm{kWh\,mol_{CrO_3}^{-1}}$)	1.6	2.5

Process parameters: $T = 30\,°C$.
[a] Overall current efficiency.

velocity was calculated for the empty space of the cell chamber. Before each experiment the voltage drop over the cell was determined using 0.2 M H_2SO_4 in all cycles at 30 mA cm^{-2} and found constant at 2.7 V. Then, 0.1 M chromic acid solution was placed into the anode and central compartment and the experiment started. After 20 min of operation, the cell voltage for velocities 5 and 7 cm s^{-1} was nearly the same and ∼1 V higher than the voltage for 16 cm s^{-1} (Fig. 7c). At higher velocities, the concentration polarisation effects, i.e., concentration decrease at the membrane surface facing the diluate compartment could be reduced and overall cell resistance could be kept lower [43]. In our application, the voltage could be only reduced by 1 V through application of higher flow rates.

5. Conclusion and future work

Our work showed that the fumasep® FAP membrane seems to be a promising membrane for the chromic acid recovery EED process having better performance than the other two commercial membranes studied (IONAC MA 3475 and PC 100 D). The main factors influencing the current efficiency of the Cr transport seem to be the chromic acid concentration in the anode compartment and the process temperature. Low chromic acid concentration in the anode compartment and high temperature result in significantly higher chromate transport. A significant process limitation is the high membrane resistance due to the formation of polychromates inside the membrane. It was shown that low initial current densities and high flow rates could improve the process performance.

Our results suggest that successful up-scaling of the EED process requires:

- low initial current density (10–20 mA cm^{-2});
- high process temperature (between 40 and 50 °C);
- high flow rates (above 7 cm s^{-1}).

Our future work will be focused on the process up-scaling and long-term investigation of the fumasep® FAP membrane under these optimised conditions.

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References

[1] V.S. Donepudi, N.R. Khalili, R. Kizilel, J.R. Selman, Purification of hard chromium plating baths—options and challenges, Plat. Surf. Finish. (4) (2002) 62.

[2] S.A. Katz, H. Salem, The toxicology of chromium with respect to its chemical speciation: a review, J. Appl. Toxicol. 13 (3) (1993) 217–224.

[3] E. Groshart, Finishing in the green—chromium, Met. Finish. 95 (3) (1997) 59–61.

[4] E. Nieboer, A.A. Jusys, Biologic chemistry of chromium, in: J.O. Nriagu, E. Nieboer (Eds.), Chromium in the Natural and Human Environments, John Wiley & Sons Inc., 1988.

[5] G. Pourcelly, R. Marquínez, B. Bauer, R. López, S. Viala, A. Mahiout, G. Istvan, Acid Chromic Recycling from Rinse Water in Galvanic Plants by Electro-Electrodialysis. Workshop on Environmentally Clean Technologies for Sustainable Production and Consumption, Vancouver, Canada, Canmet-Cari-European Commission, 2003.

[6] A. Baral, R.D. Engelken, Chromium-based regulations and greening in metal finishing industries in the USA, Environ. Sci. Pol. 5 (2) (2002) 121–133.

[7] E.A. Cohen Hubal, M.R. Overcash, Net-waste-reduction analysis applied to zero-water discharge systems for chromic acid electroplating, J. Cleaner Prod. 3 (3) (1995) 161–167.

[8] R. Audinos, Liquid waste concentration by electrodialysis, in: N.N. Li, J.M. Calo (Eds.), Separation and Purification Technology, Marcel Dekker, 1992, pp. 229–301.

[9] J. Audran, P. Baticle, M.-M. Letord, Recycling of Chromic Acid by Electro-Electrodialysis, Fifth World Filtration Congress, Nice, France, 1990.

[10] J. Audran, M.-M. Letord, A. Ducourroy, Electrochemical cell, especially for recycling of chromic acid, Patent EP 0483015 (1992).

[11] T. Cohen, F. Duclert, Récupération des acides et des métaux par de nouvelles membranes échangeuses d'ions, Rev. gén. électr. (3) (1992) 17–19 (in French).

[12] Y. Çengeloğlu, A. Tor, E. Kir, M. Ersöz, Transport of hexavalent chromium through anion-exchange membranes, Desalination 154 (3) (2003) 239–246.

[13] E. Castillo, M. Granados, J.L. Cortina, Chromium(VI) transport through the Raipore 1030 anion-exchange membrane, Anal. Chim. Acta 464 (1) (2002) 15–23.

[14] E. Castillo, M. Granados, J.L. Cortina, Chemically facilitated chromium(VI) transport throughout an anion-exchange membrane: application to an optical sensor for chromium(VI) monitoring, J. Chromatogr. 963 (1–2) (2002) 205–211.

[15] R.F. Dalla Costa, M.A.S. Rodrigues, J.Z. Ferreira, Transport of trivalent and hexavalent chromium through different ion-selective membranes in acidic aqueous media, Sep. Sci. Technol. 33 (8) (1998) 1135–1143.

[16] M.E. Vallejo, P. Huguet, C. Innocent, F. Persin, J.L. Bribes, G. Pourcelly, Contribution of Raman spectroscopy to the comprehension of limiting phenomena occurring with a vinylpyridinium anion-exchange membrane during the electrolysis of Cr(VI) solutions, J. Phys. Chem. B 103 (51) (1999) 11366–11371.

[17] M.E. Vallejo, F. Persin, C. Innocent, P. Sistat, G. Pourcelly, Electrotransport of Cr(VI) through an anion-exchange membrane, Sep. Purif. Technol. 21 (2000) 61–69.

[18] S. Roualdes, N. Kourda, J. Durand, G. Pourcelly, Plasma-grafted PVDF polymers as anion-exchange membranes for the electrotransport of Cr(VI), Desalination 146 (2002) 273–278.

[19] R.F. Dalla Costa, J. Zoppas Ferreira, C. Deslouis, Electrochemical study of the interactions between trivalent chromium ions and Nafion perfluorosulfonated membranes, J. Membr. Sci. 215 (2003) 115–128.

[20] P. Ng, D. Snyder, Combining electrolysis and dialysis for regeneration of chromic acid etching solution, J. Membr. Sci. 13 (1983) 327–336.

[21] M.A.S. Rodrigues, R.F. Dalla Costa, A.M. Bernardes, J. Zoppas Ferreira, Influence of ligand exchange on the treatment of trivalent chromium solutions by electrodialysis, Electrochim. Acta 47 (5) (2001) 753–758.

[22] K.-L. Huang, T.M. Holsen, J.R. Selman, Impurity partitioning in nafion and ceramic separators used for purification of spent chromium plating solutions, J. Membr. Sci. 210 (2002) 137–145.

[23] K.-L. Huang, T.M. Holsen, T.-C. Chou, J.R. Selman, Comparing nafion and ceramic separators used in electrochemical purification of spent chromium plating solutions: cationic impurity removal and transport, Environ. Sci. Technol. 37 (9) (2003) 1992–1998.

[24] K.-L. Huang, T.M. Holsen, J.R. Selman, Impurity diffusion through nafion and ceramic separators used for electrolytic purification of spent chromium plating solutions, J. Membr. Sci. 221 (2003) 135–146.

[25] M.I. Ahmed, H.T. Chang, J.R. Selman, T.M. Holsen, Electrochemical chromic acid regeneration process: fitting of membrane transport properties, J. Membr. Sci. 197 (2002) 63–74.

[26] M.I. Ahmed, T.M. Holsen, J.R. Selman, Electrochemical chromic acid regeneration process with fuel-cell electrode assistance. Part I: removal of contaminants, J. Appl. Electrochem. 31 (2001) 1381–1387.

[27] M.I. Ahmed, T.M. Holsen, J.R. Selman, Chromic acid regeneration process with fuell cell electrode assistance. Part II: electrochemical characterization, material compatibility and energy consumption, J. Appl. Electrochem. 31 (2001) 1389–1394.

[28] H. Bergman, T. Iourtchouk, Verfahren und Zelle zur Regenerierung chromhaltiger Systeme, Patent DE 19733064 A1 (1999).

[29] T. Iourtchouk, H. Bergmann, Elektrochemische Regenerierung vorzugsweise chromhaltiger Systeme, in: A. Zielonka (Ed.), Jahrbuch der Oberflächentechnik, Bad Saulgau, Eugen G. Leuze Verlag, 2003, pp. 206–221 (in German).

[30] N. Shuster, A.D. Babinsky, W.E. Kidon, Chromic acid production process using a three-compartment cell, Patent US 4,290,864 (1981).

[31] W.E. Kidon, N. Shuster, A.D. Babinsky, Production of chromic acid using two-compartment and three-compartment cells, Patent US 4,273,628 (1981).

[32] H. Wendt, G. Kreysa, Electrochemical engineering: science and technology in chemical and other industries, Springer-Verlag, Heidelberg, 1999.

[33] R. Sarmaitis, V. Dikinis, V. Rezaite, Equilibrium in solutions of chromic acid, Plat. Surf. Finish. 83 (6) (1996) 53–57.

[34] R. Sarmaitis, V. Dikinis, V. Rezaite, V. Stasiukaitis, Distribution of Cr(VI) particles in solutions of acids, in: Proceedings of the AESF Annual Technical Conference, 1996, p. 89.

[35] G.A. Lausmann, J.N.M. Unruh, Die galvanische Verchromung. Schriftenreihe Galvanotechnik (1998) (in German).

[36] E. Korngold, F. De Körösy, R. Rahav, M.F. Taboch, Fouling of anionselective membranes in electrodialysis, Desalination 8 (1970) 195–220.

[37] H. Holdik, Impedanzspektroskopische Charakterisierung von tensidverursachten Foulingvorgängen an Ionenaustauscher-Membranen, Ph.D. Thesis, Saarland University, 1999 (in German).

[38] H. Strathmann, Ion-exchange membranes, in: W.S. Winston Ho, K.K. Sirkar (Eds.), Membrane Handbook, Van Nostrand Reinhold, New York, 1992, p. 235.

[39] B.J. Robbins, R.W. Field, S.T. Kolaczkowski, A.D. Lockett, Rationalisation of the relationship between proton leakage and water flux through anion-exchange membranes, J. Membr. Sci. 118 (1996) 101–110.

[40] Y. Lorrain, G. Pourcelly, C. Gavach, Influence of cations on the proton leakage through anion-exchange membranes, J. Membr. Sci. 110 (1996) 181.

[41] F. De Körösy, E. Zeigerson, Breakthrough of poisoning multivalent ions across a permselective membrane during electrodialysis, J. Phys. Chem. 71 (11) (1967) 3706–3709.

[42] D. Kertész, F. De Körösy, E. Zeigerson, Advances in the electrochemistry of permselective membranes, Desalination 2 (1967) 161–169.

[43] W.S. Winston Ho, K.K. Sirkar, Membrane Handbook, Van Nostrand Reinhold, New York, 1992.