

# Influence of $\text{CH}_3\text{SO}_3\text{H}$ and $\text{AlCl}_3$ in direct and pulse current electrodeposition of trivalent chromium

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Comparison of direct and pulse current electrodeposition of the trivalent chromium from urea formic acid as a complexing agent was studied in detail. The influences of  $\text{CH}_3\text{SO}_3\text{H}$  and  $\text{AlCl}_3$  on the properties of the deposit were also studied. The presence of  $\text{CH}_3\text{SO}_3\text{H}$  exhibits higher current efficiency and better corrosion resistance because of its higher hydrogen overpotential. The pulse current electrodeposition leads to growth of  $\beta$ -Cr. The corrosion studies were conducted by potentiodynamic polarisation and electrochemical impedance spectroscopy. The morphology of the deposits was characterised by scanning electron microscopy (SEM) and X-ray diffraction.

**Keywords:** On time, Off time, Coatings, Chromium, Pulse electrodeposition

## Introduction

Electrodeposition of chromium is extensively used in the field of surface finishing and engineering applications. In the case of the two forms of chromium, the chemistry and toxicology of each form is markedly different. Chromium can exist in oxidation states ranging from +2 to +6. However, only Cr(III) and Cr(VI) are stable enough to actually be used. Cr(VI) is readily reduced to more stable Cr(III) and in this process substances in contact with the Cr(VI) are oxidised. Cr(VI) compounds are very soluble compared to Cr(III) compounds. Therefore, in the environment Cr(VI) is much more likely, upon release into a stream or an aquifer, to dissolve and move with flow. In fact, one method that has been used to stabilise Cr(VI) (make it less mobile) in the environment is to reduce it to Cr(III).

The chemistry of chromium provides a basis for understanding the toxicology. Cr(III) is rather insoluble and does not oxidise organic material. Cr(III) is poorly absorbed from the gastrointestinal track and is not considered to be a carcinogen. On the other hand, Cr(VI) is very reactive and causes ulceration of the nasal septum and other tissues upon exposure as well as reproductive, gastrointestinal and dermal effects. Even so, Cr(III) is not without toxic effects and should be handled appropriately.

As described above, Cr(III) plating has numerous environmental, health and technical advantages relative to Cr(VI) plating. Attempts to deposit chromium from aqueous trivalent chromium solution can be traced to the early 1900s. Since 1933, many patents and papers have been issued for deposition of chromium alone and then as an alloy with elements like nickel, manganese, irons, cobalt and molybdenum.<sup>1-10</sup> Considerable

research has been conducted to study Cr(III) plating, including the effects of the plating bath chemistry on plating thickness, brightness, hardness, and corrosion resistance<sup>11-17</sup> and the effect of current wave forms on chromium deposit structure, distributions, brightness and hardness.<sup>18-22</sup>

Trivalent chromium electroplating was first used only for decorative purpose due to thickness limitations. During the 1980s and 1990s, studies were performed on electrodeposition of chromium from trivalent chromium baths, most of which contained carboxylic acids.<sup>23-26</sup>

Electrodeposition by pulse plating has been shown to have advantages over dc plating by producing deposition with reduction of porosity, lower gas content, high purity and deposits having low electrical resistance.<sup>27-30</sup> Crystalline morphology of the deposits is also controlled by the condition of pulsed electrolysis,<sup>31-45</sup> which affects the concentration of ionic species in the vicinity of the substrate for deposition. Nomura *et al.* reported that Ni films were formed by pulsed electrolysis and the preferred orientation of the Ni films was changed into the preferred one by pulse parameters.<sup>46</sup> Ghosh *et al.* demonstrated that the grain size of nano crystalline Ni-Cu alloy was decreased by pulsed electrolysis and improved its microhardness and corrosion resistance.<sup>47</sup> The present work is to study the effect of  $\text{CH}_3\text{SO}_3\text{H}$  and  $\text{AlCl}_3$  on current efficiency and corrosion resistance of chromium deposit from Cr(III) urea formate bath. Using dc and pulse current. Only very few literature report explain the effect of  $\text{AlCl}_3$  in trivalent chromium bath till now. Similarly there is no literature available for the effect of  $\text{CH}_3\text{SO}_3\text{H}$  on trivalent chromium electrodeposition by direct and pulse current (pc) technique. From the present study, the authors can know the advantage of  $\text{CH}_3\text{SO}_3\text{H}$  on the chromium deposit. By adding metahne sulphonic acid, current efficiency and corrosion resistance of the deposit increases.

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## Experimental

### Electrolyte, dc and pc plating

Electrodeposited chromium was prepared by the electrolysis of dc and pc methods from a trivalent chromium bath I consisting of  $159.87 \text{ g L}^{-1} \text{ CrCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $26.74 \text{ g L}^{-1} \text{ NH}_4\text{Cl}$ ,  $29.22 \text{ g L}^{-1} \text{ NaCl}$ ,  $18.55 \text{ g L}^{-1} \text{ H}_3\text{BO}_3$ ,  $200 \text{ mL CH}_3\text{OH}$ ,  $7.5 \text{ mL HCOOH}$  and  $120 \text{ g L}^{-1} (\text{NH}_2)_2\text{CO}$ . The bath I plus  $2 \text{ mL CH}_3\text{SO}_3\text{H}$  and bath I plus  $96.57 \text{ g L}^{-1} \text{ AlCl}_3$  are represented as baths II and III respectively. Analytical grade chemicals and distilled water were used to prepare the electrolytes. The solution was maintained at the pH value of  $1.3 \pm 0.1$  and the temperature of  $30 \pm 1^\circ\text{C}$ . Electrodepositions were performed galvanostatically using dc and pc and the pulse parameters are shown in Table 1. Cathodically cleaned copper plates were used as cathode with the exposed surface area of  $2.5 \times 2.5 \text{ cm}$ . The insoluble graphite anode was placed at a distance of  $6 \text{ cm}$  from the cathode.

### Electrochemical procedures

The electrochemical corrosion behaviour was studied using potentiodynamic polarisation tests and electrochemical impedance spectroscopy in a stagnant solution of  $3.5 \text{ wt}\% \text{ NaCl}$ . A standard measuring cell with three electrodes was used. The samples from high current efficiency condition of both dc and pc coatings of baths I–III were used as working electrode and they are represented as I dc, I pc, II dc, II pc, III dc and III pc respectively. A platinum foil and a saturated calomel electrode were used as auxiliary electrode and reference electrode respectively. The electrodes were connected to an advanced electrochemical system (Princeton applied Research, USA, model PARSTAT 2273). All potentials in the present work are referred to saturated calomel electrode.

Potentiodynamic polarisation curves were measured with open circuit potential for all the samples between  $-0.25$  and  $+0.25 \text{ V}$  at a scan rate of  $10 \text{ mV s}^{-1}$  and impedance spectra were conducted at frequency range from  $100 \text{ KHz}$  to  $10 \text{ Hz}$ . The amplitude of potential modulation was  $5 \text{ mV}$ . All the recorded impedance spectra were shown as Nyquist diagrams.

## Results and discussion

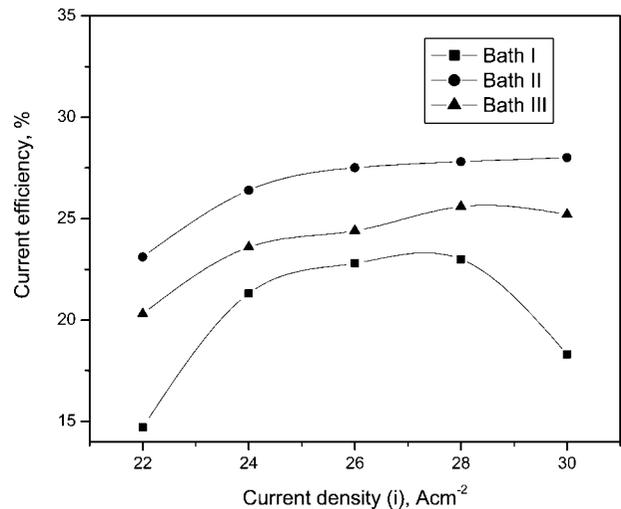
### Effect of current density on current efficiency

Current efficiency varied with current density, as shown in Fig. 1. Whereas an increase in current density up to  $28 \text{ A dm}^{-2}$  in baths I and III and  $30 \text{ A dm}^{-2}$  in bath II are led to an increase in current efficiency. In baths II

**Table 1** Details of pulse conditions

	Pulse frequency, Hz				
	10	20	50	100	
Duty cycle, %	Pulse on-off time, ms				
	10	10–90	4–36	2–18	1–9
	20	20–80	8–32	4–16	2–8
	40	40–60	16–24	8–12	4–16
80	80–20	32–8	16–4	8–2	

$$\text{Duty cycle} = \frac{\text{on time}}{\text{on time} + \text{off time}} \times 100; \text{ peak current} = \frac{\text{average current}}{\text{duty cycle}}$$



**1** Effect of current density on current efficiency of Cr deposits using dc

and I it is an advantage that the current efficiency increases with increase in current density because it causes uniform metal distribution. In contrast, metal distribution would not be uniform in bath III because more metal was deposited in high current density areas such as edges and corners than in low density areas such as the centre of the substrate.

### Two types of experiments for comparison of dc and pc plating

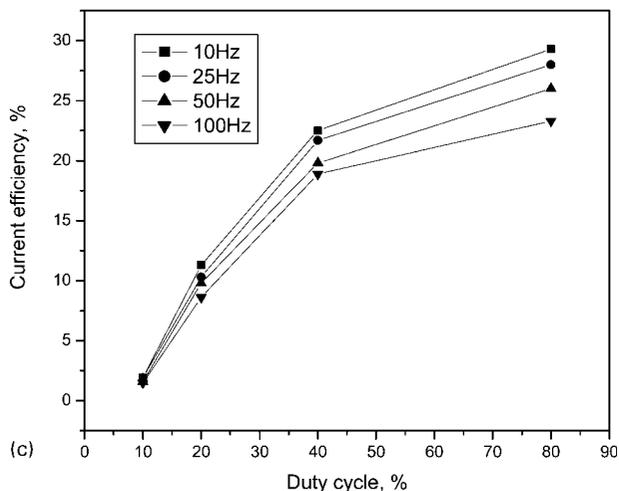
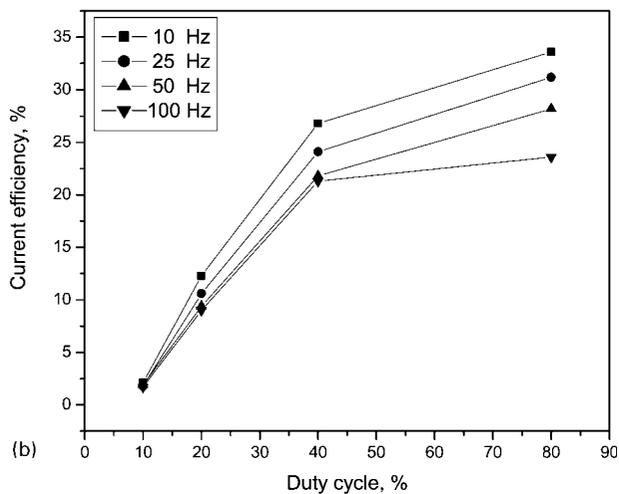
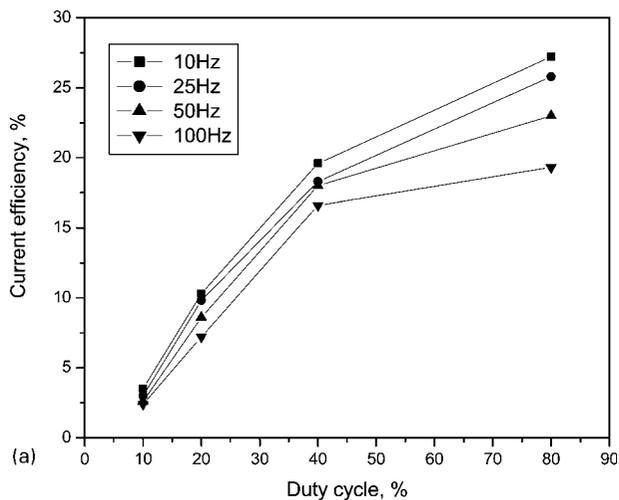
To compare the effect of dc and pc plating on the rate of deposition, two sets of experiments were conducted for baths I–III. They were:

- pc plating at different frequencies and duty cycle with the average current density of  $26 \text{ A dm}^{-2}$  for baths I and II and  $24 \text{ A dm}^{-2}$  for bath III and the duration of electro deposition was  $15 \text{ min}$
- the effect of time on current efficiency was carried out at high current efficiency conditions of both dc and pc methods.

### Effect of pulse parameters

Current efficiency varied with pulse duty cycle, as shown in Fig. 2. The higher current efficiency ( $27.2$ – $19.3\%$  in Fig. 2a,  $33.6$ – $23.6\%$  in Fig. 2b and  $29.3$ – $23\%$  in Fig. 2c) was obtained for deposition of chromium at  $80\%$  pulse duty cycle, while at  $10\%$  duty cycle, the current efficiency were decreased  $<5\%$ . The current efficiency of pc plating is higher at  $80\%$  duty cycle, when compared to dc plating at same average current and duration of plating in all baths. The pc electrodeposition, during the off time period, leads to the relaxation of the pulsating diffusion layer, in turn to increased replenishment of chromium ion and desorption of hydrogen gas and hence increases the current efficiency.<sup>38</sup> In contrast the current efficiency decreases with pulse frequency increases because the current on-off time decreased. Therefore, there is no time for sufficient replenishment of chromium ion at the cathode surface.

Moreover, the effect of  $\text{CH}_3\text{SO}_3\text{H}$  and  $\text{AlCl}_3$  on current efficiency of both dc and pc deposits are listed in Table 2. The addition of  $\text{CH}_3\text{SO}_3\text{H}$  in bath I accelerates the deposition of chromium and increases its current efficiency by  $4$ – $7\%$  because of a higher hydrogen overpotential. But it does not affect the rate of the

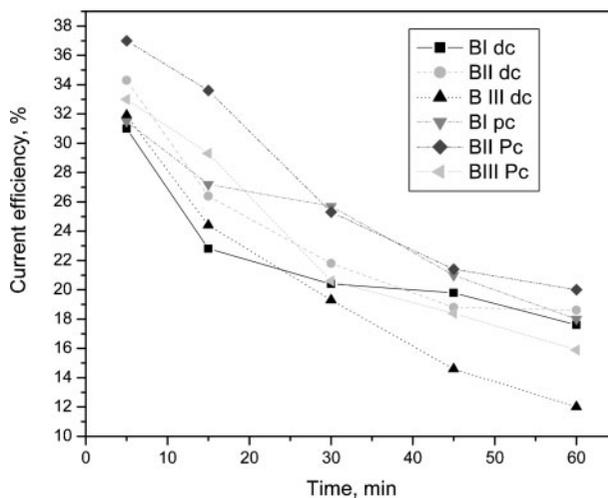


**2 Effect of pulse parameters on current efficiency of Cr deposits of a bath I, b bath II and c bath III**

reduction in chromium.<sup>48</sup> The addition of AlCl<sub>3</sub> in the bath I improves the current efficiency (1–2%), bath stability and quality of chromium deposits.<sup>11–13</sup> El-Sharif *et al.*

**Table 2 Effect of CH<sub>3</sub>SO<sub>3</sub>H and AlCl<sub>3</sub> on current efficiency**

System	Current efficiency, %	
	dc deposit at average current density	pc deposit at 80% duty cycle and 10 Hz
Difference between the baths I and II	4–7	6–4
Difference between the baths I and III	1	2–1



**3 Effect of time on current efficiency of Cr deposits**

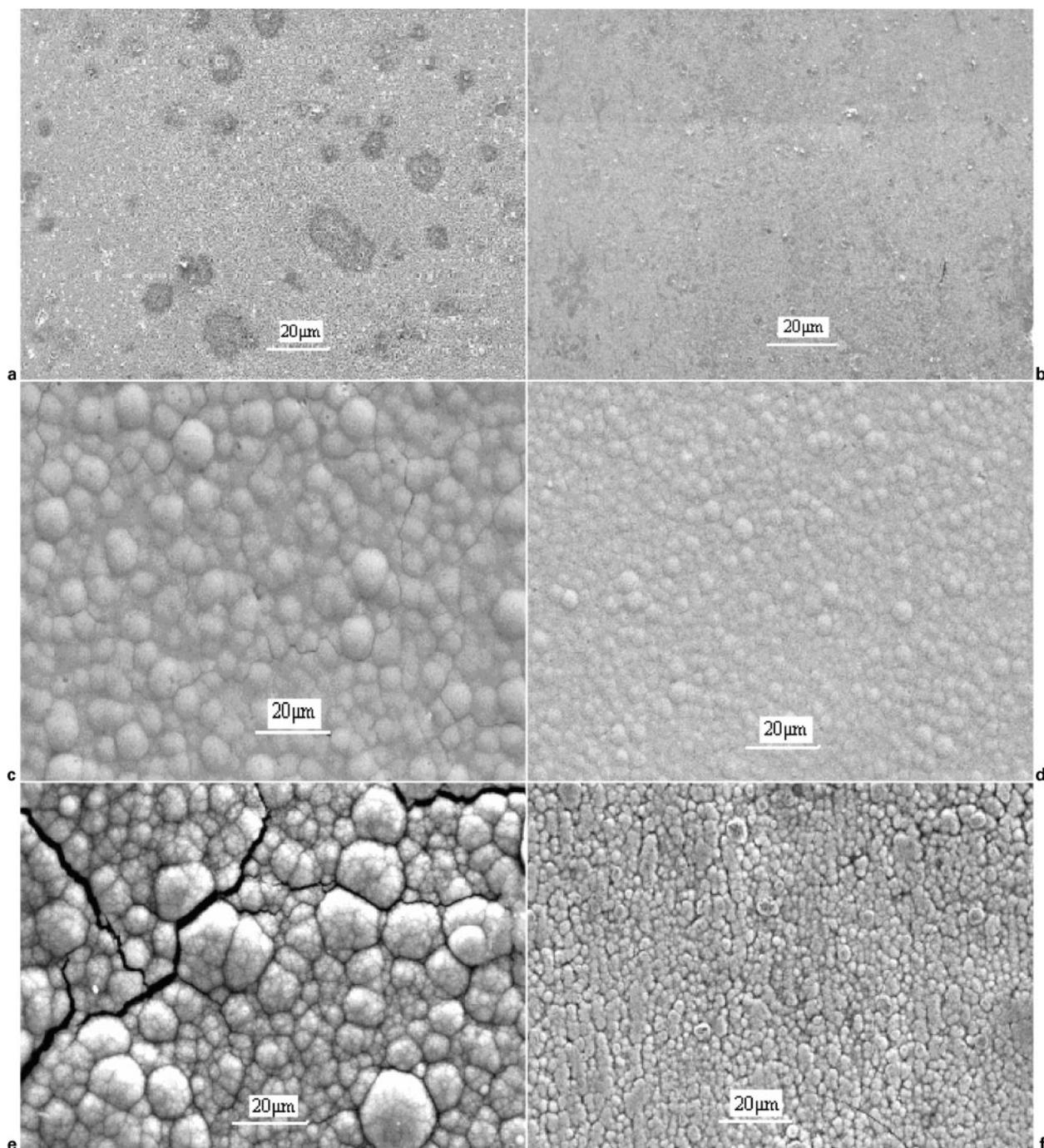
proposed that aluminium chloride prevents olation reaction during electroplating. As pH in the vicinity of the cathode rise due to reduction in hydrogen ions, [Al (H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> will hydrolyse and exert its buffering effect to prevent formation of μ-hydroxy bridged chromium (III) species<sup>49,50</sup> that lead to electrochemical deactivation of chromium complexes.

**Effect of duration of deposition**

The effect of duration of deposition on current efficiency was carried out at high current efficiency conditions of both dc and pc methods and the results are illustrated in Fig. 3. From this figure, a decline in current efficiency was observed as the duration increases. However, the rate of decline in pc deposition was lower than the corresponding dc deposition of all baths. In addition, the rate of decline was more rapid in bath III in both electrolysis methods than the other and it was relatively same in both electrolysis methods of baths II and I. Cathode surface pH increases with increasing duration of deposition, as was established by Tu *et al.*<sup>51</sup> They found that the pH quickly rose to ~8.4 from an initial pH of 3.5 in 45 min in carboxylic acid based baths. This rise in pH causes the formation of the oxy and hydroxyl chromium (III) species, consistent with the reduction in glossiness of the deposit with increase in deposition time because of accumulation of chromium oxide/ hydroxide on the deposit in the case of baths II and I. This is why it is difficult to obtain thick films even with extended plating in baths I–III.

**Morphology**

Figure 4 shows the surface morphologies of electro-deposited chromium obtained from I dc and pc, II dc and pc as well as III dc and pc respectively. Among these, I dc and pc are amorphous with some very fine grains and smooth surface form, but there are numerous pinholes on the surface. Therefore, they will be



a I dc; b I pc; c II dc; d II pc; e III dc; f III pc

#### 4 Surface morphologies of electrodeposited Cr

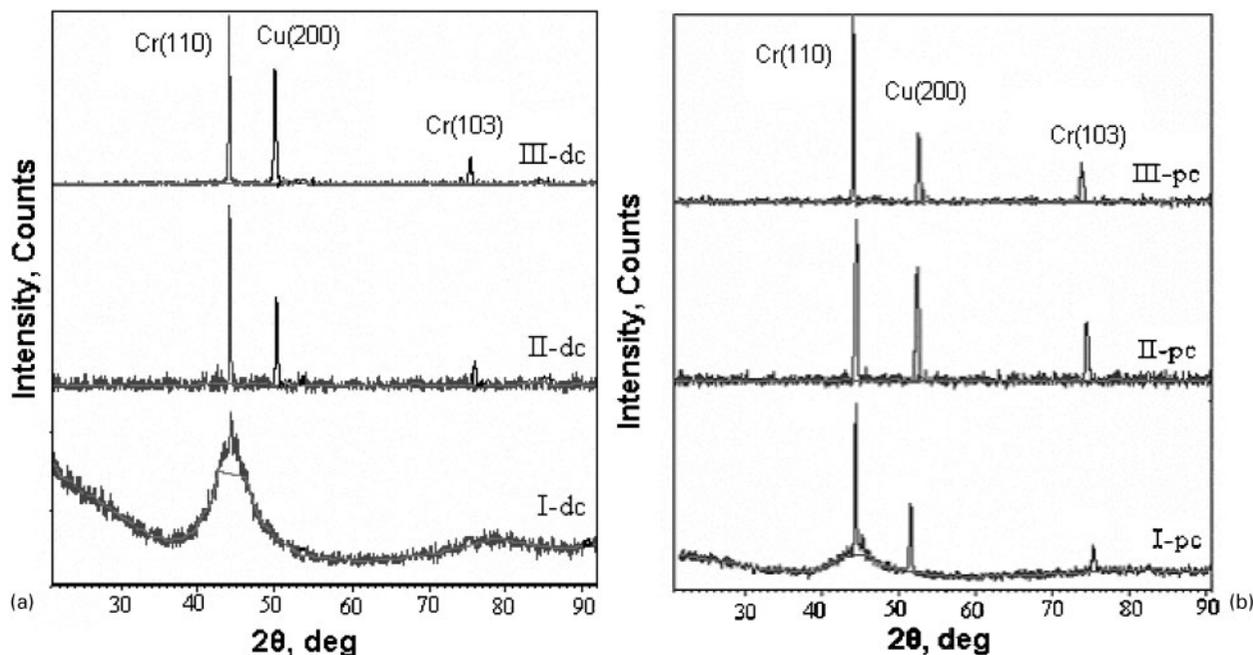
facilitates the corrosion rapidly. The nodular grains are formed on the II dc and pc as well as III dc and pc samples. But III dc has some microcracks and both II dc and pc have crack free, compact microstructure of electrodeposits. Moreover, the pc electrodeposits exhibit small nodular grain size, when compared to dc electrodeposits of all baths.

The X-ray diffraction patterns of electrodeposited chromium consist of three peaks except I dc and figures are shown in Fig. 5. They are strong (110) plane of  $\alpha$ -Cr, weak (103) plane of  $\beta$ -Cr and another one is (200) plane of substrate copper. Both I dc and I pc consist of mixture of amorphous and some crystalline grains of chromium and the other samples are polycrystalline grains. Preferred orientation is represented by the X-ray

peak ratio of  $I_{(110)}/I_{(103)}$ . Grain size is assessed by the Scherrer equation. The value of the preferred orientation and grain size are tabulated in Table 3. The pc method is preferred to growth of  $\beta$ -Cr. Under the suitable T on and T off period, the deposition is nearly pure  $\beta$ -Cr.<sup>27</sup> Grain size of the pc deposition of all samples is decreased, when compared with its corresponding dc deposition samples because the evolution of hydrogen is low.<sup>52</sup> The modification of the growth interface by hydrogen changes the surface energy and growth mechanisms, and then facilitates the formation of smaller grain size.

#### Corrosion experiments

The result from the potentiodynamic polarisation measurements of the Cr coating on the substrates of

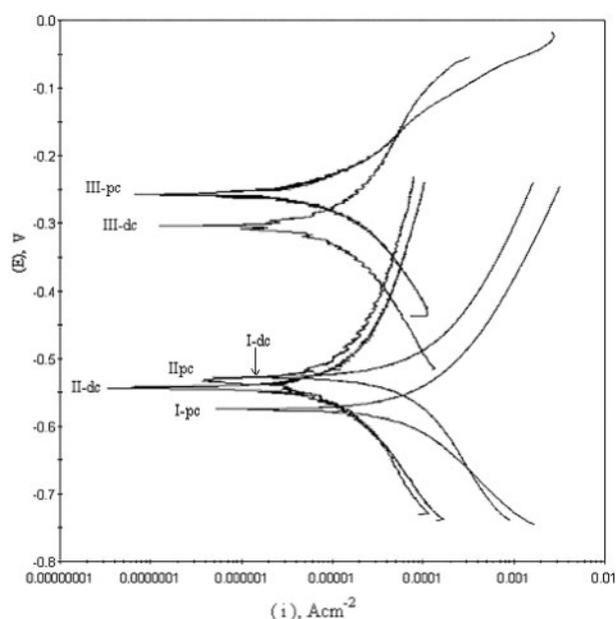


a dc deposit; b pc deposit  
**5 X-ray diffraction patterns of electrodeposited Cr**

**Table 3 Preferred orientation and grain size of electrodeposited Cr**

Bath	dc coatings			pc coatings		
	$I_{(110)}/I_{(103)}$	110 $\alpha$ -Cr grain size, nm	103 $\beta$ -Cr grain size, nm	$I_{(110)}/I_{(103)}$	110 $\alpha$ -Cr grain size, nm	103 $\beta$ -Cr grain size, nm
I	–	42	–	7.4	32	25.15
II	14.2	48	20.6	3.57	36.6	24.7
III	14	51.06	27.4	6.53	38.05	30.85

mild steel in the 3.5 wt-% aqueous NaCl solution are shown in Fig. 6. The curves representing the dc and pc coatings on a mild steel substrate are shown for comparison. The corrosion current density  $I_{corr}$  and corrosion potential  $E_{corr}$  calculated from the intercept of

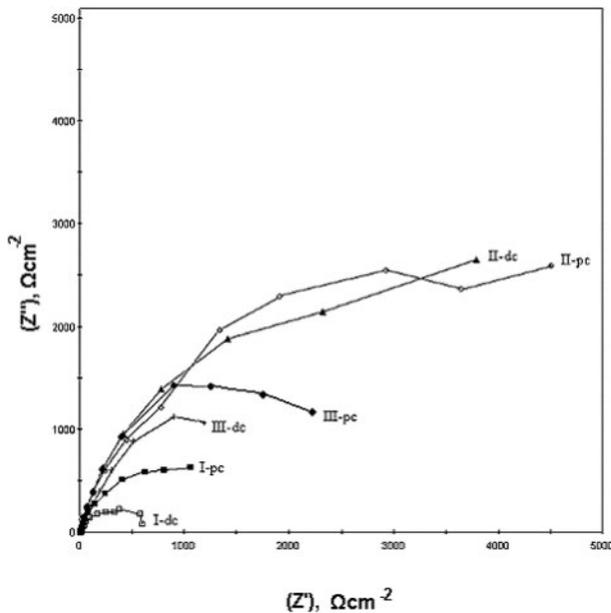


**6 Polarisation curves of electrodeposited Cr in 3.5% NaCl solution**

the Tafel slopes. The corrosion rate in miles per year was estimated from the polarisation curves, and then tabulated in Table 4. In pc coatings corrosion potential were shifted to positive direction and corrosion current were shifted to negative direction, when compared to the corresponding dc coatings. This relation indicates that the pc coatings exhibit better corrosion protection than the dc coatings. In the case of I pc, coating of  $E_{corr}$  was shifted to negative direction even though its corrosion current density value is lower than the dc coating. The corrosion protection is normally proportional to the corrosion current density. Therefore, the I pc coating has more corrosion protection than the dc coating. Moreover, the II pc coating exhibits the best corrosion protection, which is attributed to the compact microstructure.

**Table 4 Electrochemical parameters obtained from potentiodynamic polarisation curves of electrodeposited Cr in 3.5% NaCl solution**

Bath	Electrolysis method	$E_{corr}$ , mv	$I_{corr}$ , $\mu$ A	Corrosion rate, mpy
I	dc	-527	146.2	45.66
	pc	-574.9	132.6	41.43
II	dc	-303.03	18.71	5.84
	pc	-256.7	8.23	2.57
III	dc	-542.9	28.17	8.80
	pc	-533.52	18.7	5.84



7 Nyquist diagrams for electrodeposits in 3.5%NaCl solution

The information about the coating/solution interface and substrate/solution interface can be obtained from electrochemical impedance spectroscopy. Figure 7 shows the impedance response of the Cr coatings in a Nyquist representation. The impedance plots exhibit depressed semi circles, corresponding to a charge transfer resistance in parallel with an equivalent capacitance. The calculated values of circuit elements are (solution resistance  $R_s$ , charge transfer resistance  $R_{ct}$  and double layer capacitance  $C_{dl}$ ) listed in Table 5. The pc coatings of  $R_{ct}$  value of all baths are greater than that of its dc coatings. In addition, it can be found that all fitted corrosion parameters of the electrodeposits vary with the changes of the microstructure. So CH<sub>3</sub>SO<sub>3</sub>H not only reduces hydrogen evolution it also reduces grain size so surface covered fine grained nodular deposit occurred. The corrosion resistance  $R_{ct}$  of II pc coating is greater than that of other samples. Conductivity of the bath III is higher because of lower solution resistance  $R_s$ . Addition of AlCl<sub>3</sub> to the electrolyte,<sup>13</sup> i.e. bath III led to a higher conductivity, improved the brightness of deposits and stabilised the electrolyte over its lifetime to gave ore consistent good quality of deposits.

Table 5 Values of equivalent circuit parameters determined by impedance spectra of electrodeposited Cr in 3.5%NaCl solution

Bath	Electrolysis method	$R_s$ , $\Omega$	$R_{ct}$ , k $\Omega$	$C_{dl}$ , mF
I	dc	6.6	0.653	1.501
	pc	25.9	1.624	0.411
II	dc	58.9	5.314	0.265
	pc	72.5	5.497	0.177
III	dc	8.7	1.840	0.368
	pc	19	2.964	0.299

## Conclusions

Based on the authors' study using dc and pc methods, the authors carried out optimisation of the current efficiency of trivalent chromium electrodeposition from urea formic acid bath with the influence of CH<sub>3</sub>SO<sub>3</sub>H and AlCl<sub>3</sub>. The results indicate that the pc deposition increases the current efficiency and it is preferred to growth of  $\beta$ -Cr than dc deposition. Extended electrodeposition exhibits a decline in current efficiency in all cases. The addition of CH<sub>3</sub>SO<sub>3</sub>H accelerated the deposition of chromium and increases its current efficiency (4–7%) because it increases the hydrogen over potential. The addition of AlCl<sub>3</sub> improved bath stability and brightness of chromium deposits. Corrosion behaviour of electrodeposited II pc in 3.5 wt-%NaCl solution is provided with the best corrosion resistance because the CH<sub>3</sub>SO<sub>3</sub>H reduces the grain size of the chromium by reducing the evolution hydrogen.

## Acknowledgement

One of the authors (Doctor S. Mohan) thanks the Department of Science and Technology New Delhi for a research grant under SERC (Engineering Sciences) scheme no. SR/S3/ME/047/2005.

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