Electrodeposition of Chromium From Eutectic-Based Ionic Liquid

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Abstract: The electrodeposition of chromium from a solution containing chromium chloride ($CrCl_3.6H_2O$) in choline chloride-ethylene glycol (EG) based ionic liquid has been carried out onto a copper cathode by constant current and constant potential methods at different temperature. The influences of various experimental conditions on electrodeposition and the morphology of the deposited layers have been investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It is found that bright metallic coloured chromium coating has been obtained from choline chloride-EG based ionic liquid in presence of 0.10 $g \cdot L^{-1}$ polyethylene glycol and 40 $mL \cdot L^{-1}$ formic acid mixture as surfactant. A very smooth, shiny and crack free Cr coating has been obtained at applied deposition potentials up to -0.70 V and current densities up to -15 $A \cdot m^{-2}$ between 50° C and 80° C. The cathodic current efficiency for the deposition of chromium is about 98.4%.

Keywords: *Electrodeposition; Reline; Ethaline; Chromium; Cyclic voltammetry*

Introduction: Chromium coatings are extensively used for the purposes of decorative, anti-wear and anti-corrosion. It is also used for surface coating of precision mechanical parts, molds, surgical tools, etc. Usually, chromium coatings are electrodeposited from aqueous solutions containing hexavalent chromium (Cr(VI)) [1]. Cr(VI) poses serious health and environmental concerns: is sharply irritating to the mucous membranes of the nose and throat and potentially carcinogenic, so contact with these solutions as well as inhalation of the mist formed during electrodeposition must be avoided. Moreover, due to its toxicity, treatment of waste waters before disposal is mandatory. Legal restriction to the use of Cr(VI) have already been introduced and others are to be expected in the near future [2]. Furthermore European Union has passed the "WEEE" and "RoHs" directives to restrict Cr(VI) in electrical and electronic equipment [3, 4]. United States Environmental Protection Agency (EPA) implicates Cr(VI) as a Group A known human carcinogen, while the same agency classifies the Cr(III) as much as less toxic, being included in Group D carcinogen, not classifiable as to carcinogenicity in humans [5].

These considerations are responsible for the increase interest in less toxic trivalent chromium baths as a greener alternative to hexavalent chromium baths [1]. A number of attempts have been made to offer effective trivalent chromium baths [6-8], unfortunately with limited success due to the complex chemistry of Cr(III) ions [9]. Several proposals have been made to explain the low rate of Cr(0) deposition from Cr(III) baths which involved olation or formation of polymers [10,

11]. The use of ionic liquids might avoid the problems of Cr (III) baths thus representing an attractive alternative for chromium electrodeposition.

Ionic liquids have a number of unique properties that make them extremely interesting solvents for electrodeposition. They can dissolve many organic and inorganic compounds, present a wider electrochemical window and better chemical stability than water, negligible vapour pressure and high thermal and chemical stability. A wide range of metals, metal alloys and semiconductors has been electrodeposited from ionic liquid solutions, including reactive materials such as aluminium, silicon, germanium and titanium, impossible to obtain by electrodeposition from aqueous solutions [12-15]. There have been only few reports using these types of ionic liquids. Abbott et al. reported the deposition of chromium from Cr (III) solutions based on eutectic mixtures of choline chloride with a hydrogen bond donor species. By using this electrolyte the authors obtained an amorphous pale/grey crack-free deposit [16, 17]. These liquids, also known as deep eutectic solvents (DESs), have been used for the deposition of a range of metal coatings including Zn [18], Cu [19], Ni [20], Ag [21] and Co-Sn [22] at high current efficiency and also for metal dissolution processes such as electropolishing [23, 24]. The Effect of water presence on choline chloride-2urea ionic liquid and coating platings from the hydrated ionic liquid has been reported by Cuiling Du et al. [25] In many cases, the use of ionic liquids solvents overcomes the need for strong inorganic acids (e.g., chromic acid, HF, H_3PO_4, H_2SO_4) and highly toxic salts (e.g., cyanide).

The purpose of this present work is to develop a coating of chromium thin films on copper substrate by electrodeposition method from ionic liquids contain Cr(III) ions. The ionic liquid used as solvent is based on eutectic mixtures of choline chloride and hydrogen bond donors such as ethylene glycol.

Experimental Details:
Chemicals: Choline chloride ($HOC_2H_4N^+(CH_3)_3$ Cl^-) ChCl (Aldrich 99%) was, when necessary, recrystallized from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) ($HOCH_2CH_2OH$) (Aldrich>99%) was used as received. Chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) (BDH 98%) was used as obtained. Solution was generally made up to a metal halide concentration in the ranging from 0.01 to 0.1 $mol \cdot L^{-1}$.

The organic additives (surfactants) polyethylene glycol ($HO(CH_2CH_2O)_nCH_2CH_2OH$) (RDH 97%) and formic acid (HCOOH) (Merck 98%) were used as received. Generally, the organic additives were added to the plating bath to a concentration of 0.1 $g \cdot L^{-1}$ polyethylene glycol and 40 $mL \cdot L^{-1}$ formic acid mixture. All other chemicals were used as received.

Preparation of ionic liquid: The eutectic mixture was formed by stirring the two components together, in the stated proportions, at 75° C until a homogeneous, colourless liquid formed. The molar ratio for the eutectic compositions was found to be 1:2 for choline chloride (ChCl) with

ethylene glycol (EG). The ionic liquid, once formulated, was kept in a thermostatic oven at 30° C prior to use.
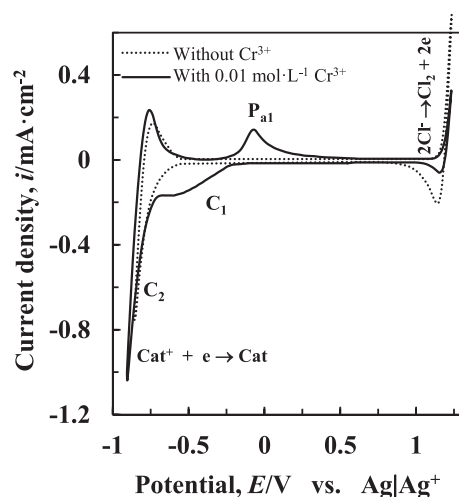

Fig. 1: Cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquid containing 0.01 mol·L^{-1} CrCl$_3$·6H$_2$O at 30° C with a scan rate of 10 mV·s^{-1}
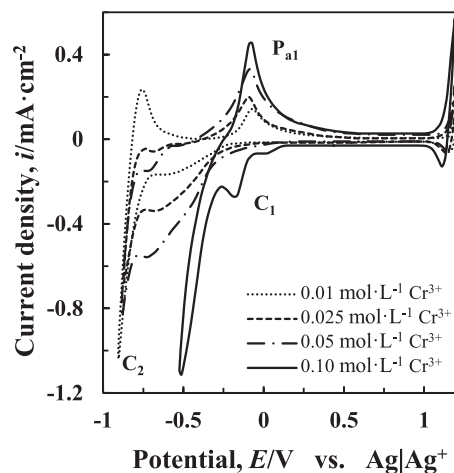
Fig. 2: Effect of CrCl$_3$·6H$_2$O concentrations on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquid at 30° C with a scan rate of 10 mV·s^{-1}

Electrochemical measurements: Electrochemical investigations including potential step chronoamperometry, chronopotentiometry and cyclic voltammetry were carried out using a Hokudo Denko HAB-151 Potentiostat/Galvanostat, Tokyo, Japan, equipped with a potential sweeper. Data were recorded in a computer through data acquisition system (USA) using WinDaq software. A three electrode system consisting of a platinum (50×5×0.1mm^3) working electrode, a platinum (50×5×0.1mm^3) counter electrode and a silver wire quasi-reference electrode were used in all electrochemical studies. The working and counter electrodes were cleaned electrochemically in 1.5 mol·L^{-1} H$_2$SO$_4$–1.5 mol·L^{-1} H$_3$PO$_4$ mixtures, then rinsed with deionised water, and finally dried with acetone prior to use in all measurements. All voltammograms were obtained at 30° C with various scan rates ranging from 5 to 100 mV·s^{-1}. A silver wire (immersed in ethaline) quasi-reference electrode was used in all electrochemical experiments which have been shown to have stable reference potential in chloride based eutectics. All potentials in this work are quoted with respect to this Ag|1:2 ChCl-EG reference electrode which will be written as Ag|Ag(I) (note the reference potential will change slightly with melts of different compositions).

Deposition of chromium: The electrodeposition of chromium was carried out onto copper cathode under constant current and constant potential methods from ionic liquid (ethaline) containing CrCl$_3$·6H$_2$O in the temperature ranging from 50 to 80°C. The applied current densities and potentials for depositing chromium in different plating operations were -5.0 ~ -21.0 A·m^{-2}

and -0.40 ~ -0.80V, respectively. The depositing time in different plating operations was 2 ~ 3 h. Following each deposition, the resulting deposit was soaked firstly in toluene, then in deionised water, and finally washed with acetone to remove the residual ionic liquid. The deposit was then dried with cold air.

Deposit characterization: The surface morphologies of the chromium electrodeposits obtained on copper from 1:2:0.1 (mole ratio) ChCl:EG:CrCl$_3$·6H$_2$O ionic liquid in presence of 0.10 g·L^{-1} polyethylene glycol and 40 mL·L^{-1} formic acid mixture at 80°C by constant potential and constant current methods were examined with scanning electron microscope (XL 30 SEM, PHILIPS). X-ray diffraction analysis of chromium electrodeposit obtained on copper from ChCl:2EG:0.1CrCl$_3$·6H$_2$O ionic liquid in presence of surfactant at -0.50 V and 80°C was performed with a Philips PW 1716 diffractometer using Cu$K\alpha$ radiation (40 kV, 25mA) to explore the crystal structure of the deposits.
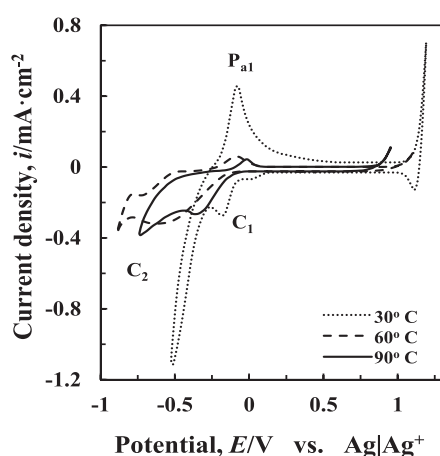

Fig. 3: Effect of temperature on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquid containing 0.1 mol·L^{-1} CrCl$_3$·6H$_2$O with a scan rate of 10 mV·s^{-1}.
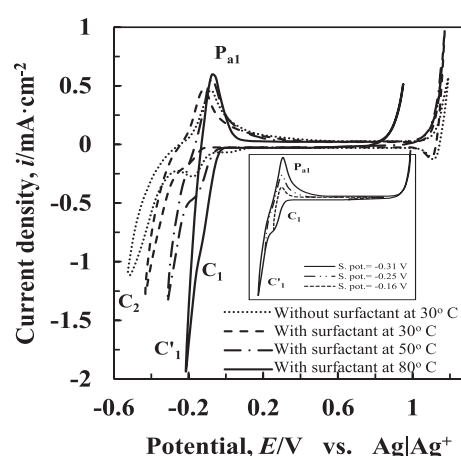
Fig. 4: Effect of surfactant and temperature on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquids containing 0.10 mol·L^{-1} CrCl$_3$.6H$_2$O.

Results and Discussion:

Cyclic voltammetry of Cr(III) in ChCl:2EG (ethaline): The cyclic voltammogram recorded on a platinum electrode in 1:2:0.01 (mole ratio) ChCl:EG:CrCl$_3$·6H$_2$O ionic liquid at 30°C with a scan rate of 10mV·s^{-1} is shown in Fig. 1. The rest potentials is +0.549V. The scan towards negative direction consists of first reduction wave C$_1$ with the current starting to increase at -0.144 V. Additional reduction wave C$_2$ is observed with the current again starting to increase at -0.677 V. The reverse scan consists of first oxidation peak P$_{a1}$ (-0.062 V). Additional oxidation wave is observed with the current again starting to increase at +1.113 V. Compared with the voltammogram obtained in the absence of CrCl$_3$·6H$_2$O, the dotted curve in Fig. 1, the reduction wave appeared at -0.72 V correspond to the reduction of cationic species (Cat^{+}) into this ionic

liquid, while the oxidation wave appeared at +1.05 V to the oxidation of chloride ions (anions) to molecular/gaseous chlorine according to following reaction [19, 20]:

$$2Cl^-_{(ad)} \rightarrow Cl_2\uparrow + 2e^-$$
eq.1

Figure 2 shows the effect of $CrCl_3 \cdot 6H_2O$ concentrations on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquid at 30°C with a scan rate of 10 mV·s^{-1}. It is readily seen from these voltammograms that the magnitudes of current densities are increased with the increase of $CrCl_3 \cdot 6H_2O$ concentrations added into the ionic liquids. The same phenomena are also observed on the oxidation peak P_{a1} in Fig. 2, which also shows the magnitude of peak current densities are increased with the increase of the $CrCl_3 \cdot 6H_2O$ concentrations added into the ionic liquid. The increase of the magnitudes of the reduction current densities with the increase of $CrCl_3 \cdot 6H_2O$ concentrations added into the ionic liquid indicate the higher discharge rates of chromium ions at low over-potentials. Similar result has been reported for the deposition of Cu [19] and Ag [21] in this ionic liquid.
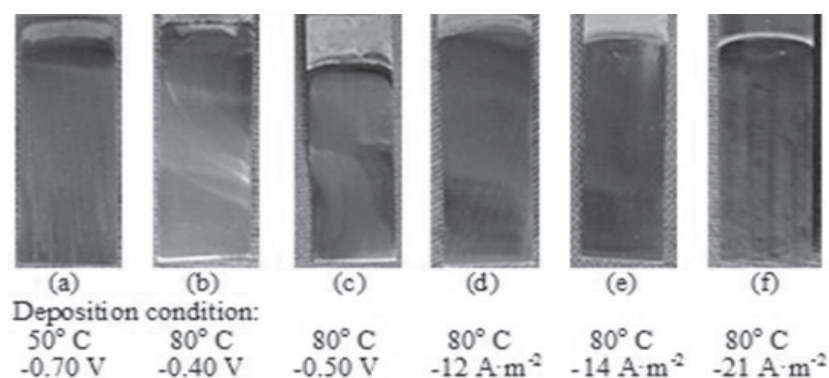

Fig. 5: Camera images of electrolytic chromium deposits on copper from ChCl:2EG:0.1CrCl$_3$·6H$_2$O ionic liquid in presence of 0.10 g·L^{-1} polyethylene glycol and 40 mL·L^{-1} formic acid mixture as surfactant at different deposition conditions.

Figure 3 shows the effect of temperature on the cyclic voltammograms recorded on a platinum electrode in 1:2:0.10 (mole ratio) ChCl:EG:CrCl$_3$·6H$_2$O ionic liquid with a scan rate of 10 mV·s^{-1}. It is readily seen from the voltammograms that the onset potentials of chromium deposition and dissolution are unchanged with the rise of temperature. On the other hand, the magnitudes of the deposition and dissolution current densities decrease with the increase of temperature. This indicates the formation of inert metallic complex on increasing the temperature.

Figure 4 shows the effect of surfactant (0.10 g·L^{-1} polyethylene glycol and 40mL·L^{-1} formic acid mixture) and temperature on the cyclic voltammograms recorded on a platinum electrode in 1:2:0.1 mole ratio of ChCl:EG:CrCl$_3$·6H$_2$O ionic liquid with a scan rate of 10 mV·s^{-1}. It is readily seen from the voltammograms that the onset potential of chromium deposition and

dissolution moves towards anodic and cathodic direction, respectively on the addition of 0.10 g·L⁻¹ polyethylene glycol and 40 mL·L⁻¹ formic acid mixture as surfactant and with the rise of temperature. The difference between the onset voltage of chromium deposition and dissolution is 0.137 V (0.280 V without surfactant) indicating the quasi-reversible nature of chromium deposition changes to reversible in nature in this ionic liquid on the addition of surfactant at 80° C. The reason behind this may be due to the change of the metallic complexes in this ionic liquid at high temperature. On the other hand, the magnitudes of the reduction and oxidation current densities are also increase on the addition of surfactant and with the rise of temperature. Cathodic sweeping potential studies on the cyclic voltammograms (inside of Fig. 4) show that the first (C_1) and second (C'_1) reduction waves correspond to the first oxidation peak (P_{a1}). Pure chromium has been deposited from this ionic liquid containing $CrCl_3.6H_2O$ in presence of 0.10 g·L⁻¹ polyethylene glycol and 40 mL·L⁻¹ formic acid mixture as surfactant at temperature above 45°C by constant potential and constant current methods.
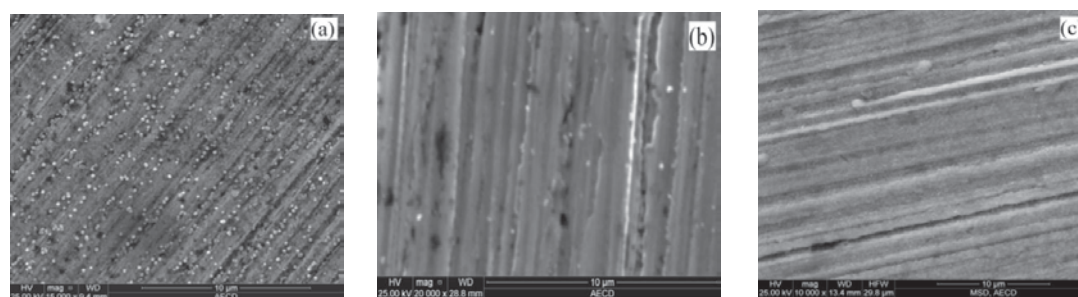

Fig. 6 SEM images of chromium electrodeposits on copper substrate obtained from 1:2:0.1 (mole ratio) ChCl:EG:CrCl₃·6H₂O ionic liquid in presence of 0.10 g·L⁻¹ polyethylene glycol and 40 mL·L⁻¹ formic acid mixture as surfactant at 80°C. Applied deposition potential/current density: (a) -16.0 A·m⁻², (b) -0.60 V, (c) -0.50 V.

Electrodeposition of Chromium from ethaline: The camera images of the electrodeposited chromium layers on copper cathode under constant potential and constant current methods from EG based ionic liquid containing $CrCl_3.6H_2O$ in presence of 0.10 g·L⁻¹ polyethylene glycol and 40 mL·L⁻¹ formic acid mixture as surfactant are shown in Fig. 5. All of the deposits obtained on copper substrate at the applied deposition potentials up to -0.70 V (Fig. 5(a), 5(b) and 5(c)) and applied deposition current densities up to -14.0 A·m⁻² (Fig. 5(d) and 5(e)) in the temperature ranging from 50 to 80°C appear to be smooth, shiny and bright metallic coloured chromium. There is no apparent rupture on the deposit surface and the deposits do not peeling off by hand scratching. However, the deposit obtained at the applied current density >-20.0 A·m⁻² is not smooth and bright metallic coloured (Fig. 5(f)) due to high deposition over potential.

Figure 6 shows the SEM images of chromium electrodeposit obtained from ChCl:2EG:0.1CrCl₃·6H₂O in presence of 0.10 g·L⁻¹ polyethylene glycol and 40 mL·L⁻¹ formic acid mixture by constant potential (Fig. 6(a)) and constant current (Fig. 6(b) and 6(c)) methods. The electrodeposited crystals are nodular in shape and in the order of 0.25~ 0.5 μm in size (Fig.

6(a)). There is no rupture on the deposit surface and it does not peeling off. The thickness of the deposited layers are approximately 3 ~ 5 μm, which has been calculated by weight gain method.
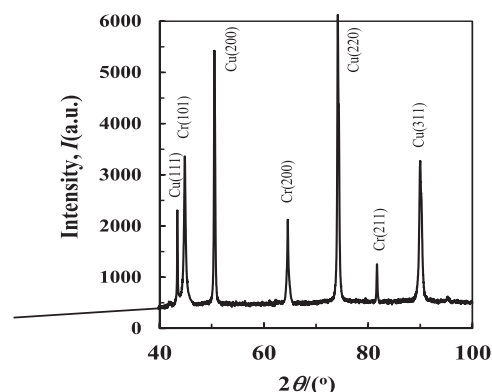

Fig. 7: X-ray diffraction pattern of chromium electrodeposit obtained on copper from molar ratio of 1:2:0.1 in ChCl:EG:CrCl$_3$·6H$_2$O ionic liquid containing 0.10 g·L^{-1} polyethylene glycol and 40 mL·L^{-1} formic acid mixture as surfactant at 80° C and -0.50 V.

The acquired diffraction pattern for the deposit obtained from 1:2:0.1 mole ratio of ChCl:EG:CrCl$_3$·6H$_2$O ionic liquid in presence of surfactant (0.10 g·L^{-1} polyethylene glycol and 40 mL·L^{-1} formic acid mixture) at applied deposition current density of -12.0 A·m^{-2} and deposition temperature of 80°C is shown in Fig. 7. The diffraction peaks at $2\theta = 44.4°$, 64.6° and 81.7° are for Cr(100), Cr(200) and Cr(211), respectively. The diffraction peaks are very sharp, indicating the deposit has crystalline structure. The deposits obtained with this type of crystal structure are very smooth, shiny and have good adherence to the surface. The current efficiency for the deposition of pure chromium is about 98.4%. However, additional diffraction peaks at 2θ = 43.31°, 50.45°, 74.126° and 89.94° corresponding to Cu(111), Cu(200), Cu(220) and Cu(311) (base metal) respectively, are also observed in Fig. 7. The same experiment has also been carried out by urea based ionic liquid (reline); however chromium deposit could not obtain at any temperature and even on the addition of surfactant.

Conclusions: This work shows that ionic liquid based on eutectic mixtures of choline chloride and hydrogen bond donors such as ethylene glycol can be used as electrochemical solvents. Smooth and good adhering bright metallic coloured chromium can only be electrodeposited onto copper cathode from EG based ionic liquid (ethaline) containing CrCl$_3$·6H$_2$O in presence of 0.10 g·L^{-1} polyethylene glycol and 40 mL·L^{-1} formic acid mixture as surfactant between 50° C and 80° C. The chromium electrodeposits obtained at applied deposition potentials up to -0.70 V and applied deposition current densities up to -15 A·m^{-2} are very smooth, shiny, good adhering and of uniform size. SEM images indicate the electrodeposited Cr crystals are nodular in shape and in the order of 0.25~ 0.5 μm in size. The deposits obtained at high applied deposition current densities (>-20 A·m^{-2}) are black in colour. The diffraction pattern indicates the deposited Cr has crystalline structure. Chromium electrodeposits cannot be obtained from urea based ionic liquid (reline) at any temperature and even on the addition of surfactant.

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