



EFFECT OF SOME PARAMETERS ON CYCLIC VOLTAMMETRY OF CHROMIUM IN RELINE

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ABSTRACT

Studies of cyclic voltammetry (CV) were used to investigate the interaction behavior of chromium from a solution containing chromium chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) in ionic liquid based on choline chloride urea called reline. The interaction experiments were performed in variation of cathodic sweeping potential, scan intensity, concentration of metal ions, temperature effects and surfactants. The effects of different experimental conditions and some parameters on cyclic voltammetry were investigated using a potentially sweeper-equipped Potentiostat/Galvanostat. The electrochemical activity of Cr(III) on platinum substrates was studied at various scan rate values and different potential windows within the temperature range from room temperature to 90 °C. The method of cathodic reduction has received special attention. The cyclic voltammograms obtained at different scan rate values showed that the reduction process for Cr(III) is strongly governed by the diffusion of the electro-active species to the electrode surface. It was suggested that the chromium ion reduction mechanism occurs in a one-step process that exchanges three electrons and is controlled by the diffusion of chromium ions in the ionic liquid.

1. INTRODUCTION

The most commonly used technique for gathering qualitative knowledge about electrochemical reactions is cyclic voltammetry. This provides a fast location of the redox potentials of the electro active cells. Diagnostic criteria may be established by correlating kinetic and experimental parameters such that unknown structures can be identified by observing the variations of peak current, half peak potentials, or anodic peak currents ratio and cathodic peak currents as a function of the voltage scan rate. When the electron transmission reaction is irreversible system, the peak to peak distance is wide while the peak to peak distance is low in the reversible system. The effect on the voltammetric wave of a chemical reaction would depend on its rate, as opposed to the time taken to perform the experiment. In the kinetic parameter the ratio of the rate constant to the voltage scan rate appears. This, in addition, allows such relationships to be used to determine diagnostic standards for examining unknown structures. The author investigated the reduction of Cr(III) in reline using cyclic voltammogram.

Chromium is used widely for cosmetic, antiwear, and anti-corrosion coating purposes. This is also used for surface coating of mechanical precision components, molds, surgical equipment, etc. Chromium coatings are normally electrodeposited from aqueous solutions that contain hexavalent chromium (Cr(VI))[1]. Cr(VI) poses serious health and environmental concerns: it is highly irritating to nose and throat mucous membranes and is potentially carcinogenic.

There have been a number of attempts to give successful trivalent chromium baths [2],[3],[4],[5],[6][7], unfortunately with limited success due to the complex Cr(III) ion chemistry [8]. Many suggestions have been made to explain the low Cr(0) deposition rate from Cr(III) baths that involved polymer formation [9],[10]. The use of ionic liquids could avoid the problems of baths with Cr(III) thus representing an attractive alternative for electrodeposition with chrome.

Ionic liquids possess a number of unique properties which make them extremely interesting electrodeposition solvents. We can dissolve many organic and inorganic compounds, have a broader electrochemical range, and have higher chemical stability than water, low vapor pressure, and good thermal and chemical stability. A wide range of metals, metal alloys and semiconductors were electrodeposited from ionic liquid solutions, including reactive materials such as copper, silicon, germanium and titanium, which could not be obtained from aqueous solutions by electrodeposition [11],[12],[13],[14]. These types of ionic liquids have been used only in few reports. Abbott *et al.* reported chromium deposition from Cr(III) solutions based on eutectic mixtures of choline chloride with a donor hydrogen bond species. The authors obtained an amorphous pale/gray crack-free deposit by using this electrolyte [15],[16]. Such liquids, also known as Deep Eutectic Solvents (DESs), were used to deposit a number of metal coatings like Zn [17], Sn [18], Cu [19], [20], Ni [21], [22], and Ag [23],[24] at high current efficiency and also for metal dissolution processes such as electropolishing [25],[26]. The use of ionic liquid solvents in certain situations overcomes the need for strong inorganic acids (e.g., chromic acid, HF, H₃PO₄, H₂SO₄), and extremely toxic salts (e.g., cyanide).

This paper presents an electrochemical analysis of the actions of Cr(III) ions in an ionic liquid called reline, in the presence of surfactants, on the platinum electrode at room temperature range up to 90 ° C using cyclic voltammetric technique. The ionic liquid used as solvent is based on the choline chloride and urea eutectic mixtures.

2 EXPERIMENTAL DETAILS

2.1 Chemicals

Choline chloride (HOC₂H₄N⁺(CH₃)₃Cl⁻) ChCl (Aldrich 99%) was recrystallized from absolute ethanol, filtered and dried under vacuum. Ethylene glycol (EG) (HOCH₂CH₂OH) (Aldrich >99%) was used as obtained. Chromium chloride hexahydrate (CrCl₃·6H₂O) (BDH

98%) was used as received. Generally 0.01 to 0.1 mol·L⁻¹ ranging concentration of metal halide solution was made.

The organic additives (surfactants) polyethylene glycol (HO(CH₂CH₂O)_nCH₂CH₂OH) (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·L⁻¹ polyethylene glycol and 40 mL·L⁻¹ formic acid mixture. All other chemicals were used as received.

2.2 Preparation of ionic liquid

The eutectic mixture was formed by mixing together the two components at 75 °C in the specified proportions, until a homogeneous, colorless liquid was formed. For choline chloride (ChCl) with urea, the molar ratio for the eutectic compositions was found to be 1:2. When developed, the ionic liquid was stored in a thermostatic oven at 30 °C until use.

2.3 Electrochemical measurements

A Hokudo Denko HAB-151 Potentiostat/Galvanostat, Tokyo, Japan, fitted with a potential sweeper, was used to perform electrochemical investigations including potential phase chronoamperometry, chronopotentiometry and cyclic voltammetry. Using WinDaq software, data were recorded in a computer via a data acquisition system (USA). A three electrode system consisting of a platinum (50 × 5 × 0.1 mm³) working electrode, a platinum (50 × 5 × 0.1 mm³) 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 H₂SO₄–1.5 mol·L⁻¹ H₃PO₄ mixtures, then rinsed with deionised water, and finally dried with acetone prior to use in all measurements. All voltammograms with varying scan levels ranging from 5 to 100 mV·s⁻¹ were obtained at 30 °C. In all electrochemical experiments, a silver wire (immersed in ethaline) quasi-reference electrode was used which has been shown to have stable reference potential in chloride dependent eutectics. All potentials in this work are quoted with respect to this Ag|1:2 ChCl-urea reference electrode which will be written as Ag|Ag(I) (note the reference potential will change slightly with melts of different compositions). The overall instrumental cell set-up for the cyclic voltammetry experiment is shown in figure 1.



Fig. 1 The instrumental set-up of the three electrodes cell connected with the potentiostat/galvanostat via transducer with winDaq software installed computer system.

3. RESULT AND DISCUSSION

3.1 Cyclic voltammetry of Cr(III) in ChCl:2urea (Reline)

Figure 2 shows the cyclic voltammogram recorded on a platinum electrode in 1:2:0.01 (mole ratio) ChCl:urea:CrCl₃·6H₂O ionic liquid at 30 °C with a scan rate of 10 mV·s⁻¹. The rest potentials is +0.742 V. The scan towards negative direction consists of first reduction wave C₁ with the current starting to increase at -0.126 V. Additional reduction wave C₂ is observed with the current starting to increase again at -0.732 V. The reverse scan consists of first oxidation peak P_{o1} (-0.498 V). Additional oxidation wave is observed with the current starting to increase again at +1.233 V. Compared with the voltammogram obtained in the absence of CrCl₃·6H₂O, the

dotted curve in Fig. 2, 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 +1.108 V to the oxidation of chloride ions (anions) to molecular/gaseous chlorine according to following reaction.

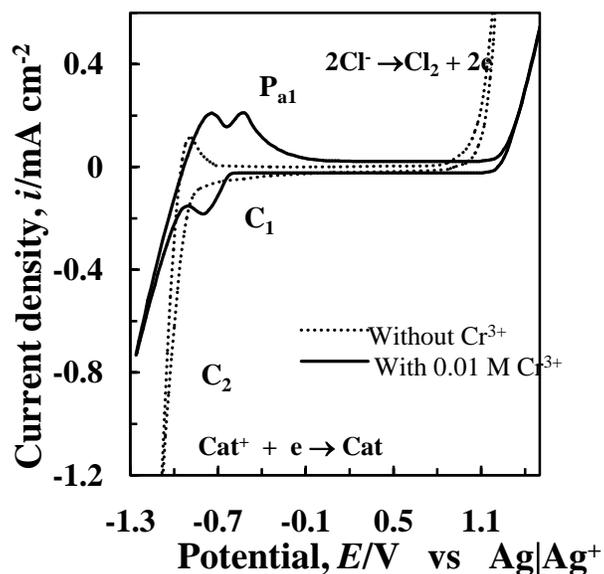


Fig. 2 Cyclic voltammograms recorded on a platinum electrode in ChCl:2 urea ionic liquid containing 0.01 mol·L⁻¹ CrCl₃·6H₂O at 30 °C with a scan rate of 10 mV·s⁻¹.

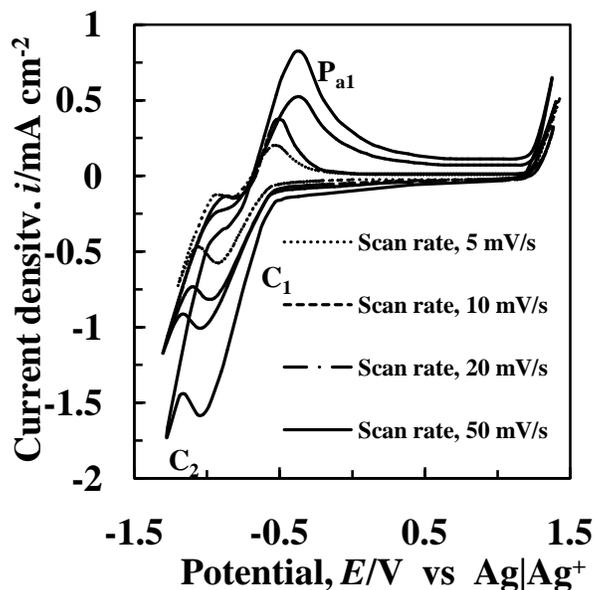


Fig. 3 Effect of scan rate on the cyclic voltammograms recorded on a platinum electrode in 1:2:0.10 (mole ratio) ChCl:urea:CrCl₃ ILs with surfactant at 30°C.

Figure 3 shows the effect of scan rate on the cyclic voltammograms recorded on a platinum electrode in 1:2:0.10 (mole ratio) ChCl:urea:CrCl₃ ILs at 30 °C. It is readily seen from the voltammograms that the first reduction waves C_1 and C'_1 correspond to the oxidation peaks P_{a1} . The increase of the negative current in the first reduction wave (C_1) is obviously associated with the reduction of chromium ion to metallic state according to the following reaction:



In ChCl:2urea IL, only a single stripping peak is observed in the voltammogram at -0.64 V (P_{a1}). It is also clear from the voltammograms that the magnitude of the current densities is much smaller in ChCl:2urea IL this is a consequence of slow mass transport due to the high viscosity of reline.

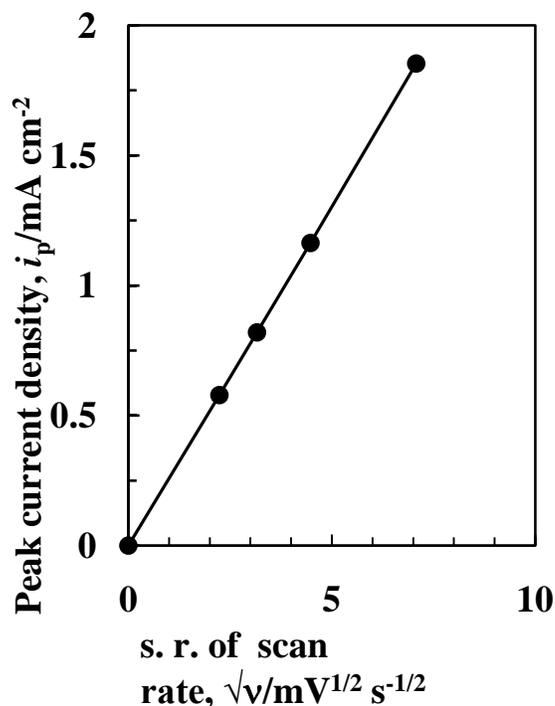


Fig. 4 Square route of scan rate Vs peak current density recorded on a platinum electrode in ChCl:2urea:0.1 CrCl₃ ILs at 30 °C.

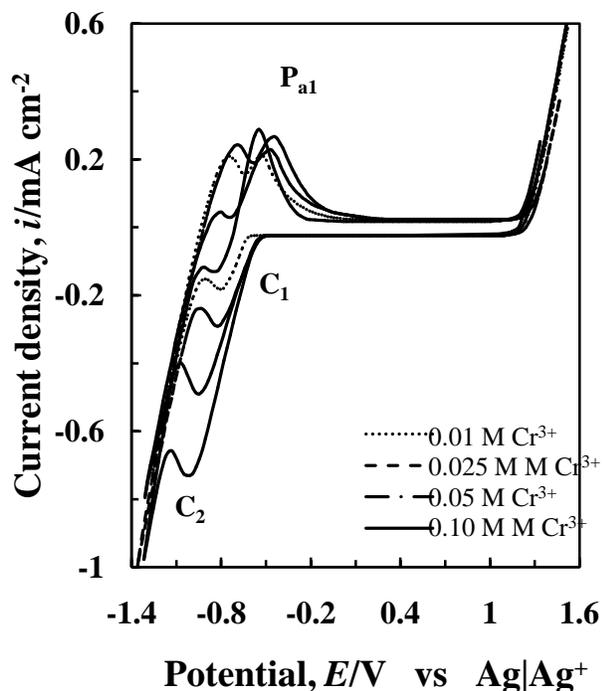


Fig. 5 Effect CrCl₃·6H₂O concentrations on the cyclic voltammograms recorded on a platinum electrode in ChCl:2urea ionic liquid at 30 °C with a scan rate of 10 mV·s⁻¹.

From Fig. 4, it is evident that for a reversible system, peak potential E_p is independent of scan rate (v), and peak current density (i_p) is proportional to the square root of scan rate ($v^{1/2}$). It is evident from Fig. 4 that the peak potential for the redox reaction of Cr(III)/Cr(0) couple show linear feature. But the peak potentials for the redox reaction are believed to be almost independent of the low scan rates indicating reversible in nature. According to Randles-Sevcik equation [27], the linear increases in the cathodic peak current densities i_p with the square root of scan rate, as shown in Fig. 4, indicate that the reduction process of chromium ions in ChCl:2urea based IL is controlled by diffusion.

Figure 5 shows the effect of CrCl₃·6H₂O 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. Through these voltammograms it is readily seen that the magnitudes of current densities are increased with the increased concentrations of CrCl₃·6H₂O applied to the ionic liquids. The same phenomena are also observed on the oxidation peak P_{a1} in Fig. 5, which also shows the magnitude of peak current densities are increased with the increase of the CrCl₃·6H₂O concentrations added into the ionic liquid. The increase in the magnitudes of reduction current densities with the rise in concentrations of CrCl₃·6H₂O applied to the ionic liquids shows the higher discharge levels of chromium ions at low overpotentials.

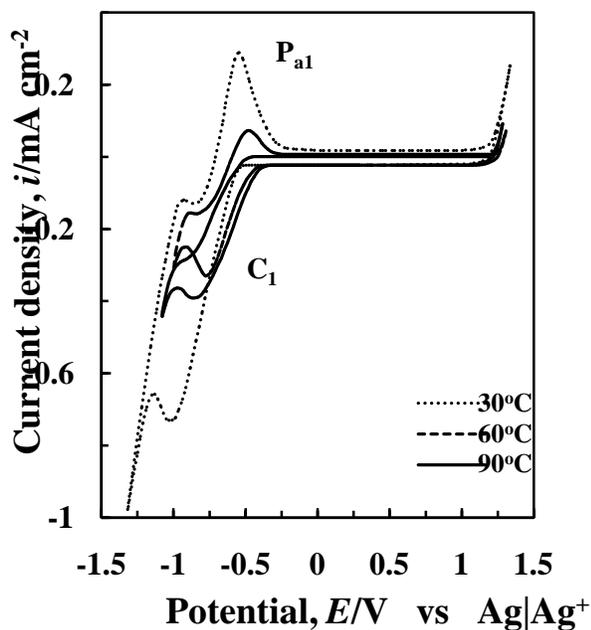


Fig. 6 Effect temperature on the cyclic voltammograms recorded on a platinum electrode in ChCl:2urea ionic liquid containing $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ CrCl}_3\cdot 6\text{H}_2\text{O}$ with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$.

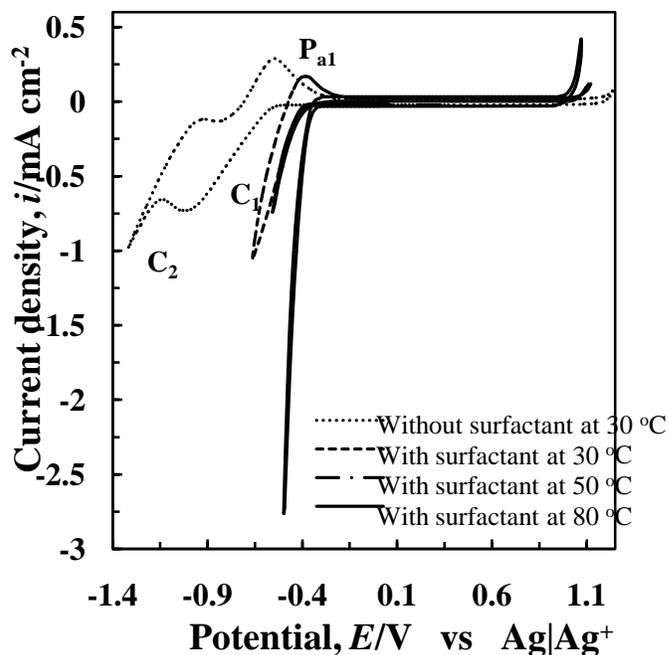


Fig. 7 Effect of surfactant and temperature on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG ionic liquids containing $0.10 \text{ mol}\cdot\text{L}^{-1} \text{ CrCl}_3\cdot 6\text{H}_2\text{O}$.

Figure 6 shows the temperature effect of ChCl:EG: $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ ionic fluid with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$ on the cyclic voltammograms measured on a platinum electrode in 1:2:0.10 (mole ratio). From voltammograms it is readily seen that the starting potentials of chromium deposition and dissolution are unchanged with temperature rise. At the other hand, with the rise in temperature the magnitudes of the deposition and dissolution current densities decrease. This implies inert metallic complex being formed to increase the temperature.

Figure 7 shows the effect of surfactant ($0.10 \text{ g}\cdot\text{L}^{-1}$ polyethylene glycol and $40 \text{ mL}\cdot\text{L}^{-1}$ formic acid mixture) and temperature on the cyclic voltammograms obtained on a platinum electrode in 1:2:0.1 mole ratio of ChCl:EG: $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ ionic liquid with a scan rate of $10 \text{ mV}\cdot\text{s}^{-1}$. From the voltammograms it is easily shown that the capacity for chromium deposition and dissolution starts in anodic and cathodic direction, respectively on the addition of $0.10 \text{ g}\cdot\text{L}^{-1}$ polyethylene glycol and $40 \text{ mL}\cdot\text{L}^{-1}$ formic acid mixture as surfactant and with the rise of temperature. The difference between the onset voltage of chromium deposition and dissolution is 0.168 V (0.354 V without surfactant) suggesting the quasi-reversible existence of improvements in the reversible form of chromium deposition in this ionic liquid by applying a surfactant at $80 \text{ }^\circ\text{C}$. The explanation behind this may be due to the high change in temperature of the metallic complexes in this ionic liquid. At the other hand, with the introduction of surfactant and the increase in temperature, the magnitudes of the reduction and oxidation current densities are also rising. Cathodic sweeping potential studies on the cyclic voltammograms (inside of Fig. 7) show that the first (C_1) and second (C'_1) reduction waves correspond to the first oxidation peak (P_{a1}). With the presence of $0.10 \text{ g}\cdot\text{L}^{-1}$ polyethylene glycol and $40 \text{ mL}\cdot\text{L}^{-1}$ formic acid mixture as a surfactant at temperatures above $45 \text{ }^\circ\text{C}$, pure chromium was extracted from this ionic liquid containing $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ by constant potential and constant current methods.

4. CONCLUSIONS

This research shows that ionic liquid can be used as electrochemical solvents, based on eutectic mixtures of choline chloride and hydrogen bond donors such as ethylene glycol. With the increased concentrations of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ added to the ionic liquids suggest the higher discharge levels of chromium ions at low overpotentials. Inert metallic complex is formed on temperature rises. Regardless of the transition of metallic compounds in this ionic liquid at high temperatures, the quasi-reversible aspect of chromium deposition shifts to reversible in aspect when surfactant is applied at 80 °C. The magnitudes of the existing densities of reduction and oxidation are therefore increased when the surfactant is applied and the temperature rise.

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REFERENCES

- [1] A.P. Abbott, K.S. Ryder, U. Konig, "Electrofinishing of metals using eutectic based ionic liquids", *Trans. Inst. Met. Finish.*, vol. 86, no. 4, pp. 196–204, Jul. 2008.
- [2] G. Hong, K.S. Siow, G. Zhiqiang, A.K. Hsieh, "Hard chromium plating from trivalent chromium solution", *Plat. Surf. Finish.*, vol. 88, no. 3, pp. 69-75, May. 2001.
- [3] Y.B. Song, D.-T. Chin, "Current efficiency and polarization behavior of trivalent chromium electrodeposition process", *Electrochim. Acta*, vol. 48, no. 4, pp. 349-356, Dec. 2002.
- [4] S.C. Kwon, M. Kim, S.U. Park, D.Y. Kim, D. Kim, K.S. Nam, Y. Choi, "Characterization of intermediate Cr-C layer fabricated by electrodeposition in hexavalent and trivalent chromium baths", *Surf. Coat. Technol.*, vol. 183, no. 2-3, pp. 151-156, May. 2004.
- [5] F.I. Danilov, V.S. Protsenko, T.E. Butyrina, E.A. Vasil'eva, A.S. Baskevich, "Electroplating of chromium coatings from Cr(III)-based electrolytes containing water soluble polymer", *Prot. Met.*, vol. 42, no. 6, pp. 560–569, Dec. 2006.
- [6] B.S. Li, A. Lin, "Study of hard chromium plating from trivalent chromium electrolyte", *Key Eng. Mat.*, vol. 373–374, pp. 200-203, Mar. 2008.
- [7] G. Saravanan, S. Mohan, "Structure, current efficiency, and corrosion properties of brush electrodeposited (BED) Cr from Cr(III) dimethyl formamide (DMF)-bath", *J. App. Electrochem.*, vol. 40, no. 1, pp. 1-6, Jan. 2010.
- [8] S. Surviliene, V. Jasulaitiene, O. Nivinskiene, A. Cesuniene, "Effect of hydrazine and hydroxyl aminophosphate on chrome plating from trivalent electrolytes", *App. Surf. Sci.*, vol. 253, no. 16, pp. 6738–6743, June. 2007.
- [9] S. Surviliene, O. Nivinskiene, A. Cesuniene, A. Selskis, "Effect of Cr(III) solution chemistry on electrodeposition of chromium", *J. App. Electrochem.*, vol. 36, no. 6, pp. 649–654, June. 2006.
- [10] V.N. Korshunov, L.N. Vykhodtseva, V.A. Safonov, "Reduction of trivalent chromium ions on stationary mercury electrode in concentrated LiCl solutions", *Russ. J. Electrochem.*, vol. 40, no. 4, pp. 466–469, April. 2004.
- [11] F. Endres, "Ionic liquids: Solvents for the electrodeposition of metals and semiconductors", *Chem. Phys. Chem.*, vol. 3, no. 2, pp. 144-154, Feb. 2002.
- [12] S.Z.E. Abedin, N. Borissenko, F. Endres, "Electrodeposition of nanoscale silicon in a room temperature ionic liquid", *Electrochem. Commun.*, vol. 6, no. 5, pp. 510-514, May. 2004.

- [13] F. Endres, M. Bukowski, R. Hempelmann, H. Natter, "Electrodeposition of nanocrystalline metals and alloys from ionic liquids", *Angew. Chem. Int. Ed.*, vol. 42, no. 29, pp. 3428-3430, July. 2003.
- [14] I. Mukhopadhyay, C.L. Aravinda, D. Borissov, W. Freyland, "Electrodeposition of Ti from $TiCl_4$ in the ionic liquid 1-methyl-3-butyl-imidazolium bis(trifluoromethyl sulfone)imide at room temperature: study on phase formation by in situ electrochemical scanning tunneling microscopy", *Electrochim. Acta*, vol. 50, no. 6, pp. 1275-1281, Janu. 2005.
- [15] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, "Ionic liquid analogs formed from hydrated metal salts", *Chem.-a Euro. J.*, vol. 10, no. 15, pp. 3769-3774, July. 2004.
- [16] S. Surviliene, S. Eugénio, R. Vilar, "Chromium electrodeposition from [BMIm][BF₄] ionic liquid", *J Appl Electrochem*, vol. 41, no. 1, pp. 107-114, Oct. 2011.
- [17] N.M. Pereira, C.M. Pereira, J.P. Araújo, A.F. Silva, "Zinc Electrodeposition from deep eutectic solvent containing organic additives", *J. of Electroanal. Chem.*, Vol. 801, Pages 545-551, 15 September 2017.
- [18] A.P. Abbott, G. Capper, K.J. McKenzie, K.S. Ryder, "Electrodeposition of zinc-tin alloys from deep eutectic solvents based on choline chloride", *J. Electroanal. Chem.*, vol. 599, no. 2, pp. 288-294, Jan. 2007.
- [19] A.P. Abbott, K.E. Ttaib, G. Frisch, K.J. McKenzie, K.S. Ryder, "Electrodeposition of copper composites from deep eutectic solvents based on choline chloride", *Phys. Chem.Chem. Phys.*, vol. 11, no. 21, pp. 4269-4277, July. 2009.
- [20] M.R. Ali, M.Z. Rahman, S.S. Saha, "Electrodeposition of copper from a choline chloride based ionic liquid", *J. Electrochem.*, vol. 20, no. 2, pp. 139-145, Feb. 2014.
- [21] A.P. Abbott, E.T. Khalid, K.S. Ryder, E.L. Smith, "Electrodeposition of nickel using eutectic based ionic liquids", *Trans. Inst. Met. Finish.*, vol. 86, no. 4, pp. 234-240, Jul. 2008.
- [22] M.R. Ali, M.Z. Rahman, S.S. Saha, "Electroless and electrodeposition of nickel from deep eutectic solvents based on choline chloride", *Ind. J. Chem. Technol.* Vol. 21, no. 2, pp. 127-133, March. 2014.
- [23] A.P. Abbott, S. Nandhra, S. Postlethwaite, E.L. Smith, K.S. Ryder, "Electroless deposition of metallic silver from a choline chloride-based ionic liquid: a study using acoustic impedance spectroscopy, SEM and atomic force microscopy", *Phys. Chem. Chem. Phys.*, vol. 9, no. 28, pp. 3735-3743, August. 2007.
- [24] M.R. Ali, M.Z. Rahman, S.S. Saha, "Electroless and electrodeposition of silver from a choline chloride-based ionic liquid", *Pak. J. Sci. Ind. Res. Series A: Phys. Sci.*, vol. 58, no. 2, pp. 66-73, May. 2015.
- [25] A.P. Abbott, G. Capper, K.J. McKenzie, K.S. Ryder, "Voltammetric and impedance studies of the electropolishing of type 316 stainless steel in choline chloride based ionic liquid", *Electrochim, Acta*, vol. 51, no. 21, pp. 4420-4425, June. 2006.
- [26] A.P. Abbott, G. Capper, K.J. McKenzie, A. Glidle, K.S. Ryder, "Electropolishing of Stainless Steels in a Choline Chloride based Ionic Liquid: An Electrochemical Study with Surface Characterisation using SEM and AFM", *Phys. Chem. Chem. Phys.*, vol. 8, no. 36, pp. 4214-4221, October. 2006.
- [27] A.J. Bard & L.R. Faulkner, "*Electrochemical Methods*", 2nd edition, (New York: John Wiley & Sons, Inc) p. 218, 1980.