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Characterization of Imidazolium Chloride Ionic Liquids Plus Trivalent Chromium Chloride for Chromium Electroplating

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 Supporting Information

ABSTRACT: A series of mixtures consisting of the ionic liquids (ILs) 1-ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, and 1-hexyl-3-methylimidazolium chloride ($[\text{emim}][\text{Cl}]$, $[\text{bmim}][\text{Cl}]$, and $[\text{hmim}][\text{Cl}]$, respectively) and trivalent chromium chloride have been prepared. Physicochemical and electrochemical properties of these mixtures have been studied and the potential applications of these mixtures for chromium electroplating, as an alternative to the conventional hard chromium electroplating processes using hexavalent chromium baths, have been examined. To optimize the transport properties of the mixtures, different amounts of ultrapure water were added to the Cr(III) salt–IL mixtures, although the ultimate goal is to reduce or eliminate water. As shown previously for choline chloride/Cr(III) salt mixtures, we found that the physicochemical and electrochemical properties of the mixtures are affected by the relative water content. Our preliminary electroplating results show that these types of Cr(III) salt–IL mixtures could be promising alternatives to Cr(VI) containing baths for chromium electroplating applications with the advantage of avoiding the use of highly toxic hexavalent chromium.

1. INTRODUCTION

Electroplated chromium (Cr) coatings are indispensable for a variety of industries, such as automotive, aerospace, electronics, optics, and sensors, due to their high rust and corrosion resistance, good thermal stability, and unique optical properties.¹ The most common industrial chromium coatings are usually electrodeposited from hexavalent chromium (Cr(VI)) aqueous solutions. This method, however, brings up severe health and environmental concerns because Cr(VI) is highly oxidative and toxic.^{2,3} A straightforward alternative is less toxic trivalent chromium (Cr(III)) based solutions. Unfortunately, the high stability of the hexaaquochromium(III) complex formed in aqueous electrolyte solutions can obstruct or even prevent the electrodeposition of chromium metal.^{4–9} Another considerable drawback of electrodeposition of chromium from aqueous solutions is the concomitant hydrogen evolution, which results in safety issues, reduced current efficiency, and hydrogen embrittlement of the substrate, a significant cause for parts failure.^{2,3}

Ionic liquids (ILs) have attracted increasing interest as media for metal electroplating. Key advantages that ILs offer to overcome the limits imposed by conventional aqueous or organic solutions include avoidance of water and metal/water chemistry,¹ wide electrochemical windows with some ILs reaching up to 6 V, negligible vapor pressure that enables electroplating at elevated temperature, and numerous, yet little understood, cation/anion effects that make it possible to alter the morphology of the coatings.^{3,10,11} As early as 1997, Liu et al. studied the electrochemical behaviors of Cr(III) and Cr(II) chloride complexes in basic AlCl_3 –1-ethyl-3-methylimidazolium chloride ($[\text{emim}][\text{Cl}]$) room temperature molten salts and they found that Cr(III) can be reduced to Cr(II) on a glassy carbon (GC) electrode. The forms of Cr(III) and Cr(II) complexes were discussed, and the charge transfer kinetics constant and the formal potential of the Cr(III)/Cr(II)

electrode reaction were determined in a basic mixture with a AlCl_3 : $[\text{emim}][\text{Cl}]$ mole ratio of 44.4/55.6.¹² Of course, the chloroaluminate ILs can produce hydrochloric acid when in contact with water, which limits their applicability. Interest grew tremendously when Abbott et al. demonstrated that chromium can be electrodeposited from a 2:1 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ /choline chloride ($[\text{Ch}][\text{Cl}]$) system resulting in an amorphous pale blue/gray deposit on a nickel electrode. In addition, they reported that no reduction current for water decomposition was observed suggesting that hydrated waters behave differently from bulk water with less electrochemical activity.² In 2006 Abbott and McKenzie¹ discussed the effect of water as a diluent in ILs and reported that “it is beneficial for the deposition of metals such as Cr.” Of course, the addition of significant amounts of water could reduce the electrochemical window and result in hydrogen evolution during electroplating. Subsequently, Abbott and co-workers¹³ reported the successful electrodeposition of hard, bright chromium from ILs based on CrCl_3 / $[\text{Ch}][\text{Cl}]$ mixtures. Mares et al. reported the temperature dependent physicochemical properties (density and viscosity) and electrochemical behavior of a series of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ / $[\text{Ch}][\text{Cl}]$ mixtures with different mole ratios, as well as mixtures of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $[\text{Ch}][\text{Cl}]$, and oxalic acid.¹⁴ Following Abbott et al.’s work,¹³ Ferreira et al. reported chromium electroplating from a mixture of 1:2.5 $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ /ChCl and 20 wt % of added water. A metallic crack-free deposit with good adherence was obtained on a GC macroelectrode.¹⁵ In 2014 Abbott et al. studied the speciation, physicochemical, and electrolytic properties of eutectic mixtures based on urea and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and chromium coatings with hardness about 600

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Vickers were obtained through bulk electroplating in a hull cell.¹⁶

In addition, there has been some work done with electrodeposition of chromium from imidazolium-based ILs. Eugenio et al.^{3,17} and Surviliene et al.¹⁸ studied electrodeposition of black chromium coatings from 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]). The reduction of Cr(III) was reported to proceed in a two-step manner,^{3,17} from Cr(III) to Cr(II) and from Cr(II) to Cr(0), as observed by other researchers.^{2,12,14,15} Amorphous black chromium coatings were obtained independent of the copper, stainless steel and carbon steel substrates used, though coatings deposited on a copper substrate presented better adherence than those obtained on the other two materials.³ Specifically, the coatings obtained on a copper substrate with a potential of -1.5 V for 1800 s at an electrolyte temperature of 85 °C were found to be an amorphous mixture of chromium oxide/hydroxide and metallic chromium.¹⁷ Surviliene et al. investigated Cr(III) speciation in [bmim][BF₄] and revealed that the surface morphology of the black chromium coatings obtained on a copper substrate from [bmim][BF₄] showed larger nodules and microcracks with increased cathodic potential from -1.5 to -2.0 V and that coatings mainly consisted of oxide and metallic chromium with impurities of other elements from surface to depth.¹⁸ A Chinese patent issued in 2014 reported electrodeposition of chromium from ionic liquid 1-butyl-3-methylimidazolium bromide ([bmim][Br]) containing CrCl₃·6H₂O and/or chromium(III) sulfate (Cr₂(SO₄)₃·12H₂O) with varied Cr(III) salt concentration and electrodeposition temperature.¹⁹ He et al. investigated the electrochemical reduction of Cr(III) on a GC electrode in [bmim][Br] containing anhydrous CrCl₃ and revealed that the electrodeposition of chromium proceeded via an instantaneous nucleation growth mechanism. Analysis of the chromium deposit suggested that [bmim][Br] could be a useful electrolyte for metal electrodeposition.²⁰ Most recently, He et al. reported electrodeposition of nanocrystalline chromium coatings from the ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate ([bmim][HSO₄]), where the reduction of Cr(III) was found to follow a two-step process, namely, Cr(III) to Cr(II) and Cr(II) to Cr(0). Dense chromium coatings with good corrosion resistance were made.^{21,22} Finally, Fischer et al.²³ attempted electrodeposition of chromium from a 1:9.7 anhydrous Cr(III)/[emim][Cl] mixture at 120 °C. They were interested in anhydrous conditions because they observed hydrogen embrittlement when electroplating chromium from CrCl₃·6H₂O/[Ch][Cl] mixtures with large amounts of added water. Unfortunately, the high temperature needed to reduce viscosity and improve transport resulted in electrolyte destruction.

In the present work, we have investigated some additional Cr(III)/IL mixtures as potential candidates for chromium electroplating. Specifically, we investigate mixtures of CrCl₃·6H₂O with three *N,N'*-dialkylimidazolium chloride ionic liquids, 1-ethyl-3-methylimidazolium chloride ([emim][Cl]), 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), and 1-hexyl-3-methylimidazolium chloride ([hmim][Cl]). We report data for [Ch][Cl] mixtures for comparison. Following the work of Abbott et al.¹ and Ferreira et al.,¹⁵ different amounts of ultrapure water were added to the Cr(III) salt/IL mixtures in order to optimize the transport properties of the mixtures at this preliminary stage of study, while the ultimate goal is to reduce or eliminate water. To our knowledge, these systems have not been studied previously with added water for

chromium electroplating. However, they are an extension of the pioneering work described above using Cr(III)Cl₃ with [Ch][Cl], [bmim][Br], and [emim][Cl] (anhydrous). The physicochemical properties, including conductivity, viscosity, and ionicity of the mixtures, were characterized over the temperature range from 10 to 80 °C. Cr(III) speciation in the mixtures was primarily investigated via UV-vis spectroscopy at room temperature. Electrochemical behavior of Cr(III) in the mixtures was examined by cyclic voltammetry at 52 °C, which is in the range of operating temperatures (50–65 °C) for industrial hard chromium electroplating from chromic acid baths.²⁴ The physicochemical and electrochemical properties of the mixtures were found to depend heavily on the water content, as well as the IL cation type for a fixed anion. Electroplating of chromium from the mixtures was achieved by chronoamperometry and the coatings were characterized by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) in terms of elemental composition, covalence state, and morphology. The new Cr(III) salt/IL mixtures present themselves as promising alternatives under carefully selected conditions to address the issues encountered in conventional chromium electroplating using Cr(VI) aqueous solutions.

2. EXPERIMENTAL SECTION

2.1. Materials. Ionic liquids [bmim][Cl] and [hmim][Cl] were synthesized in our laboratory via the alkylation reaction of 1-methylimidazole with 1-chlorobutane and 1-chlorohexane, respectively, according to the reported procedures²⁵ and were dried under vacuum at 60 °C for 48 h to remove residual organic solvents and water. The purities were determined by ¹H NMR to be more than 98%. Ionic liquid [emim][Cl] (IoLiTec Inc., >98%), choline chloride ([Ch][Cl], Acros Organics, 99%), and chromium(III) chloride hexahydrate (CrCl₃·6H₂O, Alfa Aesar, 99.5%) were used as purchased. Water contents of the ILs were measured by a V2 volumetric Karl Fischer titrator to be lower than 500 ppm. The electrolytes were prepared by mixing a 1:2 mol ratio of CrCl₃·6H₂O:IL with the desired amount of ultrapure water (Milli-Q, >18 MΩ·cm resistivity at 25 °C) and keeping the mixtures heated with stirring in a capped vial on a magnetic heating plate at 50 °C for several hours until a homogeneous liquid formed. The maximum uncertainty in the stoichiometric composition of the mixtures was 0.74%. Note that Ferreira et al. were able to obtain chromium coatings with attractive properties from a mixture of 1:2.5 CrCl₃·6H₂O:[Ch][Cl] mole ratio with 20 wt % added water.¹⁵ Other researchers have looked at mixtures varying from a CrCl₃·6H₂O:[Ch][Cl] mole ratio of 1:3 to 3:1.^{2,14} These studies, as well as our own work with CrCl₃·6H₂O/[Ch][Cl] systems, reveal that increasing mole fraction of CrCl₃·6H₂O in the CrCl₃·6H₂O:[Ch][Cl] mixtures results in viscosity decrease and conductivity increase. Here we have decided to focus on mixtures with a 1:2 mol ratio of CrCl₃:IL with different mole ratios of H₂O:CrCl₃. We report the total amount of water in the systems as the moles of water per mole of CrCl₃ (*x*). To make these mixtures, we start with CrCl₃·6H₂O and add water and the IL. The concentration of Cr(III) in these mixtures ranges from 1.3 to 2.2 M, which is in the range of Cr(VI) concentrations in commercial chromium plating solutions, which typically contain 200–400 g/L chromic acid (1.7–3.4 M).²⁴ The molar concentrations of Cr(III) and weight percent of H₂O (both the water added and the total water) in the different mixtures studied are listed in Table 1.

Table 1. Cr(III) Concentration and H₂O Content of Different Mixtures (1:2 CrCl₃·xH₂O/IL)

IL	x	concentration of Cr(III) (M)	wt % of added H ₂ O	wt % of total H ₂ O
[Ch][Cl]	9	2.2	9.0	27.1
	12	2.0	16.5	33.0
	15	1.8	23.0	38.2
	18	1.6	28.4	42.5
[emim][Cl]	9	2.2	8.8	26.4
	12	1.9	16.2	32.4
	15	1.8	22.4	37.4
	18	1.6	27.9	41.8
[bmim][Cl]	9	1.9	8.2	24.3
	12	1.7	14.9	29.8
	15	1.6	20.7	34.6
	18	1.5	26.0	39.0
[hmim][Cl]	9	1.7	7.4	22.3
	12	1.5	13.9	27.7
	15	1.4	19.4	32.4
	18	1.3	24.3	36.5

2.2. Conductivity Measurement. The temperature dependent conductivities were measured with a computer controlled electrochemical impedance spectroscopy (EIS) system, consisting of a Solartron SI 1287 electrochemical interface and a SI 1260 impedance/gain-phase analyzer, over the frequency range from 20 Hz to 1 MHz. All samples were loaded and sealed into conductivity sample cells under nitrogen in a glovebox. The sample cells were kept in an oven during measurement and were thermally equilibrated at each temperature for at least 1 h before measurement.

2.3. Density Measurement. The densities of the mixtures at ambient pressure were measured with a DMA 4500 Anton

Paar oscillating U-tube densitometer to a precision of ± 0.00001 g/cm³ and an uncertainty estimated to be ± 0.0005 g/cm³ taking the sample impurities into account. The temperature was automatically controlled by two integrated Pt 100 platinum thermometers with an uncertainty of ± 0.01 K.

2.4. Viscosity Measurement. The temperature dependent viscosities of the samples were measured with an Anton Paar automated microviscometer at ambient pressure. A capillary of 1.6 mm or 3.0 mm in diameter was used depending on the viscosity range measured. An inclination angle of 40° was employed. Quartic measurements of each sample at each temperature were performed with a reproducibility within 0.5%, and the results were averaged. The experimental uncertainty was estimated to be within $\pm 3.0\%$.

2.5. UV-vis Spectra. The UV-vis spectra of the mixtures were taken right after full dissolution of CrCl₃·6H₂O on a Jasco-V-670 UV-vis-NIR reflectance spectrometer with an integrating sphere detector at room temperature.

2.6. Electroplating and Coating Characterization. The substrates for electroplating were pretreated by polishing with abrasive sand paper (grit 600) to eliminate surface oxides, followed by activating in 1:4 H₂O/37% HCl and then subsequently rinsing with methanol and deionized H₂O and finally drying with air flow. The quasi-reference electrode and counterelectrode Pt wires were cleaned with 1:2 30% H₂O₂/98% H₂SO₄ solution after each experiment. Cyclic voltammetry and chronoamperometry were carried out with a VoltaLab50 potentiostat in an undivided three-electrode cell that was placed in an M. Braun dry glovebox (Labmaster SP MB 20, H₂O < 0.1 ppm, O₂ < 30 ppm) under N₂ atmosphere. The temperature of the electroplating bath was kept at 52 °C using an oil bath. The coatings were washed with methanol and then deionized water and finally dried with air flow. The elemental composition and covalence states of the coatings were analyzed with a PHI

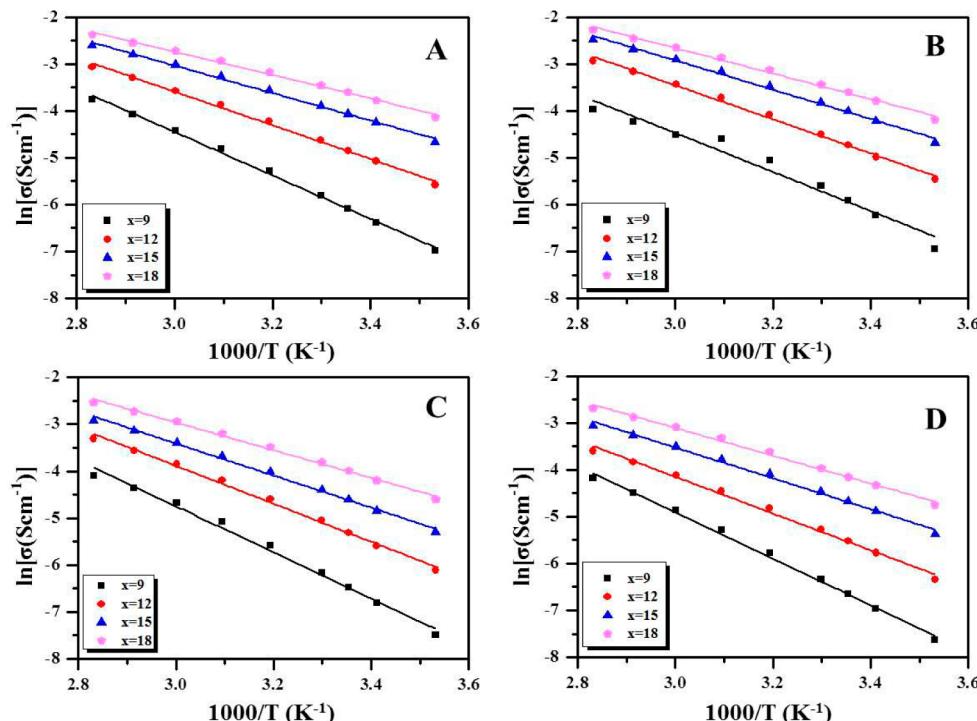


Figure 1. Arrhenius plots of temperature dependent ionic conductivities of (A) 1:2 CrCl₃·xH₂O/[Ch][Cl], (B) 1:2 CrCl₃·xH₂O/[emim][Cl], (C) 1:2 CrCl₃·xH₂O/[bmim][Cl], and (D) 1:2 CrCl₃·xH₂O/[hmim][Cl].

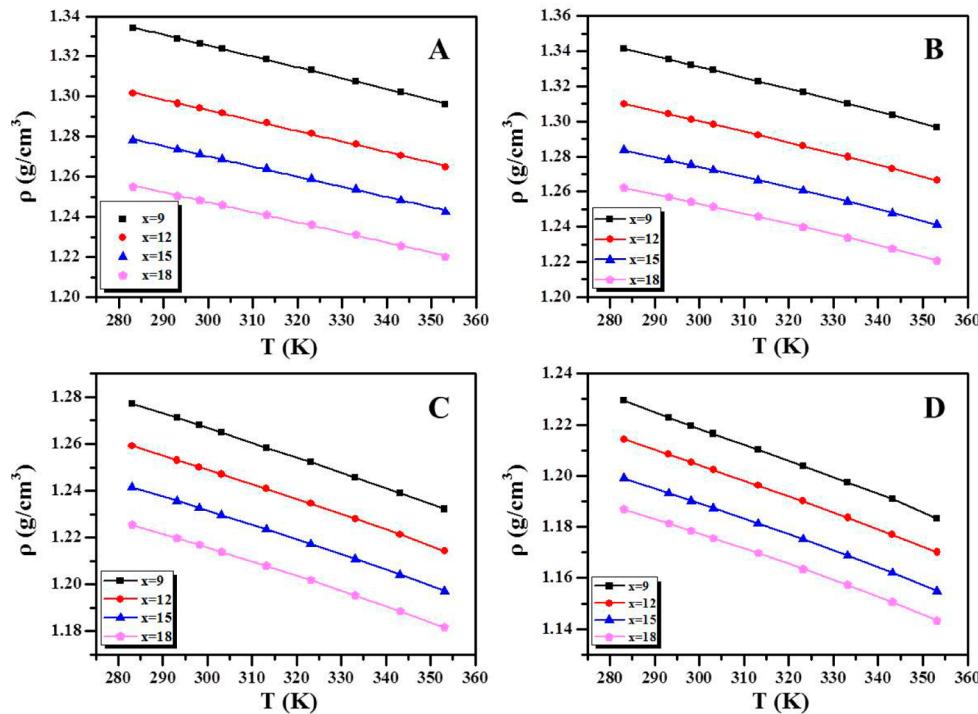


Figure 2. Temperature dependent density of (A) 1:2 CrCl₃·xH₂O/[Ch][Cl], (B) 1:2 CrCl₃·xH₂O/[emim][Cl], (C) 1:2 CrCl₃·xH₂O/[bmim][Cl], and (D) 1:2 CrCl₃·xH₂O/[hmim][Cl].

VersaProbe II X-ray photoelectron spectrometer. The morphology of the coatings was analyzed with Helios Nano Lab Dual Beam 600 (FEI) SEM/FIB workstation. The hardness of the coatings was measured with a Vicker's hardness tester with a loading of 25 gf.

3. RESULTS AND DISCUSSION

3.1. Conductivity. Conductivity is one of the most important aspects to evaluate an IL for electrochemical applications. A considerable advantage that aqueous solutions possess over nonaqueous IL solutions for metal electroplating is superior conductivity.¹ Earlier studies have revealed that the conventional Cr(VI) aqueous solutions (chromic acid solutions) provide conductivities about 2 orders of magnitude higher than those of CrCl₃·6H₂O/[Ch][Cl] mixtures.^{2,26} Conductivities of mixtures with 1:2 mol ratios of CrCl₃:IL for [emim][Cl], [bmim][Cl], [hmim][Cl], and [Ch][Cl], with different H₂O:CrCl₃ ratios, were measured over the temperature range from 283.15 to 353.15 K. The original conductivity data can be found in the Supporting Information (Table S1(a)). The conductivities were found to depend on the temperature in an Arrhenius manner as described by eq 1:^{27,28}

$$\ln \sigma = \ln \sigma_0 - E_A / RT \quad (1)$$

where E_A is the activation energy for conduction in units of kilojoules per mole, and σ_0 is a constant in units of Siemens per centimeter.¹ Arrhenius plots of the temperature dependent conductivity of all the mixtures investigated are shown in Figure 1. Generally, the conductivities of a certain mixture increase with increasing temperature, and for each type of CrCl₃/IL combination, the conductivities increase with increasing amount of water. The enhanced conductivity should be attributed to increased ion mobility since the conductivity of an ionic fluid is usually determined by the mobility of charge carriers,² and increasing temperature or addition of water helps

to improve ion mobility in the mixtures. Arrhenius equation fitting parameters for eq 1 over the temperature range from 40 to 80 °C (except for 1:2 CrCl₃·9H₂O/[emim][Cl], where points from 25 to 80 °C except 50 °C were used for curve fitting), where the linearity is better, are listed in Table S1(b). Compared with Abbott et al.'s conductivity data for 1:1 CrCl₃·6H₂O/[Ch][Cl]² conductivities of 1:2 CrCl₃·9H₂O/[Ch][Cl] measured in this work are 1 order of magnitude higher than the former for all temperatures. Considering the fact that the conductivity of CrCl₃·6H₂O/[Ch][Cl] mixtures increases with increased mole fraction of CrCl₃ in the system,^{2,14} it is clear that the effect of increasing conductivity of the electrolyte by adding ultrapure H₂O is dominant. The activation energy for conduction (E_A) of 1:1 CrCl₃·6H₂O/[Ch][Cl] reported by Abbott et al.² (43.7 kJ/mol) is comparable with the values obtained for the 1:2 CrCl₃·xH₂O/[Ch][Cl] mixtures studied here (Figure S1). It is worth pointing out that for the same CrCl₃:H₂O ratio, conductivities of the mixtures based on different dialkylimidazolium chloride ILs follow the trend of [emim][Cl] > [bmim][Cl] > [hmim][Cl]. This is consistent with the effect of alkyl chain length in imidazolium cation on the physicochemical properties of neat room temperature ionic liquids (RTILs). For example, the conductivities of pure imidazolium ILs with the bis(trifluoromethane sulfonyl)imide ([Tf₂N]⁻) anion decrease in the order of [emim]⁺ > [bmim]⁺ > [hmim]⁺.²⁹

3.2. Density. Figure 2 presents the densities of the mixtures measured over the temperature range from 283.15 to 353.15 K at ambient pressure. The original density data can be found in the Supporting Information (Table S2(a)). As shown, densities of the mixtures generally decrease with temperature in a linear relationship that can be described as

$$\rho = a + bT \quad (2)$$

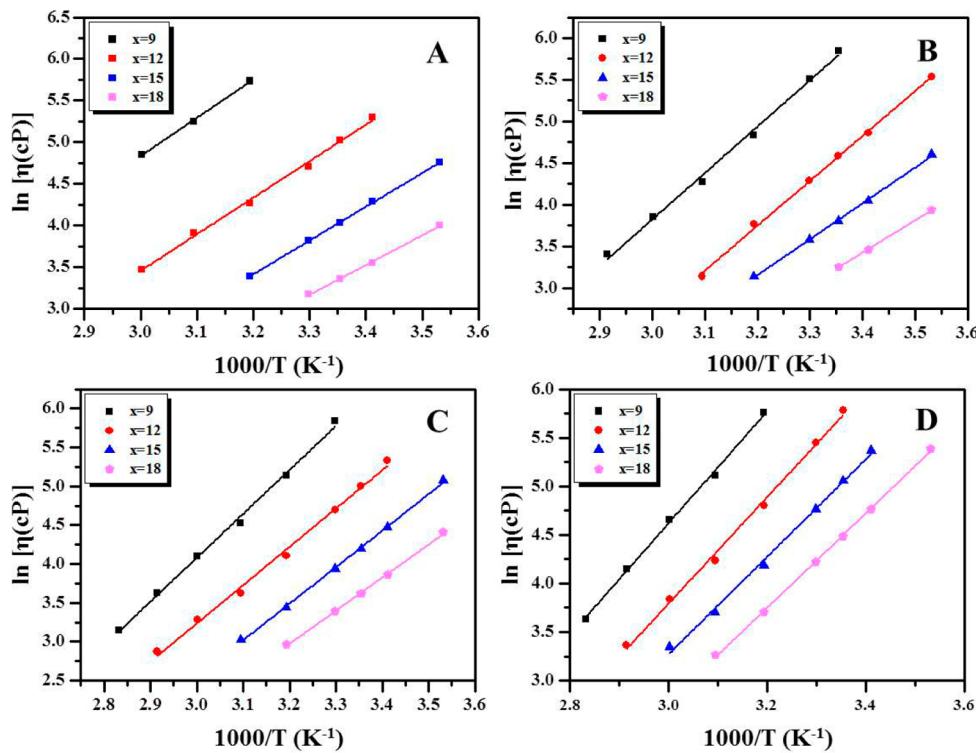


Figure 3. Arrhenius plots of temperature dependent viscosity of: (A) 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$, (B) 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{emim}][\text{Cl}]$, (C) 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{bmim}][\text{Cl}]$, and (D) 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{hmim}][\text{Cl}]$.

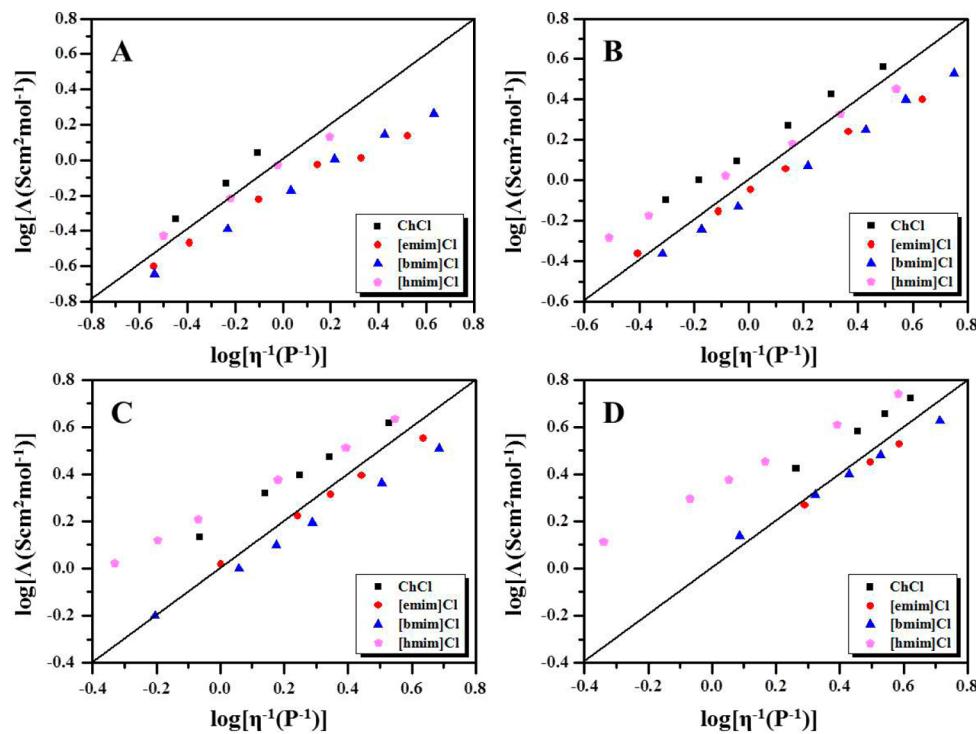


Figure 4. Walden plots for different mixtures with same Cr:H₂O ratio: (A) 9H₂O/Cr, (B) 12 H₂O/Cr, (C) 15 H₂O/Cr, and (D) 18 H₂O/Cr.

where the values of the fitting parameters, a and b in eq 2, are listed in Table S2(b). Also, for a given $\text{CrCl}_3(x\text{H}_2\text{O})/\text{IL}$ mixture, the densities decrease with increasing water content. Taking the difference in relative H₂O content into account, the density data for 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ measured in this work is in good agreement with previous available data reported

by Mares et al.¹⁴ (see Figure S2). Similar to the conductivities, for a given H₂O:CrCl₃ ratio, densities of the mixtures for different dialkylimidazolium chloride ILs decrease in the order $[\text{emim}][\text{Cl}] > [\text{bmim}][\text{Cl}] > [\text{hmim}][\text{Cl}]$. This is the same trend observed for pure RTILs with the $[\text{Tf}_2\text{N}]^-$ anion.²⁹

3.3. Viscosity. Viscosity is another important property of ILs that needs to be considered for electrochemical applications. ILs with low viscosity are generally preferable in electrochemical devices because it minimizes the power input required for mass transport. The viscosity of ILs is usually 1 or 2 orders of magnitude higher than water or other common organic solvents.³⁰ Viscosities of the same mixtures above were measured over the temperature range of 283.15–353.15 K (within instrumentation limits), and the results are shown in Figure 3 (original data can be found in the Supporting Information, Table S3(a)). Analogous to the conductivities, the viscosities are found to be dependent on the temperature in an Arrhenius manner as^{27,28}

$$\ln \eta = \ln \eta_0 + E_\eta / RT \quad (3)$$

where E_η is the activation energy for viscous flow, and η_0 is a constant. The values of the fitting parameters, E_η and η_0 , are listed in Table S3(b). Compared with Abbott et al.'s viscosity data for a 1:1 $\text{CrCl}_3\cdot 6\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ mixture,² viscosities of the 1:2 $\text{CrCl}_3\cdot 9\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ mixture measured in this work are about 1 order of magnitude lower at 323.15 and 333.15 K, respectively, and 2 orders of magnitude lower at 313.15 K, which explains the higher conductivity of the 1:2 $\text{CrCl}_3\cdot 9\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ mixture measured in this work, as mentioned above. Considering the fact that the viscosity of $\text{CrCl}_3\cdot 6\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ mixtures decrease with increasing mole fraction of CrCl_3 ,^{2,14} the effect of decreasing viscosity of the electrolyte by adding ultrapure H_2O is significant. However, the activation energy for viscous flow (E_η) of 1:1 $\text{CrCl}_3\cdot 6\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ reported by Abbott et al.² (58.5 kJ/mol) is remarkably larger than the values obtained for the 1:2 $\text{CrCl}_3\cdot x\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ mixtures studied here (Figure S3). Also, viscosities of the mixtures based on different dialkylimidazolium chloride ILs decrease in the order $[\text{hmim}]\text{Cl} > [\text{bmim}]\text{Cl} > [\text{emim}]\text{Cl}$. This follows the same trend as the viscosities of pure $[\text{Tf}_2\text{N}]^-$ -based dialkylimidazolium ILs.²⁹

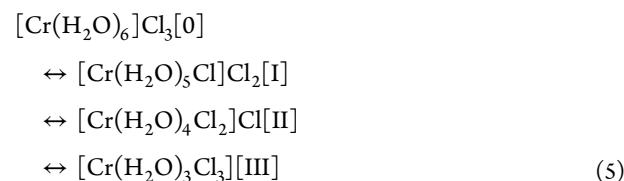
3.4. Ionicity. The relationship between conductivity and viscosity is commonly described by the empirical Walden Rule,³¹ which is expressed as^{32–34}

$$\Lambda\eta = \text{constant} \quad (4)$$

where Λ is the equivalent conductivity, $\Lambda = \sigma V_E$ (V_E is the volume containing one Faraday of positive charge, which could be calculated equivalently as $V_E = M/(\rho n)$ where ρ is the density of the electrolyte solution, and n is the moles of positive charges per mole of the electrolyte), and η is the viscosity ($\eta = \varphi^{-1}$, where φ is the fluidity). Note that for the mixtures investigated in this study, the molecular weight was calculated so that the mixture was considered a composite electrolyte with a 1:2: x $\text{CrCl}_3/\text{IL}/\text{H}_2\text{O}$ mole ratio ($x = 9, 12, 15, 18$). Figure 4 shows the equivalent conductivities of the mixtures as a function of their fluidities in a Walden plot, and different CrCl_3/IL combinations with the same $\text{H}_2\text{O}:\text{Cr}$ ratios are grouped in the same plot. The solid line running through the origin with a unit slope is the so-called ideal line determined by data for 1 M KCl aqueous solution at ambient temperature.^{32,35} The deviation from the ideal line lends a measure of ion association in an electrolyte media. In general, ionicity of $[\text{Ch}][\text{Cl}]$ -based mixtures remains almost unchanged, while ionicity of the three imidazolium IL-based mixtures increases with relative amount of H_2O (Figure S4). The ionicity of $[\text{emim}][\text{Cl}]$ and $[\text{bmim}][\text{Cl}]$ -based mixtures is similar while mixtures based on $[\text{hmim}][\text{Cl}]$ show higher ionicities. Note

that the data points mostly fall below the ideal line, which suggests the existence of strong ion interactions in the mixtures, yet mixtures containing 1:2 $\text{CrCl}_3\cdot x\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ ($x = 9, 12, 15, 18$) and 1:2 $\text{CrCl}_3\cdot x\text{H}_2\text{O}/[\text{hmim}][\text{Cl}]$ ($x = 12, 15, 18$) fall above the ideal line indicating so-called superionicity,^{33,35} which can be interpreted as diffusion of "excess" protons resulting from hydrolysis of the Cr(III) aqua complexes ($[\text{Cr}(\text{H}_2\text{O})_6]^{3+} \leftrightarrow [\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}^+$),³⁶ through the hydrogen bond network within the mixtures. This could potentially be explained by the Grotthus mechanism discussed by earlier researchers.^{35,37}

3.5. Speciation. Understanding of metal speciation in the electrolyte solution is important for electroplating. Multiple species exist in equilibrium in aqueous solutions, as expressed by eq 5, and the dominant species heavily depend on the solution environment.^{2,18,38}



Elving and Zemel observed the spectra of acidic chloroquochromium(III) solutions (the positions of the absorption bands are summarized in Table 2) and found that the addition of each

Table 2. Literature Data³⁸ on the Positions of the Absorption Bands of Chloroquochromium(III) Complex in Acid Media

species	absorption maximum (nm)		bathochromic shift (nm)	
	I	II	I	II
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	407	575		
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$	430	605	23	30
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	450	635	20	30
$[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$	475	665	25	30

chloride ligand bathochromically shifted the lower band by around 20–25 nm and the upper band by 30 nm.³⁸ Based on Elving and Zemel's results, Abbott et al. attributed the two bands observed at 470 and 669 nm in the spectrum of the 2:1 $\text{CrCl}_3\cdot 6\text{H}_2\text{O}/\text{ChCl}$ mixture to the existence of the trichloro species $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$.² UV-vis spectra of all the mixtures studied in this work are shown in Figure 5, and the positions of the two absorption bands are summarized in Table 3. Comparison between the positions of the absorption bands in Table 3 and those in Table 2 qualitatively indicates that $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ predominantly exists in all the mixtures. A small amount of $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$ may coexist in mixtures with a 1:9 $\text{Cr}:\text{H}_2\text{O}$ ratio and some $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ is present in 1:2 $\text{CrCl}_3\cdot 18\text{H}_2\text{O}/[\text{emim}][\text{Cl}]$ and 1:2 $\text{CrCl}_3\cdot 18\text{H}_2\text{O}/[\text{bmim}][\text{Cl}]$.

3.6. Cyclic Voltammograms and Electroplating of Chromium Coatings. Electrochemical behavior of the $\text{CrCl}_3\cdot x\text{H}_2\text{O}/\text{IL}$ mixtures was investigated by cyclic voltammetry in an undivided three-electrode cell. Figure 6 shows the cyclic voltammograms (CVs) of the $\text{CrCl}_3\cdot x\text{H}_2\text{O}/\text{IL}$ mixtures recorded on a GC electrode with two Pt wires as the quasi reference electrode (QRE) and the counter electrode (CE), respectively, at 52 °C with a scanning rate of 20 mV/s. Despite the fact that the shapes of the CVs vary among different combinations of CrCl_3/IL , a stepwise reduction process was

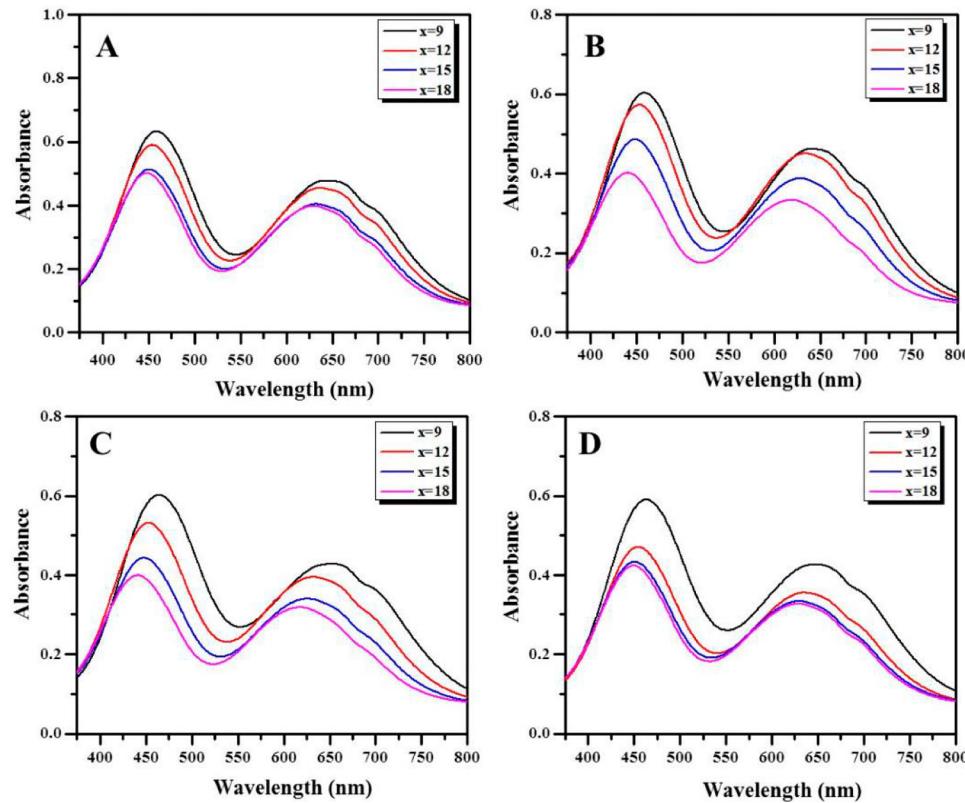


Figure 5. UV-vis spectra of (A) 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$, (B) 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{emim}][\text{Cl}]$, (C) 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{bmim}][\text{Cl}]$, and (D) 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{hmim}][\text{Cl}]$.

Table 3. Positions of the Absorption Bands of 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ and 1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{C}_n\text{mim}][\text{Cl}]$ ($n = 2, 4, 6$) Mixtures Measured at Ambient Temperature

1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$	absorption maximum (nm)	
	I	II
$x = 9$	458	644
$x = 12$	454	636
$x = 15$	450.5	632
$x = 18$	448.5	628.5
1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{emim}][\text{Cl}]$	absorption maximum (nm)	
	I	II
$x = 9$	459	641.5
$x = 12$	453.5	632.5
$x = 15$	449	628.5
$x = 18$	440.5	618.5
1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{bmim}][\text{Cl}]$	absorption maximum (nm)	
	I	II
$x = 9$	464.5	654
$x = 12$	452.5	631.5
$x = 15$	447.5	626
$x = 18$	441.5	618.5
1:2 $\text{CrCl}_3 \cdot x\text{H}_2\text{O}/[\text{hmim}][\text{Cl}]$	absorption maximum (nm)	
	I	II
$x = 9$	463	646.5
$x = 12$	454	635
$x = 15$	450.5	630.5
$x = 18$	449.5	629.5

observed in the forward scan for all the four types of mixtures. The first steep increase of reduction current should be

attributed to the reduction of Cr(III) to Cr(II). The following plateau in reduction current, which suggests an electrode passivation, was explained by Abbott et al. to be caused by a reaction of Cr(II) species yielding an insoluble product on the electrode surface, rather than the precipitation of a Cr(II) species considering the instability of Cr(II),² which might be the same case observed here. A second reduction current increase occurred after the electrode passivation at a more negative potential, which should be attributed to the further reduction of Cr(II) to metallic chromium. This process agrees with the observations by other researchers.^{2,3,12,14,15,17,18,20}

Moreover, the assignments are further supported by electroplating using a potential held at a value at the end of the first reduction wave where only Cr(II) should be formed (-1.05 V vs QRE for 1:2 $\text{CrCl}_3 \cdot 18\text{H}_2\text{O}/[\text{bmim}][\text{Cl}]$ and -0.86 V vs QRE for 1:2 $\text{CrCl}_3 \cdot 9\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$) for 20 min. In both cases a black coating was deposited that was determined by XPS to be chromium oxide throughout. Chromium(II) is easily oxidized to chromium oxide in the presence of water, which is the case here. A crossover on the reverse scans, which suggests nucleation of a new phase on the electrode surface,³ was observed in all the mixtures except the 1:2 $\text{CrCl}_3 \cdot 9\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$ and 1:2 $\text{CrCl}_3 \cdot 9\text{H}_2\text{O}/[\text{hmim}][\text{Cl}]$ mixtures, which have significantly higher viscosities. This indicates that the high viscosity of the electrolyte may inhibit mass transfer and nuclei growth on the surface of the electrode. A broad oxidation peak was observed for all the mixtures on the reversed scans. As suggested by Eugenio et al.'s cyclic voltammetry study for the $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}/[\text{bmim}][\text{BF}_4]$ system,³ this oxidation peak should be attributed to the oxidation of Cr(II), rather than the stripping/oxidation of metallic chromium formed during the forward scan.

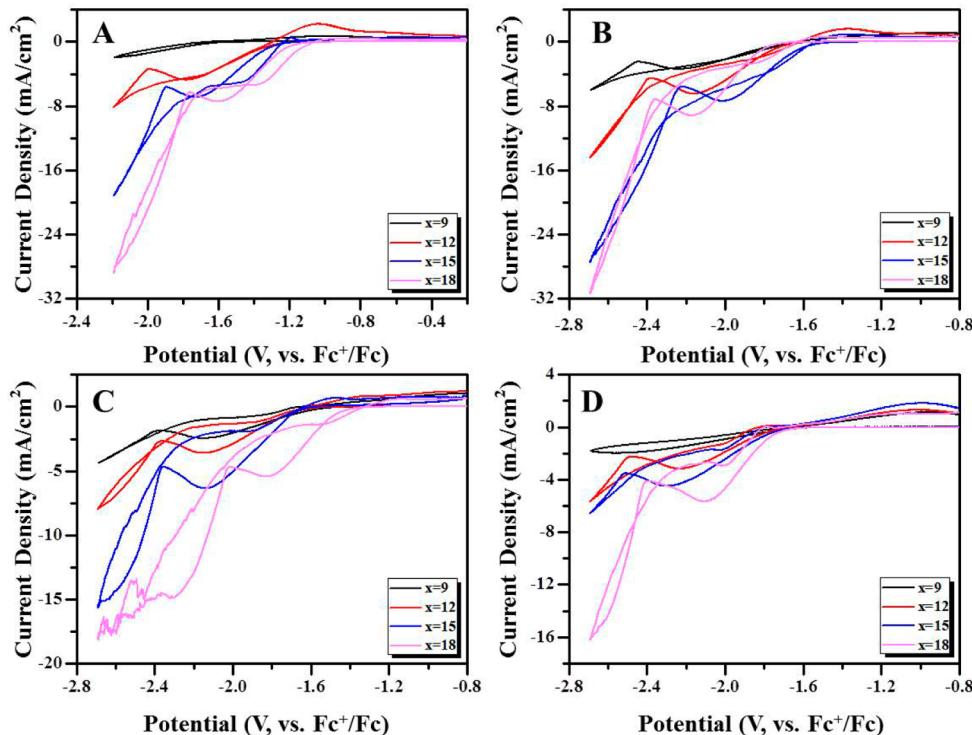


Figure 6. Cyclic voltammograms recorded on glassy carbon electrode in (A) 1:2 CrCl₃·xH₂O/[Ch][Cl], (B) 1:2 CrCl₃·xH₂O/[emim][Cl], (C) 1:2 CrCl₃·xH₂O/[bmim][Cl], and (D) 1:2 CrCl₃·xH₂O/[hmim][Cl] ($v = 20$ mV/s, 52 °C).

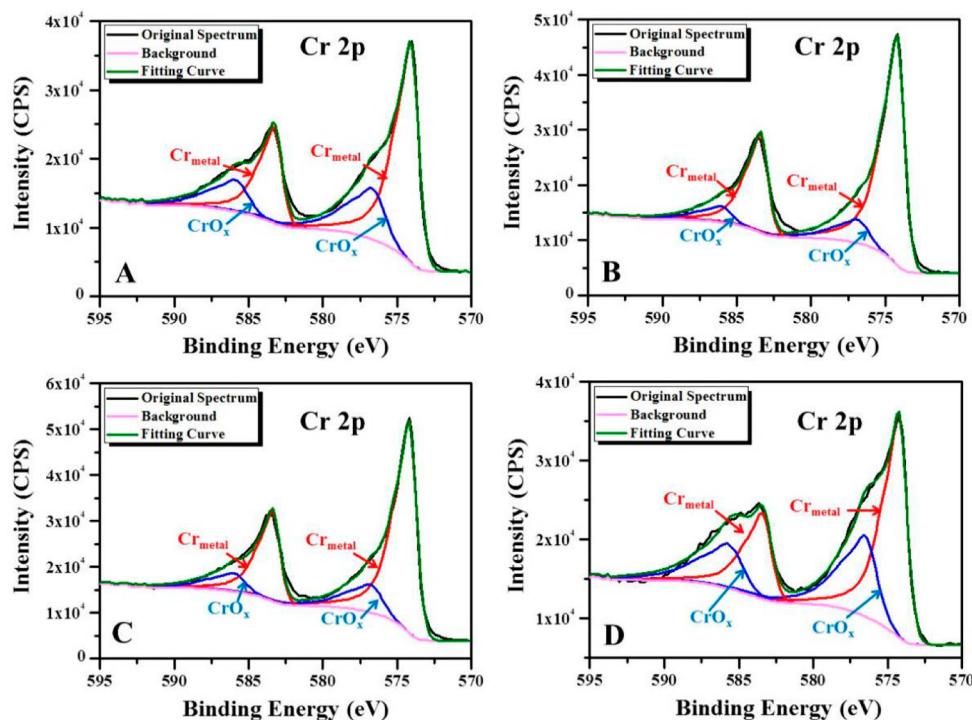


Figure 7. XPS spectra of coatings obtained on Cu substrate from different mixtures: (A) 1:2 CrCl₃·18H₂O/[Ch][Cl], (B) 1:2 CrCl₃·18H₂O/[emim][Cl], (C) 1:2 CrCl₃·18H₂O/[bmim][Cl], and (D) 1:2 CrCl₃·18H₂O/[hmim][Cl] (−2.5 V vs QRE, 52 °C, 20 min).

Our preliminary results show that mixtures with a 6:1 H₂O:Cr ratio (e.g., 1:2 CrCl₃·6H₂O/[emim][Cl] and 1:2 CrCl₃·6H₂O/[bmim][Cl]) do not give good coating coverage on the substrate (Cu), most likely because of the large mass transfer resistance in the highly viscous mixtures at the temperature used for electroplating in our study. Therefore,

we adopted mixtures with a 18:1 H₂O:Cr ratio for electroplating and the temperature was fixed at 52 °C in all the experiments.

3.7. Characterization of Electrodeposited Coatings (XPS, SEM, and Hardness). The chromium coatings plated out of the four types of mixtures based on [Ch][Cl],

[emim][Cl], [bmim][Cl], and [hmim][Cl], respectively, at -2.5 V (vs QRE) for 20 min at 52 °C onto a Cu substrate were found to be silvery in color and exhibited good adherence to the substrate. The elemental composition and the valence states of the elements of the coatings obtained from the mixtures were analyzed with X-ray photoelectron spectroscopy (XPS) and compared with standard references in the XPS database.³⁹ The photoemission features of the coatings indicate the presence of Cr, O, C, Cl, and Cu peaks, as well as a very small peak for Ca impurity (Figure S5). It has been generally accepted that the chrome coatings obtained from Cr(VI) containing baths are a composite of metallic chromium and chromium oxide in the bulk^{18,40,41} while the surface composition varies according to different reports.⁴¹ The binding energy of Cr 2p_{3/2} was found to be 576.9 eV for the as-deposited surface of all our coatings, higher than that of metallic Cr, suggesting Cr on the coating surface is in an oxidized state. By integration of the peak areas of Cr and O and considering the relative sensitivity factors, the atomic ratio of surface O to Cr was calculated to be larger than 1.5, with some reaching up to 3.0. This suggests the presence of large amount of chromium hydroxide at the surface of the coatings. In order to investigate the bulk composition of the coatings, the surfaces of the coatings were sputtered with an Ar⁺ gun for a certain time. An example can be found in the Supporting Information, showing the Cr peak shift after the surface layer of the coating was removed by Ar⁺ sputtering (Figure S6). As an example, Figure 7 presents the Cr 2p photoemission spectra of the coatings obtained on a Cu substrate from mixtures with different CrCl₃·18H₂O/IL combinations and that have been sputtered by the Ar⁺ gun for 0.2 min (3 kV). As shown, the original Cr 2p_{3/2} peaks were deconvoluted and fitted into two components with one centered at about BE = 574.4 eV, corresponding to the metallic chromium, and the other centered at about BE = 576.6 eV, corresponding to chromium oxides.³⁹ It should be pointed out that although some researchers have resolved the chromium peaks into three components,¹⁸ it is challenging to differentiate Cr oxidation states in Cr₂O₃ from that in Cr(OH)₃ merely based on peak positions as they overlap. We consider the surface as covered with various nonstoichiometric chromium oxides. This consideration is also consistent with the difference in full-width-half-maximum of the metallic Cr peak and the oxide peak, suggesting the Cr oxide peak is composed of various oxidation states of Cr components. Table 4 lists the atomic

composition of the coatings, possibly by affecting ion mobility, considering the ionicity data presented above. Note that the atomic percent of metallic chromium in the coatings reported here is much higher than that for the limited reported examples of chromium coatings obtained from ionic liquid-based electroplating baths (i.e., [bmim][BF₄]).¹⁸

After successfully electroplating chromium onto a Cu substrate from the IL mixtures, we further investigated electroplating onto other substrates. Figure 8 presents the XPS spectra of the coatings obtained on brass (E) and zinc coated steel (F) from a 1:2 CrCl₃·18H₂O/[bmim][Cl] mixture and that have been sputtered by an Ar⁺ gun for 5.5 and 4.0 min (3 kV), respectively. The spectra were resolved into two components which shows that the in depth coatings consist predominantly of metallic chromium (~92 at %) with a small amount of chromium in oxide form. Note that a C 1s peak of unusually high intensity was present in the spectra of the coatings as-deposited or sputtered for a shorter time with the brass and zinc coated steel substrate, possibly because [bmim]⁺ is more adsorptive at the surface of brass and stainless steel (SS) than Cu, and a considerable amount of the organic [bmim]⁺ was captured in the deposit during electroplating. That was why a longer sputtering time was adopted for the two coatings with brass and SS substrates, than those with a Cu substrate. Also, it should be pointed out that the coatings should be graded composite,⁴¹ which means that the relative amount of the components may vary with depth from the close surface to the interface between the coating and the substrate. Since the aim of our study was to screen possible IL candidates for chromium electroplating and to know the general composition of the coatings, we did not carry out accurate composition characterization as a function of depth from surface to bulk for the coatings, as has been done by some earlier researchers.¹⁸

The morphology of the coatings was analyzed with SEM, and the boundary between the coatings and the substrate was examined with EDS. Figure 9 shows the SEM images of the morphology of the surface (numbered 1) and of the cross sections (numbered 2) of the coatings obtained on a Cu substrate for the four types of mixtures. As can be seen in the images, a compact coating without obvious micro cracks was obtained from mixtures based on [Ch][Cl], [emim][Cl], and [bmim][Cl], while there were some microcracks caused by dense pits in the coating obtained from the [hmim][Cl] based mixture. This indicates that different extents of hydrogen evolution may exist in the electroplating process in these mixtures under the investigated conditions, although no gas bubbles were visually observed in the solution during the electroplating process. Nevertheless all the coatings exhibit good adherence to the substrate and could hardly be scratched by stainless steel tweezers. The thickness of the coatings were measured to be 6.88, 4.92, >30.51, and 3.69 μm for [Ch][Cl], [emim][Cl], [bmim][Cl], and [hmim][Cl] based mixtures, respectively.

Since the [bmim][Cl] based mixture gave the largest chromium coating thickness on the copper substrate, we further investigated electroplating onto other substrates from the [bmim][Cl] based mixture. Figure 10 presents the morphology of the surface (numbered 1) and of the cross section (numbered 2) of the coatings obtained for electroplating from a 1:2 CrCl₃·18H₂O/[bmim][Cl] mixture onto brass and zinc coated steel substrates, respectively. The coatings were found to be compact and microcrackfree, and the amount

Table 4. Atomic Percent of Different Chromium States in Coatings Obtained from Different Mixtures

IL	Cr _{metal} (at %)	CrO _x (at %)
ChCl	70.6 ± 3.2	29.4 ± 3.2
[emim]Cl	85.1 ± 2.4	14.9 ± 2.4
[bmim]Cl	80.4 ± 1.5	19.6 ± 1.5
[hmim]Cl	62.2 ± 1.7	37.8 ± 1.7

percent of chromium in metallic and oxidized states in the different coatings. It shows that the bulk coatings are predominantly metallic chromium and the atomic percent of metallic chromium is significantly higher for coatings electrodeposited from [emim][Cl] and [bmim][Cl] based mixtures than from [Ch][Cl] based mixtures. It is obvious that the structure of the ILs, more specifically, the length of the alkyl chain of the imidazolium cation, plays a role in influencing the

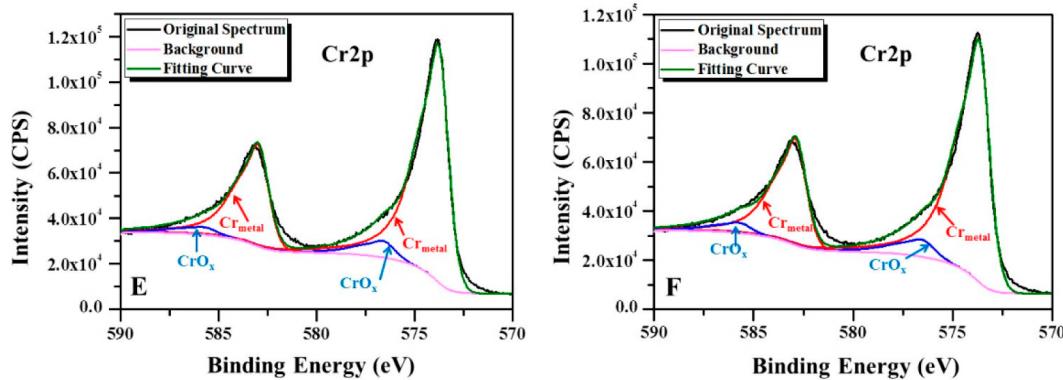


Figure 8. XPS spectra of coatings obtained from 1:2 $\text{CrCl}_3 \cdot 18\text{H}_2\text{O}/[\text{bmim}][\text{Cl}]$ onto different substrates: (E) brass and (F) zinc coated steel (-2.5 V vs QRE, 52°C , 20 min).

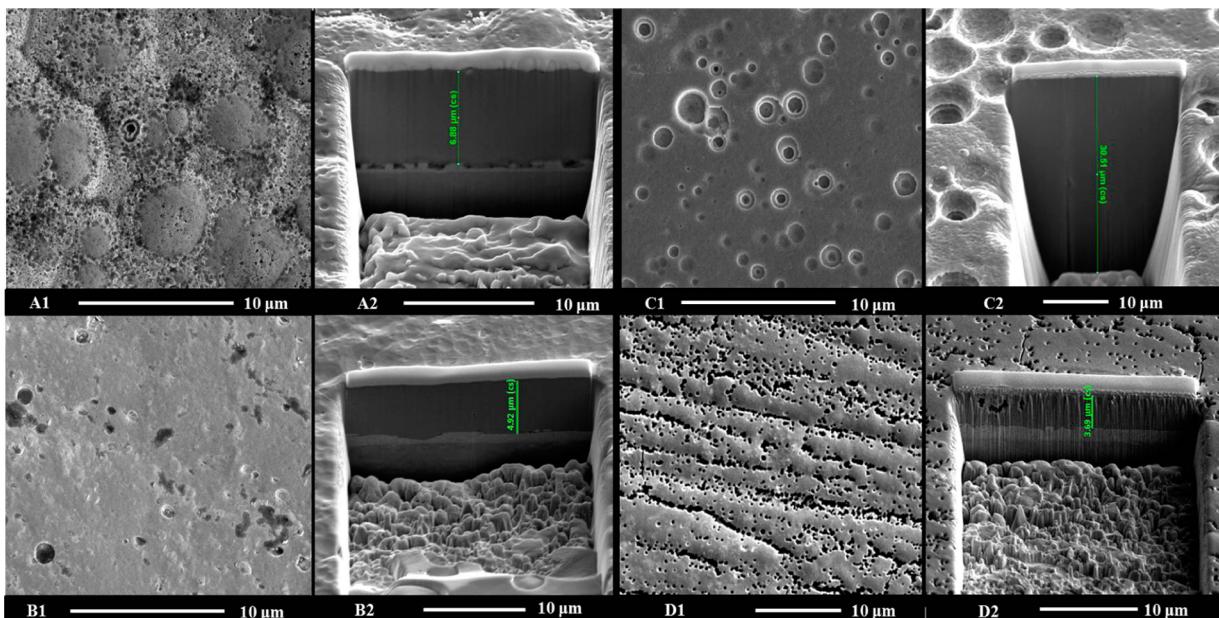


Figure 9. SEM image of coatings on a Cu substrate, from (A) 1:2 $\text{CrCl}_3 \cdot 18\text{H}_2\text{O}/[\text{Ch}][\text{Cl}]$, (B) 1:2 $\text{CrCl}_3 \cdot 18\text{H}_2\text{O}/[\text{emim}][\text{Cl}]$, (C) 1:2 $\text{CrCl}_3 \cdot 18\text{H}_2\text{O}/[\text{bmim}][\text{Cl}]$, and (D) 1:2 $\text{CrCl}_3 \cdot 18\text{H}_2\text{O}/[\text{hmim}][\text{Cl}]$ (-2.5 V vs QRE, 52°C , 20 min).

of the pits was significantly reduced compared to the coating deposited on Cu substrate. The thicknesses of the coatings were measured to be >21.75 and $2.22 \mu\text{m}$ on the brass and SS substrate, respectively. Note that the current densities were not the same for electroplating on the different substrates.

The hardness was measured for coatings with thicknesses greater than $10 \mu\text{m}$. The hardness was 441 and 681 HV for coatings obtained by electroplating from a 1:2 $\text{CrCl}_3 \cdot 18\text{H}_2\text{O}/[\text{bmim}][\text{Cl}]$ mixture on Cu and brass substrates, respectively. The hardness of the coatings is significantly higher than that of previously reported chromium coatings obtained from Cr(III)/IL baths (242 HV) and is almost as good as that of coatings produced by electroplating from conventional Cr(VI) aqueous baths (typically 800–900 HV).²

The properties of the *N,N'*-dialkylimidazolium chloride ionic liquid based mixtures containing trivalent chromium chloride, as well as the characteristics of the coatings obtained by electroplating from these mixtures, present these systems as promising alternatives to conventional chromium electroplating using hexavalent chromium sources. Yet there are many unanswered questions. For instance, we tried electroplating

out of the mixture of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{emim}][\text{Tf}_2\text{N}]$) and Cr(III) $[\text{Tf}_2\text{N}]_3$ that was synthesized in our laboratory with a 2:1:18 IL/Cr/ H_2O mole ratio, but no coating was obtained. Apparently, the chloride anion plays a key role in facilitating the process of electroplating of chromium. It is possible that the chloride anion is oxidized at the anode. Nonetheless, mixtures with a 18:1 $\text{H}_2\text{O}:\text{Cr}$ ratio are essentially aqueous solutions, where one would expect hydrogen evolution. These issues, as well as potential IL decomposition, should be investigated in the future.

4. CONCLUSIONS

We have characterized the physicochemical properties, including conductivity, density, viscosity, and ionicity, and the electrochemical behavior as well as Cr(III) speciation of a series of mixtures based on imidazolium chloride ILs and chromium(III) chloride. To the best of our knowledge, this is the first time that this type of ILs have been systematically studied for application of chromium electroplating from trivalent chromium sources. Our results show that $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$

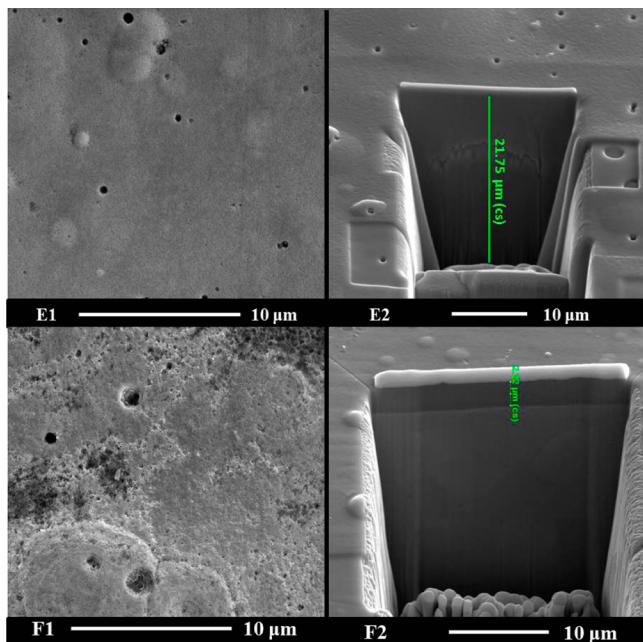


Figure 10. SEM image of coatings obtained from 1:2 CrCl₃·18H₂O/[bmim][Cl] onto: (E) brass and (F) zinc coated stainless steel.

predominantly exists in the mixtures and that the physicochemical and electrochemical properties of the mixtures are dependent on the relative amount of water in the mixture and the cation type of the IL with a fixed anion. Compact chromium coatings have been obtained from the four imidazolium chloride ILs-based mixtures with a 1:18 Cr:H₂O ratio onto copper substrates. XPS analysis shows that the percent of metallic chromium of the coatings ranges from 60% to 85%. The thickness of the coatings ranges from several up to 30 μm, and the hardness of the coatings with a thickness above 10 μm is significantly larger than that of coatings obtained from previously reported 2:1 CrCl₃·6H₂O/ChCl mixture and is comparable to coatings produced by electroplating from conventional Cr(VI) aqueous baths. Among the four types of imidazolium chloride IL-based mixtures, coatings obtained from [bmim][Cl]-based mixture have better thickness and hardness. Additional experiments showed that similar chromium coatings could be deposited onto brass and zinc coated stainless steel from the 1:2 CrCl₃·18H₂O/[bmim][Cl] mixture. Thus, this class of Cr(III)/ILs mixtures could be a promising alternative to the conventional Cr(VI) containing aqueous baths for chromium electroplating under further optimized conditions.

■ ASSOCIATED CONTENT

Supporting Information

Tables of the conductivity, density, and viscosity data on the mixtures studied in this work, as well as some sample XPS spectra. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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