

Preparation and Characterizations of High Carbon Content Cr-C Coatings Electroplated from a Trivalent Chromium-Based Bath

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A high carbon concentration chromium-carbon (Cr-C) deposits were formed from Cr(III) electroplating solution. The influences of complexing agent in Cr(III) electroplating procedure and properties of chromium-carbon deposits were studied. Our results showed that complexing agents with or without ammonium group differently affect plating rate, plating efficiency, composition, and properties of Cr electroplating. In the presence of 3 M ammonium acetate, the Cr-C layer has the highest carbon content of approximately 37.25 at.%, the smallest interfacial contact resistance among all chromium-carbon deposits studied. Generally, the hydrophobicity of chromium-carbon deposits increased with an increase of carbon content within coating, and it would be helpful for improving the working efficacy of the bipolar plates. This study clearly shows high carbon chromium-carbon deposits possess the potential to be used as bipolar plates for fuel cells.

Keywords: Cr-C alloys; coatings; Trivalent chromium; Electrodeposition; Carbon content; Complexing agents

1. INTRODUCTION

Chromium carbide coatings have some superior properties such as high hardness, toughness, chemical stability, strength and corrosion resistance [1, 2]. Due to these properties, they are widely applied on tools and dies as protective coating, and they have high potentiality to substitute the common coatings, such as the hard chrome coating used to protect a mold [3]. Chromium carbide coatings can be manufactured by physical vapor deposition (PVD) methods [4-7], pulsed laser deposition [8], arc evaporation [9, 10] and chemical vapor deposition (CVD) techniques [11]. Recently, researchers worked for preparing chromium carbide coating by means of electrodeposition from Cr(III) baths [12-15].

Chromium-carbon deposits can be formed from Cr(III) electroplating solution containing organic complexants, such as oxalate, formate, urea, carbamide and glycine [16]. Apparently, the carbon element existing in those organic complexants in the solution is co-deposited in the coating following the reduction of metal chromium [17]. By comparing with Cr(VI) deposit, chromium-carbon deposits display superior mechanical characteristics, and reveal better corrosion resistance than Cr(VI) plating. The hardness is even higher than hard chromium after heat treatment [18, 19]. Moreover, the Cr_3C_2 has a conductivity as large as $68 \times 10^6 \Omega^{-1}\text{cm}^{-1}$ [20], allowing employ as a conductive material. However, in most cases, the obtained electroplated Cr-C coatings have a low carbon content (2 to 8 wt.%) [17, 21].

Bipolar plates is a very important component in polymer electrolyte membrane fuel cells (PEMFC) [22-24]. It is generally recognized that the requirement of an excellent bipolar plate materials must include low interfacial contact resistance, high corrosion resistance, low cost, high mechanical strength, and high gas impermeability [25, 26]. Chromium carbide deposits have some advantageous properties, such as good corrosion resistance, mechanical strength, electrical and thermal conductivity, wear resistance, and hardness, meaning that chromium carbide deposits can be applied on metallic bipolar plates as a protective films for fuel cells owing to their high conductivity and corrosion resistance. Past literature indicated that the Cr-C coating was deposited on 316L stainless steel by pulsed bias arc ion plating method can to be bipolar plates for PEMFC system [27]. By comparing with pure C film and C-Cr-N film deposited on the surface of bipolar plates, the chromium carbide deposits have better corrosion resistance and interfacial contact resistance that can improve the working efficiency of bipolar plates in PEMFC system. The pack cementation method was used to the surface-chromized of 1020 carbon steel for bipolar plates [28]. The shortcoming of CVD and pack cementation technique to prepare Cr-C coatings is that it only can be used in high temperature condition. Electroplating technique provides a lower processing temperature, cut down manufacture cost, and a simple operated process. In our previous study [29], the effect of the formic acid concentration on chemical composition, microstructure, surface structure, corrosion resistance, conductivity and C concentration to chromium carbide deposits were investigated. Our results found that the highest carbon content (~28.4 at.%) of Cr-C coating was obtained at a formic acid concentration of 2 M. In addition, the electrical conductivity and corrosion resistance of the chromium carbide deposits increase with an increase of carbon concentration.

In this study, different kinds of complexing agents (formic acid, ammonium formate, acetic acid, ammonium acetate) were putted in Cr(III) electroplating solution to prepare Cr-C deposits with a high carbon content. The influence of complexing agents on the chemical composition, microstructure, surface morphology, hydrophobicity, and conductivity of the Cr-C deposits was studied.

2. EXPERIMENTAL

2.1. Materials and Electroplating

A brass plate and a platinum plate were used as the cathode and anode, respectively. Brass (30 At.% Zn, 0.05 At.% Fe, 0.05 At.% Pb, remainder Cu) substrates were prepared as square sheets (50x50x2 mm), grinded with #2000 SiC sandpaper, degreased with acetone (2 min), activated by 3% NaOH aqueous solution (1 min), and pickled in a hydrochloric acid solution (HCl (35%):water = 1:1) for 5 min prior to electroplating trivalent chromate Cr-C.

Electroplating was prepared in Cr(III) electroplating solution composed of 0.2 M $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, 0.5 M KCl, 0.01 M KBr with the addition of 3 M formic acid, 3 M ammonium formate, 3 M acetic acid or 3 M ammonium acetate as complexing agents, respectively, as listed in Table 1.

Table 1. Compositions in electroplating bath for electrodepositing Cr-C coatings

Component concentration(mol dm ⁻³)	F1	F2	A1	A2
$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	0.2	0.2	0.2	0.2
HCOOH	3			
HCOONH ₄		3		
CH ₃ COOH			3	
CH ₃ COONH ₄				3
KCl	0.5	0.5	0.5	0.5
KBr	0.01	0.01	0.01	0.01

The plating bath used $\text{B}(\text{OH})_3$ as buffering agent. The pH of the electrolyte was adjusted to 4.5-5 and all the electroplating was conducted at $25 \pm 2^\circ\text{C}$. After electroplating, all the coatings were rinsed in distilled water and dried in air at room temperature for 24 h.

2.2. Microstructure and composition analysis

The microstructure and morphology of coatings are examined by using scanning electron microscope (SEM). The phase composition of coatings were determined by X-ray diffraction (XRD) with Cu $\text{K}\alpha$ radiation ($\lambda = 0.15405$ nm) and the scanning range was from 20° to 80° . The chemical composition of coatings (including Cr, C, O, and N) was analyzed with an electron probe X-ray micro-

analyzer (EPMA). The X-ray photoelectron spectrometry (XPS) was employed to detect the concentration profiles of non-polarized samples.

2.3. Conductivity and interfacial contact resistance (ICR) measurement

The past studies had indicated the measurement technique of interfacial contact resistance [30, 31]. In this study, the interfacial contact resistance between the specimens and carbon paper gas diffusion layer (GDL) was determined by a method reported by Wang et al. [31].

3. RESULTS AND DISCUSSION

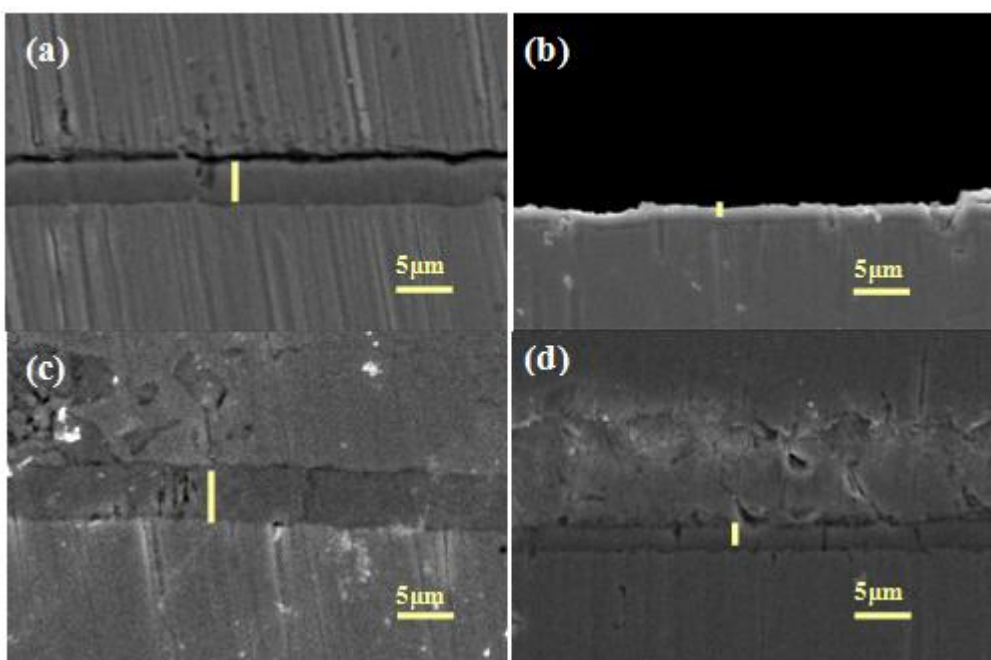


Figure 1. shows the cross-sectional micrographs of Cr-C coatings electroplated from four different baths (F1, F2, A1 and A2). The images show that the thickness of F1 and A1 were thicker than that of F2 and A2.

Table 2. Plating thickness and electroplating efficiency of electroplating Cr-C coatings from various conditions.

Sample	Thickness (μm)	Electroplating efficiency (%)	Roughness (nm)
F1	4.73	9.78	185
F2	1.52	5.23	127
A1	5.21	11.35	163
A2	1.82	6.85	145

Table 2 presents a comparison of the thicknesses of Cr-C coating and plating efficiencies in a Cr(III)-based bath with various complexing agents during electro-deposit process. The results have shown that complexing agents with and without ammonium ion differently affect on the electroreduction of the chromium plating. Chromium deposit obtained in the bath containing acetic acid (F1) had thicker thickness and higher plating efficiency compared with the chromium deposit obtained in the bath containing ammonium acetate (F2). As seen in Table 2, plating in the chromium-formic acid electrolyte (A1) also had thicker thickness and better plating efficiency than those of plating in the chromium-formate electrolyte (A2). The outcomes display that the electroplating properties of the electrolyte remarkably rely on the chemical composition of the introduced complexing agent.

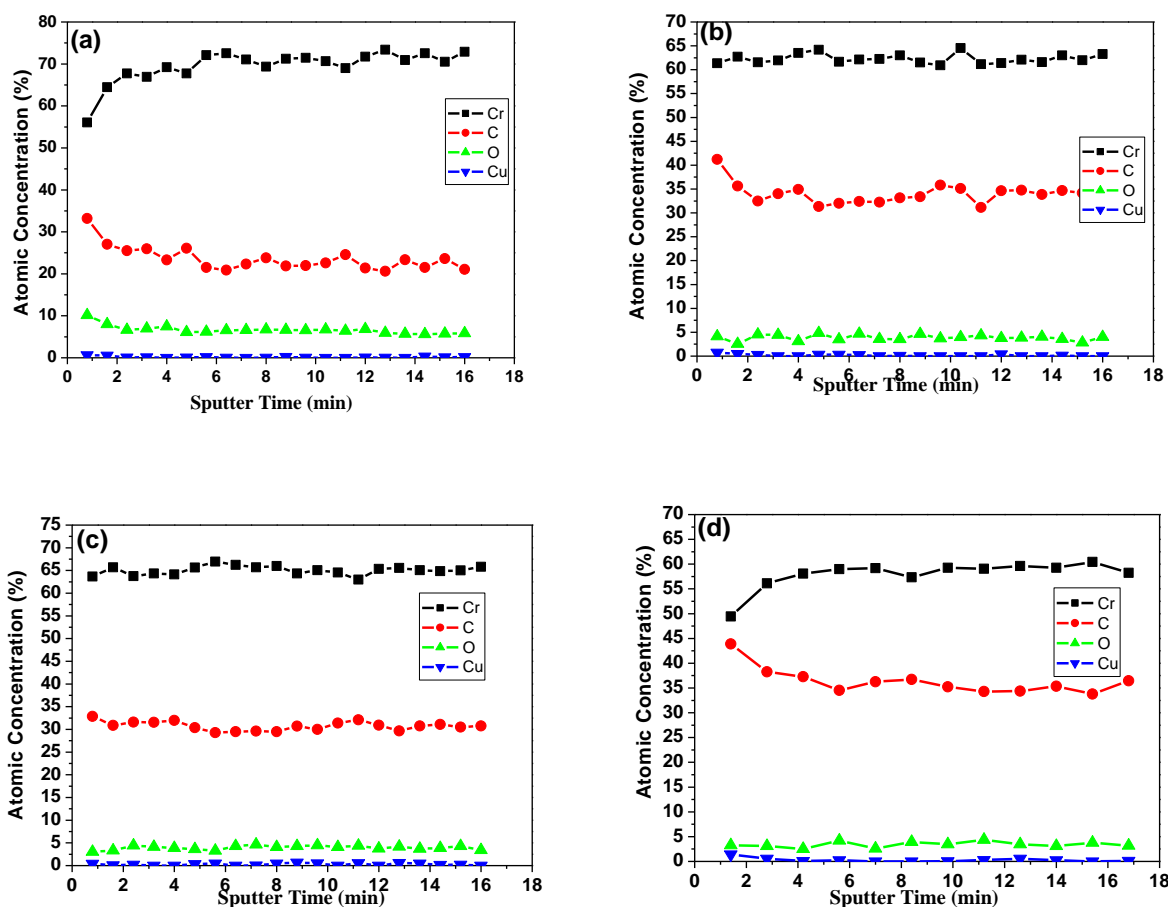


Figure 2. XPS depth profiles of the Cr-C deposits obtained from electroplating in different baths: (a) F1, (b) F2, (c) A1, and (d) A2. The estimated sputtering rate was 1 \AA s^{-1} .

Fig. 2 reveals the concentration of base elements (Cr, O and C) within Cr coatings. The concentration of these elements only varied within the top thin layer of coatings. Peaks due to C, O, Cu, and Cr are observed. It is clearly seen from Fig. 1 that Cr and carbon are distributed rather uniformly inside of the deposit. The element Cu is from the brass substrate. It is seen from Fig. 2 and

Table 3 that carbon content of all Cr deposits is more than 20 at.%. In particular, Cr coatings deposited in a bath with ammonium acetate or ammonium formate contain carbon element about 35 at.% or more.

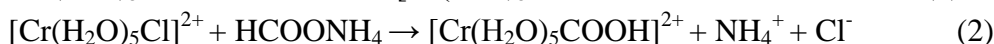
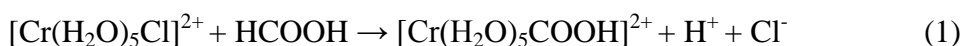
Table 3. The composition of Cr-C coatings electrodeposited from different baths for 10 min.

Sample	Cr (at%)	C (at%)	O (at%)	Cu (at%)
F1	63.64	28.37	7.91	0.08
F2	60.30	35.60	3.42	0.68
A1	63.34	31.91	4.73	0.02
A2	58.80	37.25	3.94	0.01

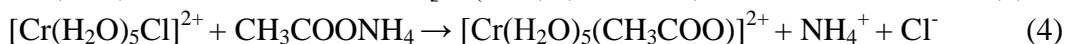
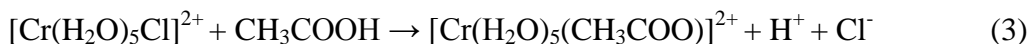
The highest ratio of carbon is observed for Cr deposited in a bath with ammonium formate (A2). Up to 7 at.% of oxygen (mainly in the form of chromium oxide) exists within the Cr coating deposited in a bath with acetic acid. When there is too much oxide, which has poor conductivity, in the coatings, the conductivity will be deteriorated.

It has been reported that thick Cr coating with acceptable quality can hardly be electrodeposited in a simple aqueous Cr^{3+} bath successfully due to a very stable esa-aquo ion ($[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$) [32]. Appropriate complexing agents, formed complexes with Cr^{3+} that are thermodynamically more stable than its esa-aquo ion; promote the reduction reaction of Cr^{3+} at the cathode. Various complexing agents such as acetic acid, formic acid, urea, glycine and oxalic acid were generally used to destabilize $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ complex. In chromium chloride solution as we used in present study, trivalent chromium ion mainly existed in the complex form of $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ [32]. In the solution containing formate and acetate complexing agents, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ ions are converted to $[\text{Cr}(\text{H}_2\text{O})_5(\text{COOH})]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_5(\text{OOCCH}_3)]^{2+}$, respectively, as described by the following reactions:

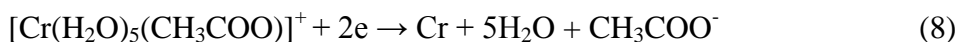
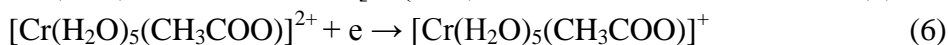
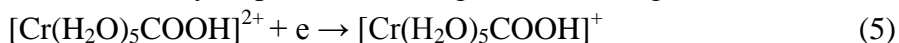
For formic acid and ammonium formate



For acetic acid and ammonium acetate



It is known [33] that the electrodeposition of Cr occurs in bath containing formate and acetate complexes of Cr^{3+} may be presented through the following reactions:



From the above equations, it shows that the formate and acetate complexes of Cr^{3+} , respectively, are reduced through a similar reaction mechanism to Cr(s) irrespective of the origin of formate and acetate ions. However, experimental results as shown in Table 2 indicate that both

deposition rate and plating efficiency are higher for baths with formic and acetic acids than those obtained from their relevant baths containing ammonium ions, whereas the carbon content is lower in the former than that in the latter. This suggests that the presence of ammonium ion in the bath play a critical role in the trivalent chromium deposition process. The reasons for effect of ammonium ion are not well understood now. It might be related to the difference in ligand ion concentration of the electrolyte. It is noted that the complexing agents used in this study are either weak acids or salts of weak acid and weak base, which means that only a portion of the molecules will dissociate into ions, while some remain as molecules. A simple calculation based on the equilibrium constant of formic acid (1.77×10^{-4}) and acetic acid (1.8×10^{-5}) shows that the concentration of ligand ions in aqueous solution are in the order of $F1 > A1 > A2 > F2$. The concentrations of formate and acetate ions in baths with formic and acetic acids are higher than those in baths with ammonium formate and ammonium acetate, resulting in a higher concentration of the available electro-active chromium complexes. As a result the plating efficiency is increased for electroplating Cr-C coating in bath with acetic or formic acid as complexing agent. However, it shows from Table 2 that the plating efficiency of bath A1 is higher than that of F1, suggesting that the ligand ion concentration does not play a decisive role in the electroreduction of the trivalent chromium, however, other factor, such as the change of chromium complex stability owing to the difference in ligand nature, might also affect the electroreduction of trivalent chromium.

Generally, the amount of carbon within the Cr-C deposit comes from the reduction of complex-formed Cr ions [34]. According to this mechanism, an increase in the electrochemically active complex concentration must result in the increase of carbon concentration in Cr-C coating. As also shown in Fig. 2 and Table 3, however, the opposite effect is found in this study that the carbon content of Cr coatings deposited in a bath with ammonium acetate (A2) or ammonium formate (F2) is much higher than that of bath with acetic acid (A1) or formic acid (F2). Our result shows the C concentration of Cr deposits increases as the available electro-active chromium complexes decrease can be illustrated with a mechanism initiated by Protsenko et al. [33]. On the basis of this theory, some of active Cr ad-atoms was produced as Cr(II) ions and the discharge may interact with adsorbed organic composition in solution (i.e. complexing agent) by "chemical" mechanism. Carbon atoms mobilized into Cr films and Cr(II) ions will participate in electrochemical reaction of Cr deposition again. It illustrated that the quantity of carbon incorporation into the coat is dominated by the amount of adsorbed complexing agent molecules on cathode surface and the concentration of Cr ad-atoms. The former is dependent on complexing agent concentration in electrolyte. Since the complexing agents remains in its original form increases with a decrease of the concentration of ligand ions in bath (i.e. the available electro-active chromium complexes), it is reasonable that more complexing agent molecules will be adsorbed on cathode surface in bath with ammonium acetate (A2) or ammonium formate (F2), resulting in an increase of carbon content of the electrocodeposited Cr-C coatings.

Fig. 3 is the surface morphology of Cr-C deposits observed by SEM. Cracks appearing in networks were observed in the deposits plated in bath F1 (Fig. 3(a)) and bath A1 (Fig. 3(c)). Cracks were hardly observed in the deposits plated in bath F2 (Fig. 3(b)) and bath A2 (Fig. 3(d)). In addition to the specimen F2, others specimens including A1, A2 and F1 all have cracks which can be observed in the cross-sectional of Cr-C deposits (see Fig. 1). Although the Cr-C coating formed in the

electroplating bath with "HCOONH₄" has the lowest plating efficiency and deposition rate, it has a dense and crack-free structure. As mentioned above, the plating efficiency and deposition rate are higher for bath A1 and F1 than those of A2 and F2. Therefore, the formation of cracks can be attributed to the stress relief during electroplating. Moreover, some dark areas with diameter of about 2-13 μm were examined from the surface of chromium-carbon coating plated in bath A2 (Fig. 3(d)), which can be ascribed to the accumulation of carbon element [35].

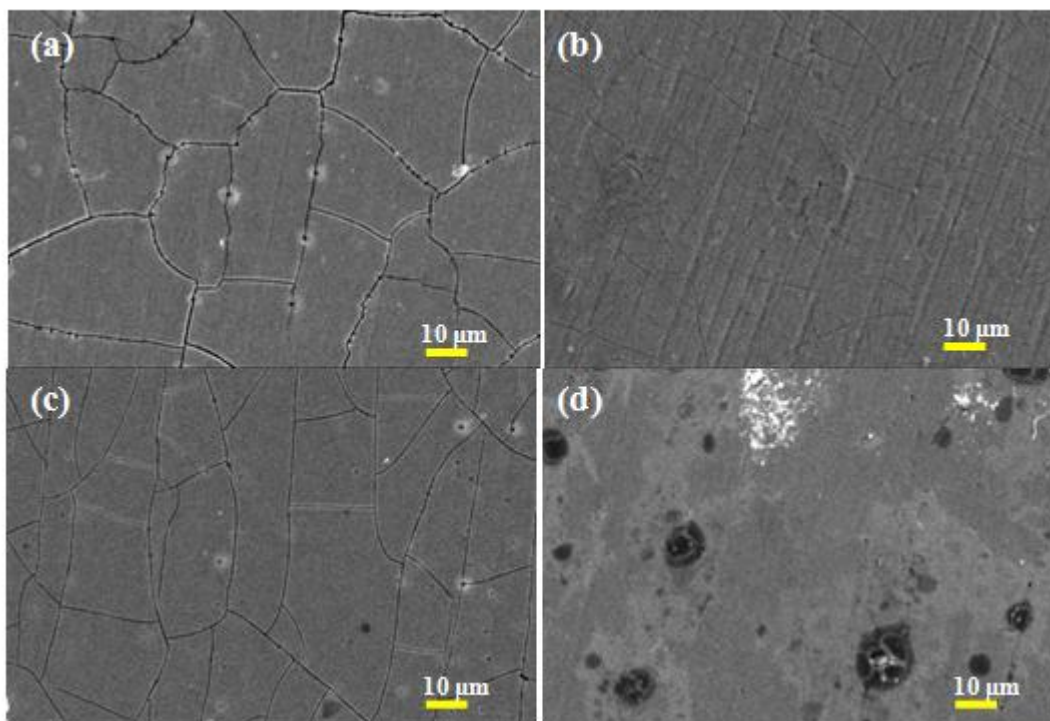


Figure 3. SEM micrographs of the Cr-C deposits obtained from electroplating in different baths: (a) F1, (b) F2, (c) A1, (d) A2, and (time 10 min)

The composition of Cr-C deposits involve Cr, chromium carbide, and minute quantity metal oxides. Although chromium carbide is an impurity within chromium coatings, it will improve the conductivity of deposits. The Cr₃C₂ has a superior conductivity about $68 \times 10^6 \Omega^{-1} \text{cm}^{-1}$ and thus can be used as a conductive ceramic [20]. Fig.4 presents the relationship of the Cr-C coatings between contact resistances and compaction pressure. From Fig.4, it revealed that the ICR reduces significantly with compaction force [31], indicating that the ICP will change slightly while the compaction force greater than 120 N/cm². Table 2 shows that the contact resistance reduces with an increase C concentration within deposits, in the following order: F1, A1, A2, F2. The Cr-C coating deposited in bath with ammonium acetate gives the lowest contact resistance (10 mΩcm² under 160 Ncm⁻²) as a result of the highest carbon concentration in the Cr-C deposit. In this work, the Cr-C film electroplated in electrolyte added ammonium acetate has good conductivity, which reaches the U.S. DOE standard applied at BPs (< 20 mΩcm² at 160 Ncm⁻²) [36].

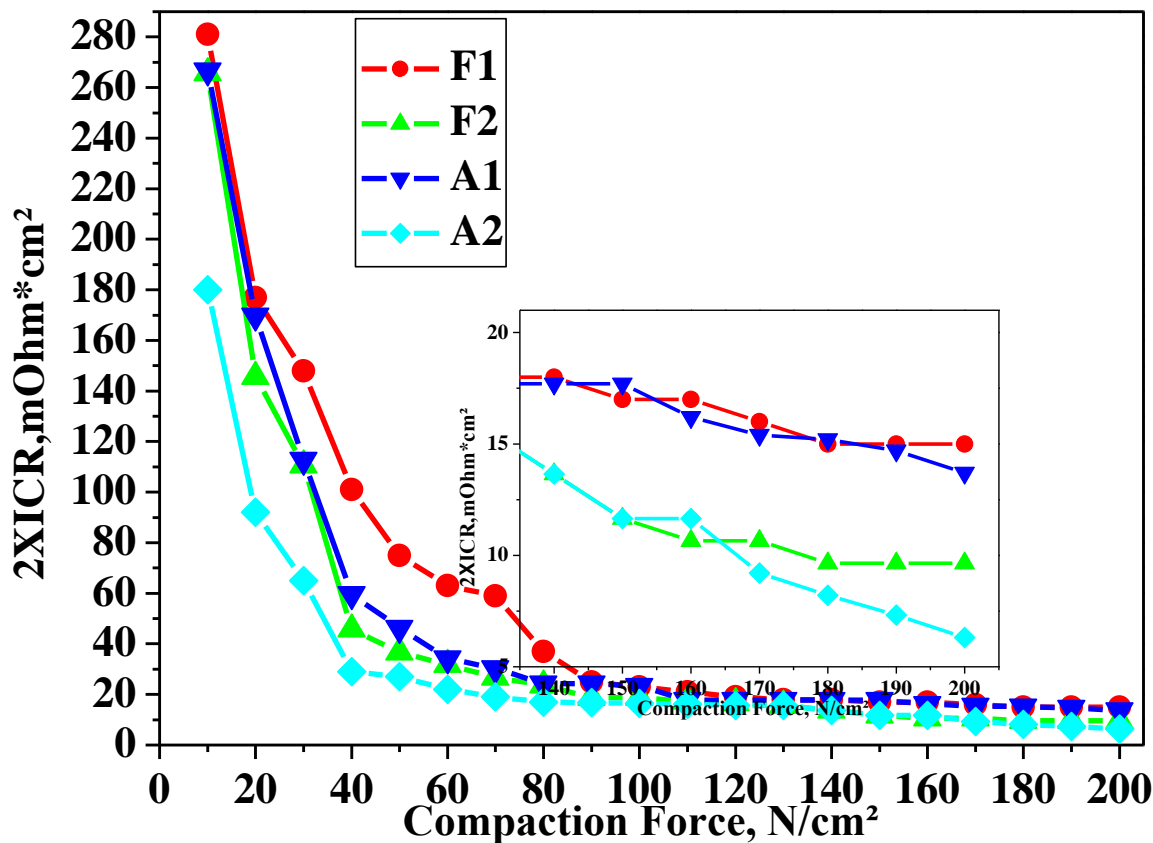


Figure 4. The relationship of the Cr-C coatings between contact resistances and compaction pressure.

Fig. 5 presents the hardness of chromium-carbon deposits obtained from different electroplating baths. By comparing the carbon content of Cr-C coatings from Table 3, the hardness of coatings enhanced with increasing of C concentration within Cr-C deposits. The carbon content within both specimen F2 and A2 exceeded 35 at.% and enhanced the hardness of coatings up to over 13 GPa. The carbon content of specimen F1 is about 28 at.% and its hardness is about 12.4 GPa. As mentioned above, the formation quantity of Cr-C compound would be controlled by the carbon content within coatings and affect the hardness of coatings. In general, the hardness of the trivalent chromium coatings was quite high (about 600 - 700 Hv) [37], but the Cr-C coatings would have a higher hardness because of precipitating Cr-C compound. Literatures [38-40] indicated that the hardness of chromium carbide is about 1350-2250 Hv (about 13-22 GPa), this also indicated that the higher carbon content the higher hardness of coatings.

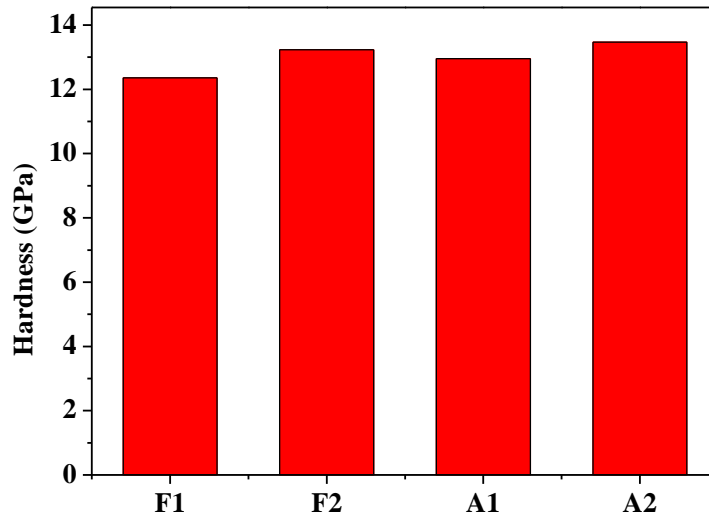


Figure 5. Hardness of the Cr-C deposits obtained from electroplating in different baths

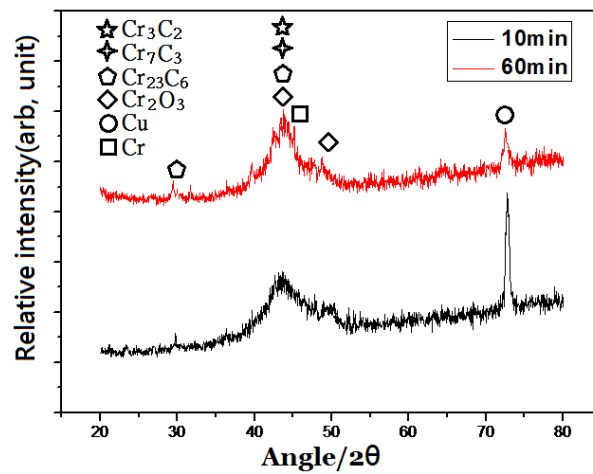
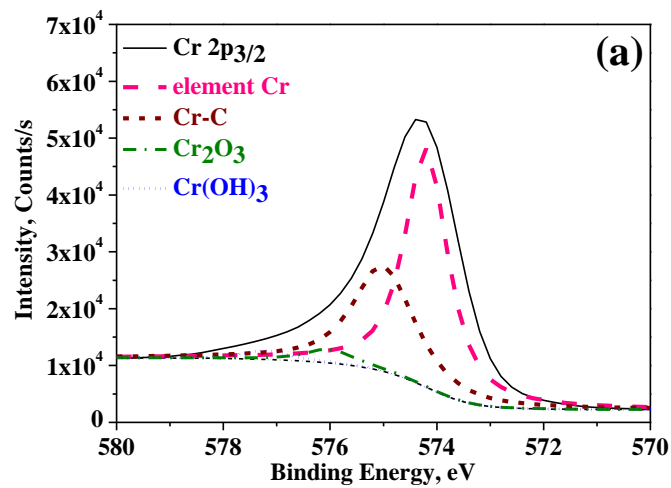


Figure 6. XRD pattern of the deposit from the trivalent bath with ammonium acetate.



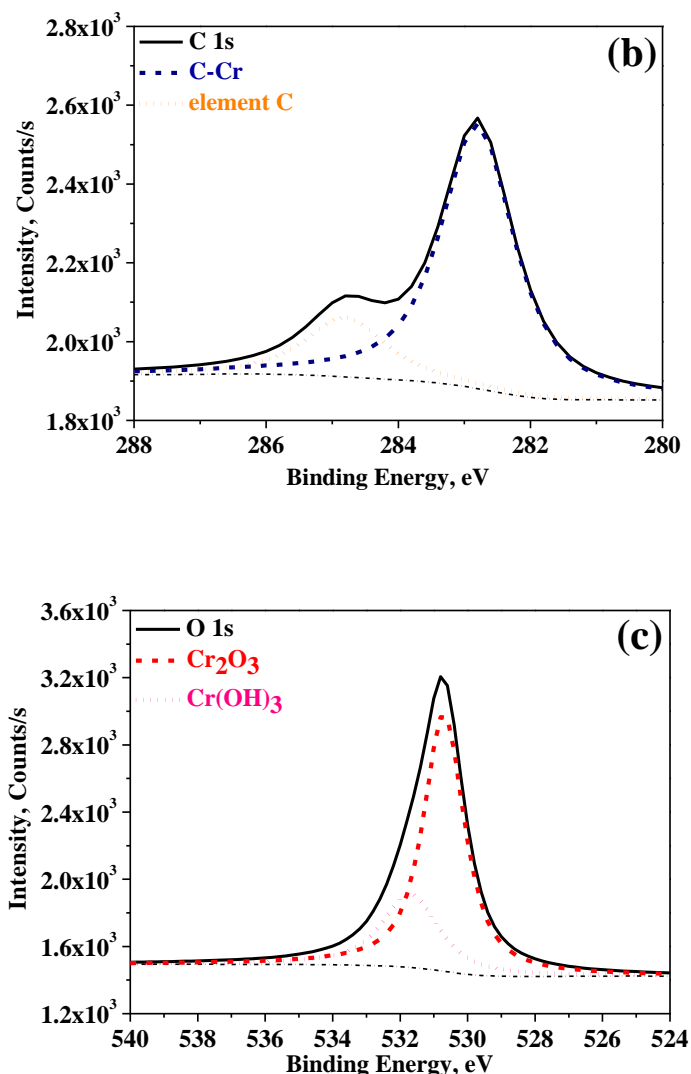


Figure 7. XPS spectra of the deposit from the trivalent bath with ammonium acetate: (a) Cr 2p_{3/2}, (b) C 1s, and (c) O 1s.

Fig. 6 presents X-ray diffraction analysis of the Cr films deposited in the bath with ammonium acetate on the brass substrate for 10 and 60 min, respectively. Both Cr-C deposits electroplated for 10 and 30 min exhibited the main phase in all coatings is amorphous, a obvious broad peak presents approximately at 43° should be the (1 1 0) diffraction peak of Cr. It is in a good agreement with the Cr-C electrodeposited formed from Cr(III) electroplating solution [41, 42]. It can attribute the amorphization of the Cr-C deposits comes from the reaction of the carbon alloying which co-deposit into the chromium crystal lattice and disturbs the setting order of Cr atoms [43, 44]. Observing carefully, however, some small sharp peaks appeared in these XRD patterns, suggesting Cr-C coatings electroplated in bath with ammonium acetate contain extremely fine crystals regardless of the plating time. A sharp peak at around $2\theta = 72.2$ corresponding to the (220) plane of CuZn alloy. The intensity of diffraction peak reduces with an increase of plating duration.

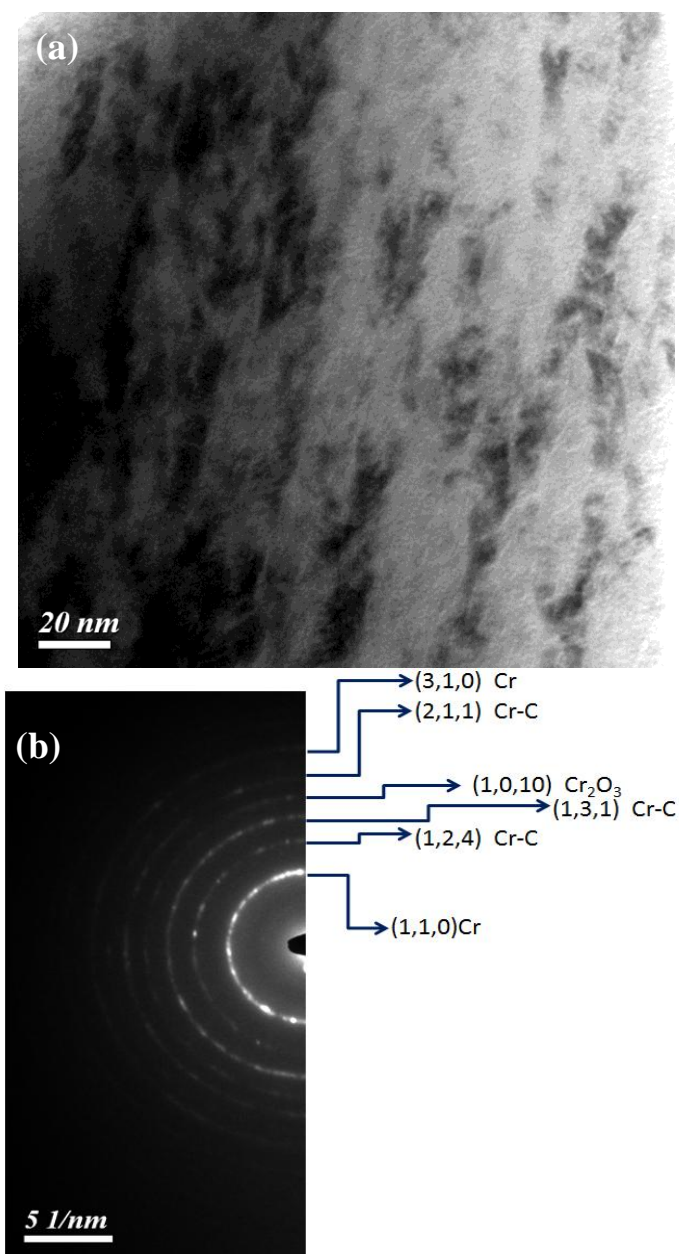


Figure 8. (a) Cross-sectional TEM micrograph and of the deposit from the trivalent Cr bath with ammonium acetate after plating at a current density of 10 A dm^{-2} for 10 min; (b) corresponding SAED pattern.

The information of existing elements in the A2 coating electrodeposited from trivalent chromium solution in the presence of ammonium acetate was analyzed by X-ray photoelectron spectroscopy (XPS). The narrow scan spectra of Cr2p, C1s and O1s band are shown in Fig. 7(a), 7(b), and 7(c), respectively. The Cr2p_{3/2} peak in Fig. 7 (a) reveals the major chromium species are elemental Cr, Cr-C, and Cr₂O₃. XPS data of C1s band is shown in Fig. 7(b). The peaks located at 282.7 and 284.4 eV are attributed to metal-carbon bond and C-C bond [45], respectively. The presence of Cr-C bond as shown in Fig. 7(a) is also verified from C1s spectra. A typical spectrum of O1s band (Fig. 7(c)) has components with binding energies of 530.1 and 532.2 eV. The oxygen peak at 532.2 eV may be the

contribution of oxygen atoms in the C=O or C–O bonds [45]. The peak located at 530.1 eV is the contribution of OH groups surrounding the Cr(III). In this study, the result of XPS profile corresponds to past literature [46].

HRTEM and selected area electron diffraction (SAED) were applied to get more precise information on the structure of coating. Fig. 8 shows cross-sectional HRTEM and SAED photograph of the Cr-C sample A2. TEM image (Fig. 8(a)) shows the presence of light and dark areas. The result explained the layers have different composition, the brighter areas indicate the lighter element (carbon) and the dark areas show the Cr element. The corresponding SAED pattern (Fig. 8(b)) presents diffraction rings, indicating the Cr-C coatings have a nano-crystalline structure. The SAED pattern from Fig. 8b indicated that the composition of coating included Cr, Cr-C and Cr₂O₃. By analyzing with TEM and XRD (Fig. 6), it is not clear why Cr-C deposit prepared in present study has a partially crystallized phase. This might be related to the carbon content (37.25 at.%) in A2 deposit is close to the composition of Cr₃C₂, thus, the nucleation is favored [47].

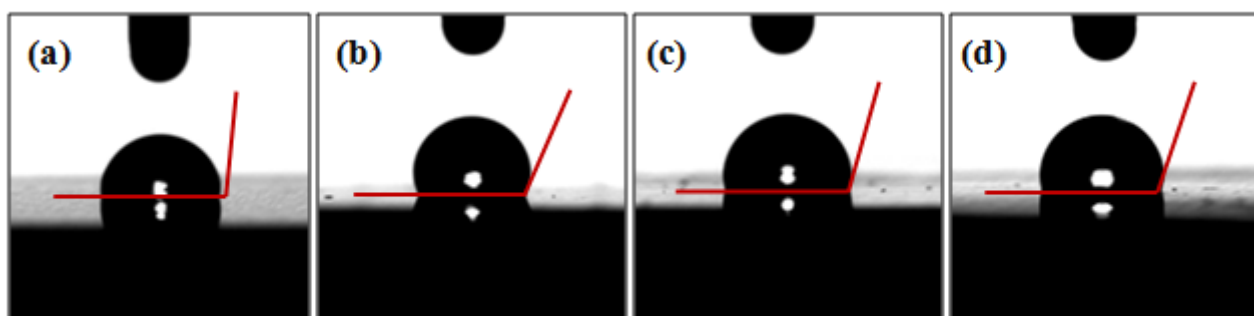


Figure 9. Contact angle of the Cr-C coatings electroplated from the bath with different complexing agents (a) F1 (93°), (b) F2 (113°), (c) A1 (106°), and (d) A2 (109°).

Fig. 9 shows the contact angle of the Cr-C coatings formed with different complexing agents. The results revealed that the contact angle would increase with an increase of carbon content within Cr-C coatings. The maximum contact angle 113° is obtained from coating F2 and this was resulted from the higher carbon content (35.6 at.%) and smoothest surface of F2 coating. Due to its coarse surface and low carbon content in the Cr-C coating, the contact angle of specimen F1 is only about 93° (the smallest contact angle among tested specimens). It has been reported in our recent study [48] that bipolar plate has good hydrophobic would improve the working efficacy of the bipolar plates.

4. CONCLUSIONS

(1) The complexing agent in plating bath significantly affects the electroplating behaviors, which, in turn, changes the physical and chemical properties of the electrodeposited Cr-C coatings. The plating bath with ammonium containing complexing agent is more favorable for improving the electrical properties of the electroplated chromium-carbon deposit than the plating bath without

ammonium containing complexing agent.

(2) The electrically conductivity of all four Cr-C deposits studied in present investigation, which having high carbon content (> 20 at.%), reaches the U.S. DOE standard applied at BPs. The Cr-C coating electrodeposited from bath A2 using the complexing agent of ammonium acetate, in particular, shows highest carbon content (37.25 at.%) and the smallest interfacial contact resistance ($10 \text{ m}\Omega\text{cm}^2$ at 160 Ncm^{-2}) among all Cr-C deposits studied, followed by Cr-C coating from bath F2 that used ammonium formate as a complexing agent.

(3) The increase of carbon content to 37.25 at.% in the Cr-C deposit favors nucleation, results in formation of nanocrystallite in the deposit. The reason for this behavior is unknown and will be studied further. Additionally, the residual stress of the Cr-C deposit and the population density of cracks are decreased when more carbon is co-deposited.

(4) The contact angle would increase with an increase of carbon content within Cr-C coatings and it is beneficial to improving the working efficacy of the bipolar plates.

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