

Electrodeposition of multicomponent alloys using phase-separated solutions

Yuki Murakami

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Yuki Murakami

Department of Materials Science and Engineering

Graduate School of Engineering

Kyoto University

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General Introduction

1. Conventional alloys and high/medium-entropy alloys

Alloy materials have been extensively studied since ancient times due to their superior mechanical properties and corrosion resistance compared to pure metals. Today, they are widely utilized as functional materials, such as stainless steel^[1] and nickel-based superalloys^[2]. The design of these alloys typically begins with the selection of primary elements, to which various alloying elements are added. The properties of alloy materials are largely determined by the primary metal, while specific functionalities, such as enhanced corrosion resistance, are imparted by the addition of elements like chromium in small amounts. Here, the type and concentration of alloying elements serve as key parameters, enabling precise control over the material's properties to suit specific applications. In contrast to conventional alloys, which have been explored in the compositional regions corresponding to the corners of phase diagrams (Figure G.1a), high-entropy alloys (HEAs) and medium-entropy alloys (MEAs) have recently attracted attention as entirely new concepts^[3,4]. These alloys are located near the center of phase diagrams, lacking a dominant principal element (Figure G.1b). These materials form single-phase solid solutions with multiple metallic elements arranged in nearly equiatomic ratios and distributed randomly. Since their pioneering report in 2004^[3,4], HEAs and MEAs have been intensely studied and have become one of the major topics in the field of inorganic materials science^[5–9]. They are named as such because their high configurational entropy contributes to their stabilization. While there are several ways to classify these alloys, the author adopts a classification based on the configurational entropy, ΔS , as described by the following equation.

$$\Delta S = -R \sum_{i=1}^n x_n \ln x_n \quad (\text{G.1})$$

where n being the number of constituent elements, and x_n being the molar fraction of the n -th metal. Alloys with $\Delta S > 1.5R$ are referred to as HEAs, while those with $1.0R < \Delta S < 1.5R$ are classified as MEAs. These alloys have been found to achieve a remarkable balance between strength and toughness^[10]—properties that were traditionally considered difficult to reconcile due to trade-offs in conventional alloys. As a result, they have been extensively studied as promising structural materials. Moreover, recent studies have revealed their unique catalytic^[11–17] and magnetic properties^[18,19], leading to the exploration of various novel applications.

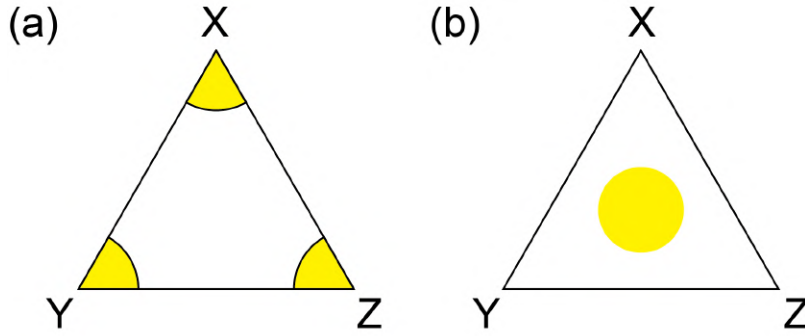


Figure G.1. Composition regions in a phase diagram: (a) conventional alloys, (b) high-/medium-entropy alloys.

The most well-known HEA is the equiatomic Cr-Mn-Fe-Co-Ni alloy, which was among the first discovered and is commonly referred to as the Cantor alloy^[3,4]. In this alloy, stacking-fault parallelepiped structure as well as nano-twinning form during deformation, resulting in exceptionally high fracture toughness, particularly under cryogenic conditions^[10]. Furthermore, compared to the microstructure of conventional alloys (Figure G.2a), HEAs exhibit a severely distorted crystal lattice (Figure G.2b). This distortion is characterized by the

mean square displacement of atomic positions from lattice points, which has been found to correlate well with the yield strength of HEAs.^[20] In addition, derivative MEAs consisting of four or three elements, obtained by excluding one or two constituent elements from the Cantor alloy, have been extensively studied^[21]. These MEAs exhibit significantly different mechanical properties depending on the combination of elements. Among them, the CrCoNi MEA demonstrates the most outstanding strength-toughness balance, even compared to the Cantor alloy and its derivatives^[22–25]. This highlights that having more constituent elements does not necessarily result in better properties. Instead, selecting the appropriate elements in optimal proportions is crucial for achieving superior performance in these alloys.

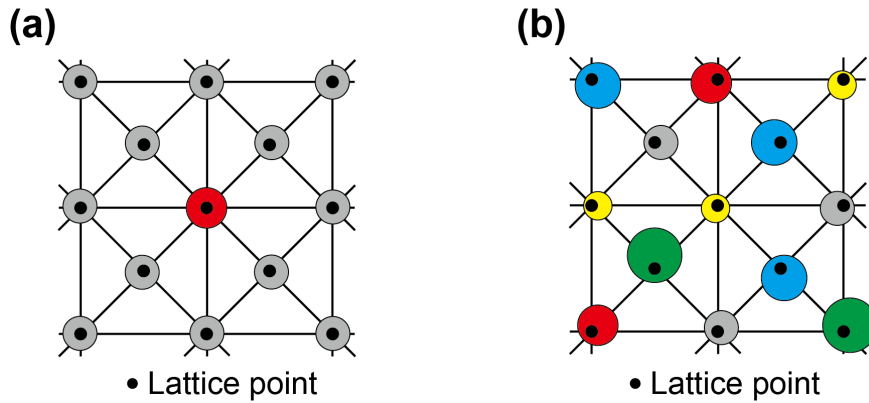


Figure G.2. Microstructure of (a) conventional alloys, (b) high-/medium-entropy alloys.

2. Fabrication methods of high/medium-entropy alloys

The current fabrication methods for HEAs and MEAs are predominantly based on casting and solidification^[3,4], which have led to a primary focus on bulk materials in research. In recent years, several studies have reported the synthesis of HEA nanoparticles targeted for catalytic applications using methods such as carbothermal shock^[11,26] and nonequilibrium chemical reduction method^[12,27]. HEAs, due to their excellent mechanical properties and corrosion resistance, are also highly anticipated for applications as surface coatings. However, methods for fabricating two-dimensional materials, such as thin films, remain limited. Recent attempts to fabricate thin films using techniques such as laser cladding^[28,29] and sputtering^[30–32] have been made. Nevertheless, challenges persist, including difficulties in forming uniform coatings on substrates with complex geometries and the tendency of alloys to undergo phase separation.

3. Electrodeposition of alloys

Electrodeposition is a process in which metal ions are electrochemically reduced to form metallic materials on an electrode. It is a key technology in industry due to its ability to produce metallic materials with various sizes and shapes, ranging from large-scale materials for electrorefining to fine structures in integrated circuits^[33]. One major application of electrodeposition is electroplating, where a thin metallic film is deposited on a substrate to impart various desirable properties to the material. For example, chromium plating using hexavalent chromium baths provides excellent wear resistance and corrosion resistance due to its high hardness and dense metal oxide layer^[33].

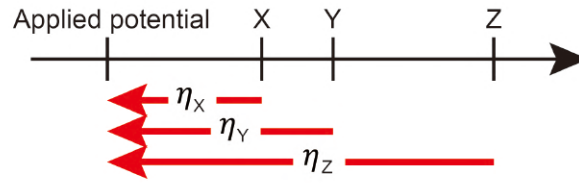
By carefully designing the electrolyte and deposition conditions, the electrodeposition process can create uniform coatings even on surfaces with complex geometries. Therefore, if HEAs and MEAs can be fabricated through electrodeposition, it could address the aforementioned challenges. However, despite the high motivation for electrodeposition of these alloys, there have been very few reports due to two major challenges associated with this process.

The first challenge is thermodynamic, arising from the differences in the electrode potentials of the constituent elements (Figure G.3a). When the potential applied to the substrate is determined, the overpotentials for the reduction of each metal vary, leading to the tendency for more noble metals to be deposited preferentially. As the number of constituent elements increases, alloy electrodeposition becomes significantly more difficult.

The second challenge is anomalous co-deposition, which is governed by kinetic factors. In such cases, less noble metals may be deposited preferentially over noble metals (Figure G.3b). As shown in this figure, the composition of the alloy can vary significantly

depending on electrolytic conditions, such as current, making it difficult to achieve controlled and uniform deposition. Anomalous codeposition is more likely to occur when the alloy contains iron-group metals, making it unavoidable when increasing the number of constituent elements or when aiming to use cost-effective metals^[34].

(a) Difference in electrode potential (thermodynamics)



(b) Anomalous codeposition (kinetics)

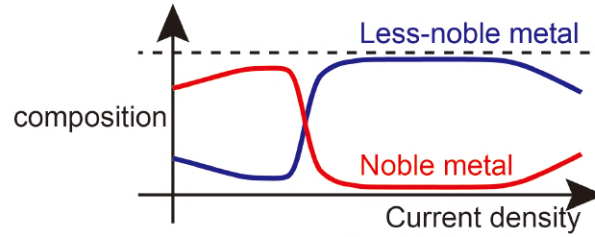


Figure G.3. Difficulties in equiatomic alloy electrodeposition: (a) thermodynamic factors, (b) kinetic factors

4. Outline of the present work

This thesis focused on electrodeposition of MEAs using phase-separated solutions. Conventional electrodeposition processes typically employ homogeneous solutions, such as aqueous solutions. However, as discussed earlier, it is challenging to control the alloy composition to be equiatomic due to the two aforementioned issues. To address these, the author hypothesized that the composition could be controlled by confining metal ions within microscale domains using phase-separated solutions. Specifically, the author began with water-in-oil emulsions

that exhibit submicron-scale phase-separated structures (Chapters 1, 2, and 3) and then extended the approach to electrodeposition using ionic liquids with mesoscopic phase separation (Chapter 4).

In Chapter 1, the author investigated the electrodeposition of CoNiCu MEA using a water-in-oil emulsion. Unlike bulk aqueous solutions, when an emulsion is used as the electrolytic solution, metal ions are immediately reduced only when droplets collide with the electrode (Figure G.4). This approach enabled the successful electrodeposition of an equiatomic alloy composed of Co, Ni, and Cu, which present widely varying deposition feasibilities. The author measured the time evolution of droplet size during the electrolysis process and observed an increase in size over time. To address this issue, intermittent sonication was applied to suppress droplet coalescence, successfully enabling the electrodeposition of MEA thin films.

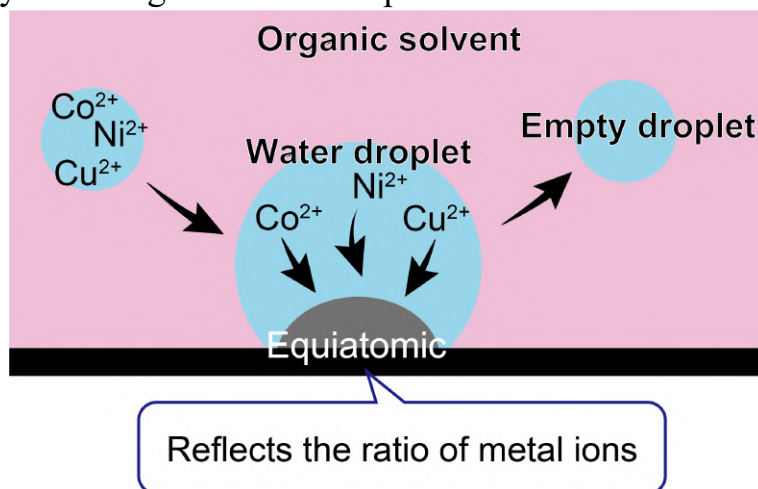


Figure G.4. Schematic of alloy electrodeposition from an emulsion

In Chapter 2, the study aimed to deposit high-quality CoNiCu MEAs by optimizing the design of emulsions. The use of appropriate surfactants resulted in a smoother surface of the deposits and an alloy composition closer to the equiatomic ratio. This improvement is attributed to the behavior of surfactant molecules, which aggregate at

the interface between the aqueous and organic phases, altering the shape of the droplets upon collision with the electrode. However, even under these conditions, the composition control was insufficient, as the proportion of Ni, the most difficult to reduce among the three elements, remained slightly lower.

To address this issue, the viscosity within the droplets was increased to uniformly suppress the diffusion of metal ions. This enabled the reduction of all metal ions under diffusion-limited conditions, successfully achieving the electrodeposition of CoNiCu MEAs with an equiatomic composition and minimal compositional variation. Furthermore, finite element simulations were employed to investigate the time evolution of metal ion concentrations within the droplets. The results demonstrated that only when the viscosity inside the droplets was increased, a thin diffusion layer was formed near the electrode, allowing reduction to occur under diffusion-limited conditions.

In Chapter 3, the focus was on the electrodeposition of composite materials composed of the CoNiCu MEA and carbon nanotubes (CNTs). While CNTs are difficult to disperse uniformly in aqueous solutions due to their hydrophobicity, they can be readily dispersed in emulsions, as the majority of the emulsion consists of a continuous oil phase. By using CNT-dispersed emulsions as the electrolyte, CoNiCu MEAs incorporating CNTs were successfully electrodeposited. Furthermore, since CNTs are conductive, they served as new nucleation sites for electrodeposition after colliding with the electrode, resulting in an enhanced deposition rate.

In Chapter 4, the electrodeposition of CrCoNi MEAs was conducted using mixtures of ionic liquids and aqueous solutions. Unlike emulsions, the ionic liquids employed in this study featured a three-dimensional interconnected structure consisting of both polar and nonpolar domains. This structure simultaneously resolved two major challenges associated with emulsions: the slow deposition rate and the difficulty of

fabricating alloys containing chromium. The mechanical properties and corrosion resistance of the CrCoNi MEA films were evaluated and compared with those of hard chromium plating from hexavalent chromium baths. The results revealed that as-deposited CrCoNi MEAs exhibited properties comparable to hard chromium plating, and these properties further improved after annealing.

Subsequently, the relationship between the length of alkyl chains attached to the ionic liquids and the characteristics of the deposits was investigated. It was found that CrCoNi MEA electrodeposition was only achievable when the alkyl chain length was equivalent to or longer than that of butyl groups. Molecular dynamics simulations were then employed to estimate the solution structure of the electrolyte, demonstrating that the mesoscopic phase-separated structure of the electrolytic solutions facilitated the successful electrodeposition of CrCoNi MEAs.

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Chapter 1

Electrodeposition of a CoNiCu medium-entropy alloy in a water-in-oil emulsion

1.1. Introduction

Multicomponent alloys containing five or more elements with a nearly equiatomic ratio have attracted keen attention from the viewpoint of mechanical properties since they are expected to exhibit excellent strength and toughness. These alloys are called *high-entropy alloys* (HEAs)^[1,2]. They were generally produced by casting; however, other production methods such as laser cladding^[3,4], and carbothermal shock method^[5,6] are intensively studied. Similarly, *medium-entropy alloys* (MEA) which contain less than five elements with a nearly-equiatomic ratio have been intensively studied as well^[7,8].

Controlling the metal composition to be a nearly equiatomic ratio is critical to produce HEAs and MEAs with excellent properties. However, such control of composition to be an equiatomic ratio is difficult using the conventional electrodeposition technique due to the difference in redox potential of each constituent metal. Recently, Glasscott et al. reported that high-entropy metallic glass (amorphous) nanoparticles can be electrochemically deposited using a water-in-oil emulsion as an electrolytic solution^[9]. They used 1,2-dichloroethane (DCE) as an oil phase and dissolved metal salts in the water phase to form a water-in-oil emulsion. Tuning the concentration ratio of the salts in the water droplets directly controlled the composition of the deposited nanoparticles. However, two issues remain from a structural materials viewpoint. First, the deposit must have a crystalline structure. Especially, HEAs and MEAs with face-centered cubic (fcc) structures are expected to show excellent mechanical

properties^[10,11]. Second, a continuous and thick film must be deposited instead of nanoparticles. Additionally, the electrodeposition mechanism in the water-in-oil emulsion should be clarified and discussed in detail from a scientific point of view although studies on emulsions from electrochemical viewpoint were reported^[12,13].

In the present paper, we report the successful production of a crystalline and nearly equiatomic CoNiCu MEA film by electrodeposition using a water-in-oil emulsion. Based on the LSV measurements, the potentials where hydrogen evolution and the cathodic decomposition of DCE occur were clarified. Using this information, we chose the applied potential, where water droplets reacted but DCE did not, to fabricate a continuous film as a deposit. Characterization of the deposited film revealed that it is a crystalline metal with nearly an equiatomic composition. We believe that this study is a milestone to electrochemically produce continuous films of MEAs and HEAs using water-in-oil emulsions.

1.2. Experimental

All the chemicals used in this study were analytical grade. We initially prepared a solution containing DCE (Nacalai Tesque Inc.) with 0.1 M $(C_4H_9)_4NClO_4$ (Nacalai Tesque Inc.) ($M = \text{mol L}^{-1}$) and an aqueous solution containing 10 mM $CoCl_2 \cdot 6H_2O$ (FUJIFILM Wako Pure Chemicals), 20 mM $NiCl_2 \cdot 6H_2O$ (FUJIFILM Wako Pure Chemicals), and 10 mM $CuCl_2 \cdot 2H_2O$ (Nacalai Tesque Inc.). Additionally, we added sodium dodecyl sulfate (SDS, Aldrich) and H_3BO_3 (FUJIFILM Wako Pure Chemicals) into the aqueous solution to be 100 mM and 400 mM, respectively. The concentration of SDS was chosen so that it is much higher than its critical micelle constant (8.5 mM)^[14]. On the other hand, that of H_3BO_3 was determined so that it is similar to conventional electrodeposition systems in aqueous solutions^[15]. H_3BO_3 , as a buffer agent, suppresses the increase of pH in the water droplet under electrolysis and SDS stabilizes the water droplets as an emulsifier. We found

a non-negligible amount of precipitation of hydroxides during electrodeposition in an emulsion without the pH buffering, and the utilization of an emulsifier is necessary because of the unstable nature of the water-in-oil emulsion formed with DCE and the aqueous solution. Then 10 mL of the DCE solution and 60 mL of the aqueous solution were mixed using a high-intensity ultrasonic processor (Vibra cell 75186) at the output power of 130 W. The pH of the aqueous solution was adjusted to 1 using hydrochloric acid (Nacalai Tesque Inc.). The size distribution of the water droplets was measured by dynamic light scattering (DLS; Otsuka Electronics, ELSZ-2Plus). The electrochemical measurements were carried out with a potentiostat (Biologic, SP-50) using a three-electrode cell with a mechanically polished molybdenum (Mo) sheet as the working electrode which was horizontally placed at the bottom of the cell, a platinum rod as the counter electrode, and Ag|AgCl in 1.0 M NaCl as the reference electrode. All the potentials in this study are referred to relative to the reference electrode. The cell geometry was reported elsewhere^[16]. The volume of the emulsion was roughly 10 mL, and the disk electrode had an area of 0.785 cm² with having a diameter of 10 mm. The reason why a Mo sheet was used as the substrate is that the characterization of the CoNiCu MEA using a Mo substrate is not complicated since the peaks of energy dispersive X-ray spectra (EDS) as well as of X-ray diffraction (XRD) of Mo are well separated from those of Co, Ni, and Cu.

To characterize the deposits, field-emission transmission electron microscopy (STEM; JEOL, JEM-2100F) together with EDS, XRD (PANalytical, X'Pert PRO Alpha-1 with Cu K α 1.542 Å), and X-ray photoelectron spectroscopy (XPS; JEOL, JPS-9010TRX) were employed. TEM samples were prepared by the focused ion beam system (FIB; Hitachi, FB2200).

1.3. Results and discussion

We initially conducted electrochemical measurements. Figure 1.1a shows three linear sweep voltammograms (LSVs). One LSV is in the 0.1 M $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ DCE solution. The other two are the in water-in-oil emulsions with and without metal salts. The LSV in 0.1 M $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ DCE solution shows two cathodic waves starting roughly from -1.0 V and -2.0 V. DCE contained a non-negligible amount of water because it was not distilled before use. Therefore, both DCE and water should undergo reduction in the DCE solution. The reduction at -1.0 V is assigned to water decomposition, while that at -2.0 V originates from DCE decomposition because water has a much narrower electrochemical window than DCE.

The LSV in the emulsion without the metal salts is similar to that in the DCE solution, except that the absolute value of the reduction current increases in the emulsion due to an increased water content. When using the emulsion with the metal salts, the LSV slightly changes in the potential region between -1.0 V and -1.3 V. The reduction current density slightly increases due to metal deposition from the water droplets in the emulsion. Additionally, the reduction of water and DCE were detected in the LSV since an increase in the reduction current density is measured both at -1.4 V and -2.0 V. To effectively promote the electrodeposition of CoNiCu MEA, the decomposition of DCE should be suppressed as much as possible, while the overpotential should be as high as possible. Consequently, we chose -1.5 V as the applied potential for MEA film deposition. The effect of ion concentration on the reduction current density was difficult to be detected so far. An estimated concentration of metal ions in the emulsion (a mixture of 10 mL of DCE and 60 mL of the aqueous solution) was quite low as 0.24 mM, and most of the reduction current density originates from the hydrogen evolution, not from the metal deposition.

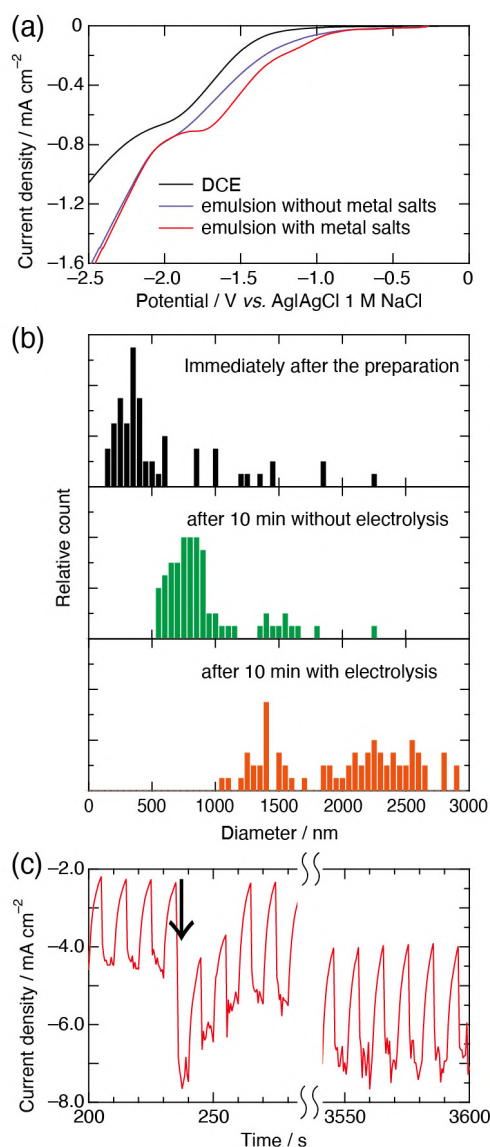


Figure 1.1. (a) LSVs measured in 0.1 M (C₄H₉)₄NClO₄ of a DCE solution (black), a water-in-oil emulsion without metal salts (blue), and a water-in-oil emulsion with metal salts (red). Scan rate is 50 mV s⁻¹. (b) Size distribution of the water droplets in the emulsion immediately after preparation (top), after 10 min without electrolysis (middle), and after 10 min with electrolysis (bottom). (c) Time development of the current density during electrodeposition. Deposition is carried out at -1.5 V vs. Ag|AgCl in 1.0 M NaCl under periodic ultrasonic irradiation in 5-second cycles of turning on/off. Arrow indicates the addition of a small amount of the aqueous solution.

Figure 1.1a suggests that the water droplets tend to decompose at -1.5 V since water is reduced to hydrogen. Thus, the lifetime of the water droplets in the emulsion may affect the electrodeposition. Figure 1.1b shows the change in the water droplet size with time by measuring the droplet size with and without electrolysis. After 10 min without electrolysis, the average size increases from ~ 350 nm to ~ 800 nm. In contrast, the emulsion is unstable under electrolysis. Indeed, the DLS results indicate that the water droplet size greatly increases. After 10 min of electrolysis, the average diameter is greater than 1000 nm. This suggests that continuous ultrasonic irradiation is necessary during electrodeposition to maintain the emulsified state. The reason why the water droplets were destabilized under electrolysis is not clear. Hydrogen evolution from the three-phase boundary may play some roles for the destabilization. The other possibility is how the water droplets behaves when they attach to and detach from the electrode surface. These issues must be studied to understand this electrodeposition method in detail. This is our future study.

Based on the above results, potentiostatic electrodeposition at -1.5 V was carried out under periodic ultrasonic irradiation (turning on/off every 5 s). Figure 1.1c shows the time development of the current density for electrodeposition. The cathodic current density fluctuates intensively with the on/off cycling of the ultrasonic irradiation. The emulsion maintained its emulsified state during electrodeposition under this periodic irradiation. During the electrodeposition under periodic ultrasonic irradiation, 40 mL of an aqueous solution containing the metal salts was added to avoid the depletion of the metal ions in every 10 min, so that the concentrations of metal ions are kept nearly constant. Although we prepared the aqueous solution so that the total concentration of metal ions was 40 mM, the apparent concentration of metal ions estimated based on the volume of the emulsion was 0.24 mM that is a quite low concentration compared with conventional electrodeposition in aqueous solutions. Thus, it is of importance to periodically supply metal ions to the emulsion. Immediately after the

additional injection of the aqueous solution, the current density slightly increases. However, it settles down to nearly the same current density after a few cycles of ultrasonic irradiation. The current density tends to increase gradually (Fig. 1.1c). This indicates that the surface roughness increases during electrodeposition. After 3 h of electrodeposition, a continuous film is obtained. Without ultrasonic irradiation, a small number of nanoparticles were certainly obtained as deposits, and continuous films have never been obtained. After the deposition, the emulsion became dark as a suspension of the deposit mechanically-detached. Also, the amount of deposit is still small; therefore, it is difficult to quantitatively discuss the electrodeposition process.

The deposited film was characterized by XRD (Fig. 1.2a). Two diffraction peaks, which do not exactly match the patterns of pure metallic Co, Ni, or Cu, appear. The peaks at 44.04° and 51.16° are respectively assigned to fcc 111 and 200 reflections. There are no diffraction peaks, except those of the Mo substrate. Since the diffraction pattern of our sample is highly symmetric and cannot be reproduced with three diffractions of pure metals especially for 200 diffraction, it is clear that the sample is not the mixtures of pure Co, Ni, and Cu. In the case of binary alloys, the diffraction exists in between those of two pure metals. Even if we consider binary alloys, the symmetric diffraction of our sample cannot be reproduced. Besides, the nano-beam electron diffraction (NBD) from a single crystal particle of the deposit was measured, and the lattice spacings for 111 and 200 diffractions derived from XRD and NBD were compared. The values of the lattice spacings matched each other. With this result together with the uniform distribution of Co, Ni, and Cu, the deposit was not a mixture but the MEA.

Then the cross-section of the sample was characterized by STEM, indicating that the film is ~ 350 nm thick. The EDS mappings of Co, Ni, and Cu confirm that these elements are distributed uniformly in the film. Note that a layered structure is observed at the cross-section, but this is attributed to the addition of a small amount of the aqueous solution to maintain the emulsified state which caused a slight change of the deposition behavior. As

previously mentioned, the composition fluctuates slightly when the aqueous solution is added.

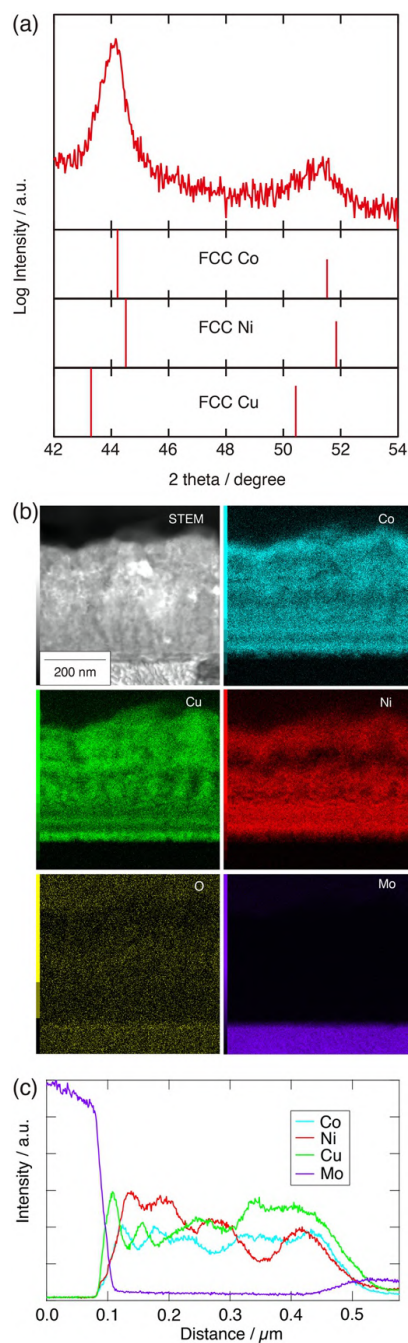


Figure 1.2. (a) XRD pattern of the film deposited at -1.5 V vs. Ag|AgCl in 1.0 M NaCl. Metallic Co, Ni, and Cu are shown as reference patterns. (b) STEM image and the corresponding EDS mapping of Co, Ni, Cu, Mo, and O at the cross-section of the film. (c) Depth profile of the elements measured by EDS.

The atomic ratio of Co, Ni, and Cu is roughly estimated based on the result of EDS. The best composition occurs at 30.0:33.6:33.2. This composition is observed near the Mo substrate. Note that small amounts of O, W (deposition on the top surface before the FIB processing), and Mo were also detected. The depth profile of EDS in Fig. 1.2c suggests that the composition of the deposit is relatively constant from the bottom to the top. It should be noted that the total concentration of metal ions was kept at 40 mM in the water phase according to the previous study by Glasscott et al.^[9]. Indeed, we tried several combinations of the concentrations of Co, Ni, and Cu, and found that the amount of Ni in the deposited film was slightly smaller than Co and Cu, when an equimolar mixture was used. Therefore, to obtain the targeted composition of the alloy, the concentration of the nickel salt was set as double of the other two salts.

It should be noted why the concentration of the Ni salt is higher than the other two. We measured LSVs in aqueous solutions containing one of the metal salts. From these results, it was clarified that the charge transfer resistance of Ni electrodeposition was quite high compared with the other two metal electrodeposition. Co and Cu electrodeposition can reach the diffusion-limitation, while Ni electrodeposition may not reach the condition. In such a case, a higher concentration of the Ni salt is necessary. Within our trials, the double concentration for the Ni salt was the best to obtain the MEA. To confirm that the deposit is an MEA, the oxidation state must be characterized. Figure 1.3a shows the XPS spectra of Co 2p_{3/2}, Ni 2p_{3/2}, Cu 2p_{3/2}, and Cu LMM. At the surface of the deposit, Co and Ni are detected as oxides. The spectrum of Cu 2p_{3/2} suggests CuO is not formed; however, it is impossible to distinguish whether metallic Cu or Cu₂O exists on the surface. Therefore, we carried out the analysis of the Auger peak between the L and M shells denoted as Cu LMM. The spectrum of Cu LMM clearly suggests the formation of Cu₂O. These results demonstrate that the surface of the deposit is partially oxidized.

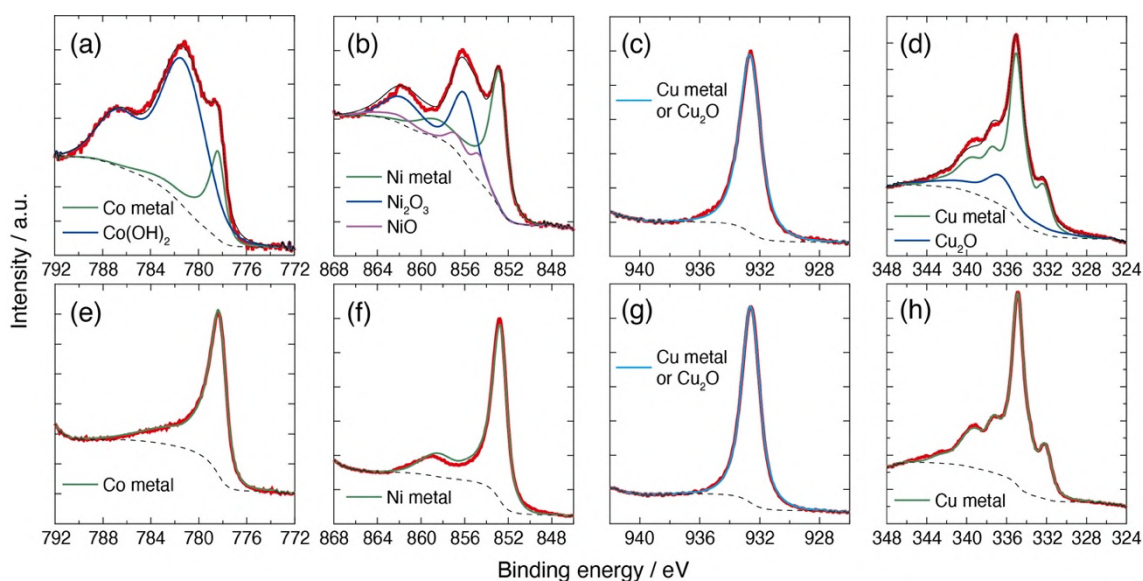


Figure 1.3. XPS spectra. (a, e) Co 2p_{3/2}, (b, f) Ni 2p_{3/2}, (c, g) Cu 2p_{3/2}, and (d, h) Cu LMM measured with the deposit. (a, b, c, d) and (e, f, g, h) show the spectra at the surface and after etching with Ar for 150 s, respectively. Red solid (thick), black solid (thin), and black dotted curves in the spectra indicate the experimental data, fitted curves, and the background, respectively.

Etching for 150 s with Ar changed the spectrum (Fig. 1.3b). The results after Ar etching clearly indicate that the deposit is metallic. Thus, the oxide at the surface may form spontaneously in the air. Actually, the backgrounds measured before and after the Ar etching were almost the same, meaning that the signals of Co(OH)₂ and the nickel oxides were relatively weak. Based on these results, we conclude that the deposit is a CoNiCu MEA.

Finally, the effect of hydrophobicity of the substrate should be discussed. We also conducted the MEA electrodeposition on a gold electrode. Also on the gold electrode, electrodeposition did not proceed without ultrasonication, while a continuous film of the CoNiCu MEA was deposited under ultrasonication. This suggests that the less-hydrophobic surface tends to be covered with a sort of “thin” aqueous layer when the water droplets attach to the surface, and the thin aqueous layer suppresses the electrodeposition of

the MEA. Although it is true that a hydrophobic substrate is advantageous for the electrodeposition of high-entropy “nanoparticles”^[9], the utilization of a hydrophobic substrate is not the optimum strategy to obtain continuous films of MEAs. This is because the electrodeposition of such alloys is expected to be self-terminated once the hydrophobic (original) surface is covered with the deposit whose surface is less-hydrophobic. Thus, to obtain continuous films of HEAs and MEAs, ultrasonic irradiation is more favorable than the utilization of a hydrophobic substrate.

1.4. Conclusions

This study examined the electrodeposition of CoNiCu MEA. A water-in-oil emulsion formed with an aqueous solution containing metal salts and DCE yielded an equiatomic CoNiCu deposit. Based on the electrochemical measurements, the applied potential for electrodeposition was chosen at -1.5 V as this was sufficient to enhance the reaction of the water droplets in the emulsion without promoting the decomposition of DCE. DLS measurements clarified that the water droplets were destroyed during electrodeposition. Consequently, continuous ultrasonic irradiation was necessary to deposit a film. Characterization of the deposit by XRD, STEM, and XPS indicated that the deposit was an equiatomic CoNiCu, namely MEA.

Electrodeposition in a water-in-oil emulsion is a promising strategy to fabricate MEA coatings. The successful production of a continuous film during electrodeposition of MEA is critical for practical applications. This electrodeposition mechanism should be applicable to prepare not only MEA coatings but also HEAs. It is highly expected that this study is a milestone for further studies of MEAs and HEAs based on electrochemistry.

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“Electrodeposition of a CoNiCu medium-entropy alloy in a water-in-oil emulsion,”

Yuki Murakami, Yuki Maeda, Atsushi Kitada, Kuniaki Murase, and Kazuhiro Fukami,

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Chapter 2

Smooth thin film of a CoNiCu medium-entropy alloy consisting of single nanometer-sized grains formed by electrodeposition in a water-in-oil emulsion

2.1. Introduction

High-entropy alloys (HEAs) are multicomponent solid solutions composed of five or more elements with a nearly equiatomic ratio and have been shown to exhibit excellent strength and toughness.^[1,2] Solid solutions composed of fewer than five elements with a nearly equiatomic ratio are known as medium-entropy alloys (MEAs). Some MEAs, such as a CrCoNi, exhibit mechanical properties comparable to those of HEAs.^[3] HEAs and MEAs can also exhibit excellent wear resistance^[4] and corrosion resistance.^[5,6] These advantages favor the use of HEAs and MEAs in surface coatings. Bulk materials of such alloys are typically produced by casting, which is not suitable for fabricating HEAs and MEAs thin films. Other fabrication methods such as the carbothermal shock method^[7,8] and nonequilibrium chemical reduction method^[9,10] have been intensively investigated; however, these methods require heating and the obtained alloys are not continuous films but nanoparticles. The production methods of HEA and MEA thin films are still very limited. The reliable method is sputtering and laser cladding. Although these methods are known as established strategies to produce HEA and MEA thin films, it is not good at producing such thin films on complex and three-dimensional geometries. On the other hand, electrodeposition is advantageous for such an objective. Hence, it is of great importance to establish a general strategy to produce HEA and MEA thin films by electrodeposition.

The electrodeposition of HEAs and MEAs faces two major obstacles. First, the compositions of alloys easily deviate from the equiatomic ratio because the overpotential of each element differs under a certain applied potential. Second, controlling the composition of an alloy is difficult because of anomalous codeposition, which occurs depending on the combination of elements. Under anomalous codeposition, the electrodeposition of a less-noble metal is enhanced while that of another noble metal is slowed.^[11] In some studies, MEAs with nearly equiatomic ratio have been deposited electrochemically by strictly controlling the concentration ratio of metal ions in the aqueous solution.^[12,13] However, these electrodeposition methods are limited to the systems where the electrode potentials of the components are not far apart from each other and phase separation does not occur, such as FeCoNi ternary system. Thus, controlling the composition to maintain an equiatomic ratio becomes increasingly difficult as the number of components and the difference in equilibrium potentials of each metal is significant. Therefore, the establishment of a general method to fabricate HEA and MEA thin films is required for the academic and industrial development of these alloys.

Glasscott et al. reported the fabrication of high-entropy metallic glass nanoparticles by electrolysis in a water-in-oil emulsion.^[14] They observed that the reduction proceeded immediately only when a water droplet collided with the electrode, resulting in the fabrication of an alloy with a composition which reflects the ion concentration ratio in the droplet. This method is unsuitable for surface coatings because their alloys were amorphous nanoparticles, whereas continuous crystalline films are strongly preferred. In our previous study, discontinuous sonication was conducted during electrodeposition in a water-in-oil emulsion. The discontinuous sonication enabled the emulsion to maintain its emulsified state, resulting in the deposition of crystalline CoNiCu film.^[15] However, the MEA film exhibited uneven distributions

of each component and a rough surface, neither of which is acceptable for a surface coating.

Here, we report that chemical stabilization of the emulsion enables the formation of a high-quality (i.e., smooth with a uniform composition) CoNiCu MEA thin film. This process requires chemical stabilization of both the oil and water phases using additives. In the oil phase, a surfactant that stabilizes the emulsions is used. In contrast, in the water phase, an additive that increases the viscosity is added. This approach enables the deposition of a smooth thin film of a CoNiCu MEA consisting of nanometer-sized fine grains. Although numerous studies on bulk materials and nanoparticles have been reported, this study is expected to inspire further studies on HEA and MEA thin films.

2.2. Experimental

Chemicals: Cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, FUJIFILM Wako Pure Chemicals, 99%), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, FUJIFILM Wako Pure Chemicals, 98%), copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Nacalai Tesque, 99%), hydrochloric acid (HCl , Nacalai Tesque, 35.0–37.0wt.%), boric acid (H_3BO_3 , Sigma-Aldrich, 98.5%), 1,2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$, Nacalai Tesque, 99.5%), tetrabutylammonium perchlorate ($(\text{C}_4\text{H}_9)_4\text{NClO}_4$, Nacalai Tesque, 98%), bis(2-ethylhexyl) sulfosuccinate sodium salt ($\text{C}_{20}\text{H}_{37}\text{Na}_7\text{S}$, Aerosol OT, Tokyo Chemical Industry, 95%), and glycerol ($\text{C}_3\text{H}_8\text{O}_3$, FUJIFILM Wako Pure Chemicals, 99.5%) were used for the preparation of the electrolytic solutions without further purification.

Electrochemical measurements: Electrochemical measurements were carried out using a potentiostat (SP-50, Biologic). A three-electrode cell was used for the measurements. A Pt rod and an Ag|AgCl in 3 M NaCl

electrode were used as the counter (CE) and reference electrodes (RE), respectively. All the potentials in this study are specified relative to the reference electrode. Electrodeposition was conducted on an Au substrate as the working electrode. The Au substrate was a thin film (250 nm in thickness) prepared on a Si wafer by electron-beam deposition.

Preparation of emulsions and electrodeposition: An aqueous solution was prepared so that the concentrations of CoCl_2 , NiCl_2 and CuCl_2 were at 40 mM. H_3BO_3 (0.4 M) was added to suppress the increase of pH in an aqueous droplet in an emulsion. Before the use, the pH of the aqueous solution was adjusted at pH=1. When using a mixture of water and glycerol, the concentrations of solutes were kept constant, but the solvent was a mixture of water and glycerol with a ratio of 1:1 by volume. The continuous phase of an emulsion was 1,2-dichloroethane (DCE) with 0.1 M tetrabutylammonium perchlorate. When adding Aerosol OT (AOT) as surfactant, its concentration was adjusted as 50 mM in DCE. The emulsion for electrodeposition was prepared by mixing the 10 mL of the DCE phase and 100 mL of the aqueous phase or the mixture of water and glycerol, followed by the sonication of the mixture (VCX-130, SONICS Co. Ltd.). During the electrodeposition, discontinuous sonication was conducted. The sonication was carried out 5 s (off) and 5 s (on) with a power density of 5.2 W mL^{-1} . We adapt discontinuous sonication in our experiments since the temperature of the emulsion increases with continuous sonication that promote the evaporation of DCE. Electrodeposition was carried out for 1 hour at -1.5 V vs. RE . Since the aqueous phase decreases by electrolysis, 20 mL of the aqueous solution or the mixture of water and glycerol was added in every 5 min.

Characterization: Samples were characterized using a field-emission scanning electron microscope (SEM, JEOL JSM-6500F), a field-emission transmission electron microscope (TEM, JEOL JEM-2100F)

together with energy dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD, PANalytical, X'Pert PRO Alpha-1 with Cu K α 1.542 Å), and X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010TRX). XPS was carried out after Ar etching of the surface of deposit. Samples for TEM observations were prepared using a focused-ion beam (FIB, Quanta 200 3DS). Size distribution of aqueous droplets was measured by dynamic light scattering (DLS, Otsuka Electronics Co. Ltd., ELSZ-2000ZS).

Numerical simulation: Numerical simulation for the concentration distribution in a 3-dimensional aqueous droplet was carried out by finite element method using a software COMSOL Multiphysics. Since the modeling of the alloy deposition involving three different metal cations is tedious, the electrodeposition of single metal, i.e. Ni, is considered to simulate the diffusion of metal ions in a water droplet for the sake of simplicity. In the simulation, we assume that a water droplet containing Ni²⁺ cations is attached to the electrode. Time (t) was determined so that the water droplet was attached to the electrode surface and the electron transfer starts at $t = 0$. Regarding the water droplet attached to the surface, the following equation was solved to simulate the diffusion of Ni²⁺ cations in a water droplet.

$$\frac{\partial c_{\text{Ni}^{2+}}}{\partial t} + \nabla J_{\text{Ni}^{2+}} = 0 \quad (\text{Eq. 2.1})$$

with $J_{\text{Ni}^{2+}}$ being the flux of Ni²⁺ cations formulated as $J_{\text{Ni}^{2+}} = -D_{\text{Ni}^{2+}} \nabla c_{\text{Ni}^{2+}}$, and $D_{\text{Ni}^{2+}}$ being the diffusion coefficient of Ni²⁺ cations. We adopted the diffusion coefficient of $0.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the aqueous droplet without glycerol^[16], which is the similar value to that in a bulk aqueous solution, and that of $0.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (one order smaller value due to the increase of viscosity) for the droplet with glycerol. At the electrode surface, the following equation was considered to model the balance between the supply and consumption of Ni²⁺ cations.

$$\frac{\partial c_{\text{Ni}^{2+}}}{\partial t} + \nabla J_{\text{Ni}^{2+}} = \frac{i_{\text{local}}}{nF} \quad (\text{Eq. 2.2})$$

with i_{local} being the local current density of the electrodeposition reaction $\text{Ni}^{2+} + 2e = \text{Ni}$, n being the number of electrons in the half-cell reaction that is fixed at 2, and F being the faradaic constant as 96,485 C mol⁻¹. i_{local} is formulated as follows based on the Butler-Volmer equation.

$$i_{\text{local}} = i_0 \left[C_R \exp\left(\frac{2(1-\alpha)F\eta}{RT}\right) - \frac{c_{\text{surf}}}{c_{\text{bulk}}} \exp\left(\frac{-2\alpha F\eta}{RT}\right) \right] \quad (\text{Eq. 2.3})$$

with i_0 being the exchange current density fixed at 4×10^{-6} mA cm⁻²,^[17] C_R being a dimensionless coefficient that is fixed at 1 in the present simulation since the oxidation reaction is the dissolution of Ni, c_{surf} being the concentration of Ni²⁺ cations at the electrode surface calculated based on the diffusion equation, c_{bulk} being that in the bulk aqueous solution fixed at 40 mM, α being the transfer coefficient that is fixed at 0.5, η being the overpotential, R being the gas constant, and T being the temperature fixed at 298 K. The cathodic overpotential was estimated as follows: We adopted the values of the electrode potential for the reaction $\text{Ni}^{2+} + 2e = \text{Ni}$ in the Ni-Co chloride bath^[18] and the liquid junction potential between DCE and water phase.^[19] In the experiment, the potential of -1.5 V vs. RE was applied, while the aforementioned references gave the electrode potential and the liquid junction potential as -0.7 V vs. RE and 0.2 V, respectively. In addition, we assume the potential drop in the oil phase is constant as 0.1 V; therefore, a cathodic overpotential η of 0.5 V is simply applied at the water/electrode interface.

2.3. Results and discussion

Before presenting the results, we explain why Co, Ni, and Cu were chosen as the components of the MEA in the present study. In HEA and MEA, difference in the atomic radius of the constituent elements leads to lattice distortion, and mechanical properties are improved when the difference in the atomic radii is more significant. However, when the atomic radii are too far apart, phase separation occurs and corrosion resistance is significantly reduced. Therefore, it is desirable to choose elements that are moderately apart in atomic radius. Since the atomic radius of Cu is not far apart from those of Co and Ni, and the stable phase of Cu has the same FCC structure as that of Co (high temperature) and Ni, Cu is considered to form a solid solution with Co and Ni. On the other hand, in terms of electrochemical deposition, the equilibrium potentials of Co^{2+}/Co and Ni^{2+}/Ni differ substantially from that of Cu^{2+}/Cu ; therefore, phase separation is expected in the electrodeposition from a bulk aqueous solution containing those metal salts. In addition, less-noble Co is well known to deposit preferentially compared with Ni in Co–Ni binary alloys (i.e., the anomalous codeposition occurs)^[18]. To deposit Co–Ni alloy with equiatomic ratio from a bulk aqueous solution, the concentration of Ni^{2+} cation needs to be much higher than that of Co^{2+} cation. Thus, a CoNiCu MEA is likely to form a solid solution and is expected to have excellent corrosion resistance due to the presence of Cu, a noble metal, but a CoNiCu MEA thin film appears to be difficult to fabricate by electrodeposition from a bulk aqueous solution. We considered it the best alloy composition to demonstrate the fabrication of high-quality thin films of an MEA by electrolysis of a water-in-oil emulsion.

In a previous study, we added sodium dodecyl sulfate (SDS) to a water phase to stabilize an emulsion. However, it turned out that the use of SDS was ineffective since surfactants should be added and dissolved

in the oil phase. Here, we explore another surfactant that is effective for our system. Because Aerosol OT (AOT) is a surfactant known to stabilize water-in-oil emulsions, we used it instead of SDS and investigated its effect when dissolved in 1,2-dichloroethane (DCE). Figures 2.1a and 2.1d show the appearance of CoNiCu thin films deposited in the absence and presence of AOT, respectively. The thin film deposited in the emulsion without AOT is black, whereas that deposited in the emulsion with AOT is gray. Figures 2.1b and 2.1e show cross-sectional field-emission scanning electron microscopy (FE-SEM) images of the films, which show that the surface roughness is several hundred nanometers in the film deposited without AOT but substantially smaller in the film deposited with AOT. These results indicate that the black appearance of the film deposited without AOT is due to its rough surface. Figures 2.1c and 2.1f show cross-sectional TEM images of films deposited without and with AOT, respectively. In the films deposited in the absence of AOT, crystal grains with various sizes are observed. Some larger grains exceeding 30 nm in size exist in the film. By contrast, the film deposited in the presence of AOT is composed of relatively uniform and fine grains of ~ 20 nm.

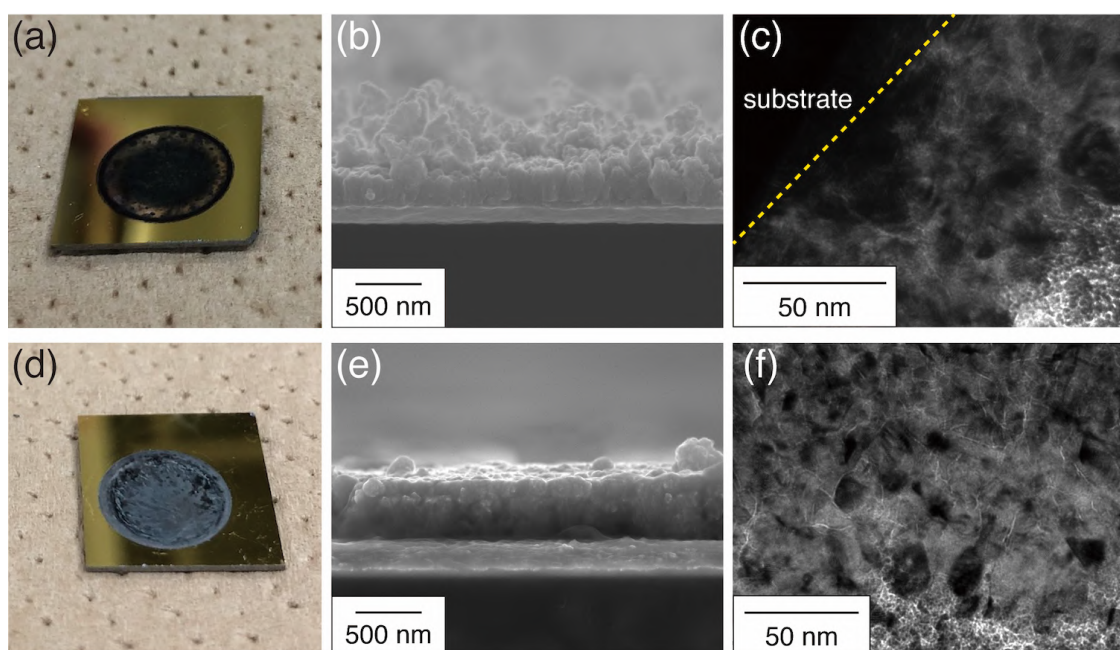


Figure 2.1. Appearance (a, d), cross-sectional FE-SEM images (b, e), and TEM images (c, f) of CoNiCu MEA samples electrochemically deposited (a, b, and c) without and (d, e, and f) with AOT.

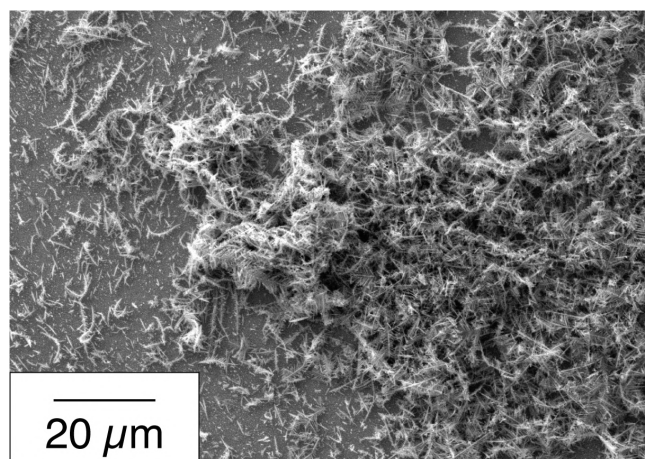


Figure 2.2. SEM image of a top surface after electrodeposition in a bulk aqueous solution. The concentrations of metal ions were the same as those used in the emulsion. Applied potential was -1.5 V vs. RE, which was the same as in the electrodeposition in the emulsion. Duration of the deposition was 10 min. Since the deposits were not attached tightly, most of the deposits were detached when washing. The composition of the deposit was Co:Ni:Cu=26:5:69.

Figure 2.2 shows a surface SEM image of the alloy electrochemically deposited not from the emulsion but from a bulk aqueous solution. This image shows that, when the electrodeposition occurs at the water/electrode (two-phase) interface, numerous dendritic crystals form, resulting in a rough surface. In the case using the emulsion without AOT, aqueous droplets are suspended in the hydrophobic DCE phase. The surfaces of the substrate and the deposited alloy are hydrophilic. When an aqueous droplet collides with the electrode, the droplet easily spreads to the electrode surface. Therefore, the electrodeposition mainly occurs at the water/electrode (two-phase) interface and the surface tends to become rough, similar to the surface of the film deposited from a bulk aqueous solution. However, when AOT is added to the DCE phase, AOT molecules assemble at the water/DCE interface and hydrophobic groups exist in the DCE phase. Consequently, the aqueous droplets exhibit hydrophobicity, even when a droplet collides with the electrode, maintaining its spherical shape without wetting; therefore, electrodeposition mainly occurs at the water/DCE/electrode (three-phase) interface. This difference in the reaction fields with and without AOT causes a difference in the smoothness of the deposits. Figures 2.3a and 2.3b show electron diffraction images of films deposited without and with AOT. In the case of the film without AOT, the Debye rings assigned to the lattice spacings of 2.11 Å, 1.82 Å, 1.28 Å, and 1.10 Å are observed. The lattice spacings correspond to 111, 200, 220, and 311 reflections of a face-centered cubic (FCC) structure. Similarly, in the case of the film with AOT, the Debye rings indicate the lattice spacings of 2.10 Å, 1.82 Å, 1.28 Å, and 1.10 Å, suggesting that the film obtained has an FCC structure as well.

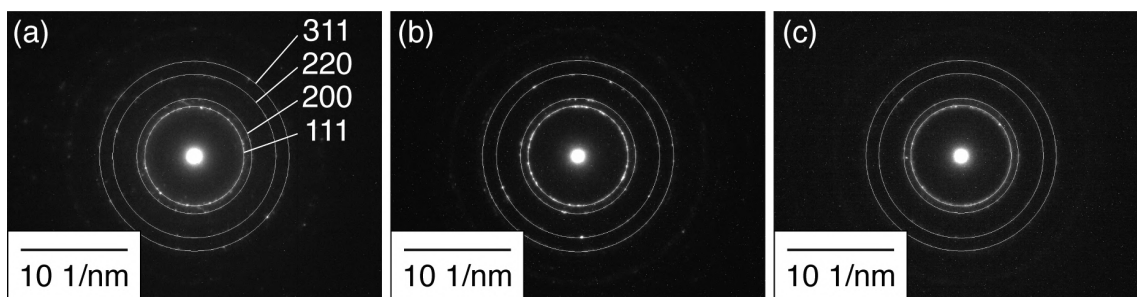


Figure 2.3. Electron diffraction patterns of samples deposited in the emulsions. Images (a), (b), and (c) show the patterns of samples prepared in the emulsion (a) without the additives, (b) with AOT in the oil phase, and (c) with both AOT in the oil phase and glycerol in the aqueous phase.

We subsequently investigated the atomic ratio of alloys by energy-dispersive X-ray spectroscopy (EDS). The atomic ratio of the alloy obtained from the bulk aqueous solution was Co:Ni:Cu = 26:5:69 (the sample shown in Figure 2.2). The content of Cu, which is the most noble of the three metals, is the highest, followed by the content of Co, which is more easily deposited than Ni because of anomalous codeposition; the Ni content was the lowest. Figure 2.4 shows the scanning transmission electron microscopy (STEM)–EDS mapping images of a film deposited without AOT. Similar to the results reported in a previous study^[15], a somewhat uneven distribution of each component is observed in the vicinity of the substrate. The average atomic ratio in the mapping area was Co:Ni:Cu = 31:14:55. The tendency is the same as that of the alloy deposited from the bulk aqueous solution, but the atomic ratio of Co and Ni in the alloy deposited from the emulsion without AOT becomes higher than that in the alloy deposited from the bulk aqueous solution. This difference can be explained as follows: In the case of the bulk aqueous solution, Cu²⁺ cations are continuously supplied from the bulk, resulting in the higher Cu content.

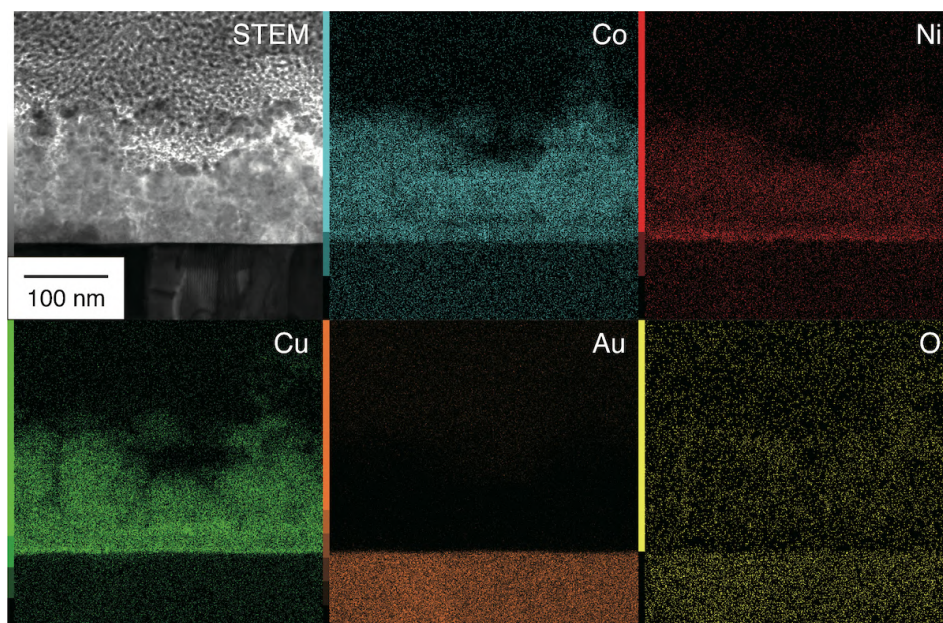


Figure 2.4. STEM image and corresponding EDS mappings of Co, Ni, Cu, Au, and O elements for the sample prepared in the absence of AOT.

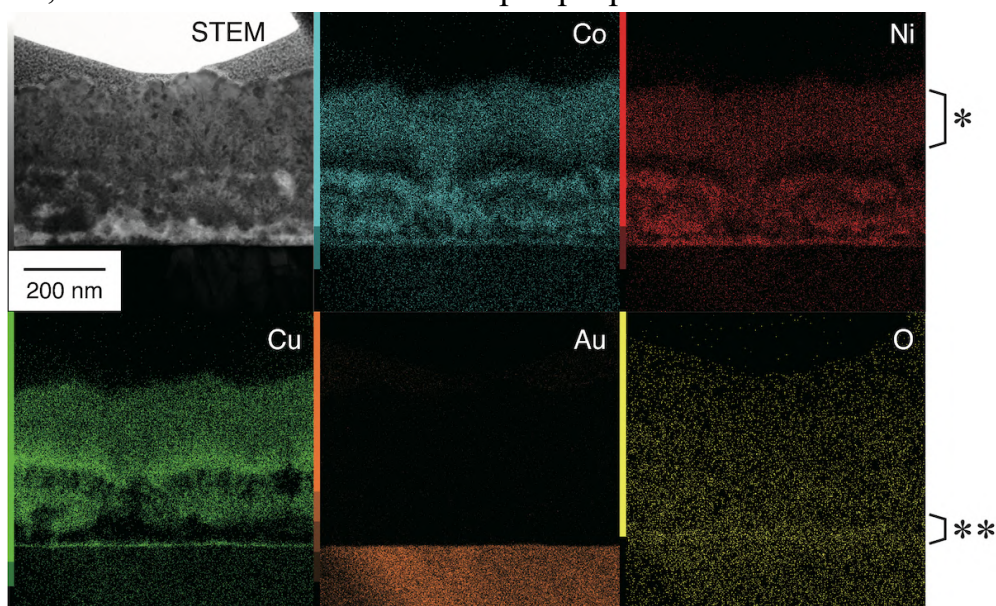


Figure 2.5. STEM image and corresponding EDS mappings of Co, Ni, Cu, Au, and O elements for the sample prepared in the presence of AOT. The * mark in the figure indicates the area where each component of the alloy is uniformly distributed. The ** mark in the figure indicates the area where cobalt hydroxide and/or nickel hydroxide form by pH increasing.

By contrast, in the case of emulsion, the confinement of the metal ions in each droplet prevents the metal ions from being continuously supplied from the bulk solution. Because the amount of Cu^{2+} cations being supplied to the electrode in a droplet is limited, the electrodeposition of Co and Ni are promoted simultaneously.

Figure 2.5 shows the STEM-EDS mapping images of a film deposited in the presence of AOT. In the upper half of the deposited film marked with *, each of the components is uniformly distributed, and the average atomic ratio in this area was $\text{Co:Ni:Cu} = 37:24:39$. Cu and Co, whose electrode potentials greatly differ, are well mixed in approximately the same atomic ratio as the ionic ratio in the water droplet because the reduction of the metal ions occurs under the diffusion-limited condition. This result is related to the aforementioned difference in the reaction fields when AOT is present. Clarke et al. have reported that reactions of ions confined in droplets preferentially occur at the water/oil/electrode (three-phase) interface rather than at the water/electrode (two-phase) interface.^[20] They experimentally revealed that electron transfer reactions tend to be accelerated at a three phase boundary rather than at the water-electrode interface (two phase boundary). The change in wettability, which changes the main reaction field from a two-phase interface to a three-phase interface, increases the reaction rate, resulting in a diffusion-limited condition. It should be noted that each droplet moves randomly after the adsorption onto the electrode surface; therefore, the three-phase and two-phase boundaries dynamically move during the electrodeposition, and it becomes impossible to distinguish the positions of the boundaries by observation of the electrode surface. Although the atomic ratio of Ni increases compared with that in the absence of AOT, it is still lower than the ratios of Co and Cu. Thus, the reduction of Ni^{2+} cation is not perfectly diffusion-limited probably because of the anomalous codeposition with Co. On the other hand, oxygen is detected along with Co and Ni near

the substrate marked with **, indicating that this precipitate on the substrate is cobalt hydroxide and/or nickel hydroxide. Such hydroxides form because water is decomposed into hydrogen at the cathode, which increases the local pH near the substrate. By contrast, when AOT is not present, hydroxide is not observed (Figure 2.4). This suggests that the aggregation of AOT at the water/oil interface increases the charge density in the droplet, resulting in the decrease in the solubility of the hydroxides. In addition, a relatively large amount of Cu is deposited on the hydroxide layer, most likely due to the higher concentration of Cu^{2+} cations remained in the droplet as a result of the consumption of Ni^{2+} and Co^{2+} cations as hydroxides. To further characterize the precipitation, XPS was carried out after Ar etching of the surface of deposit. Although we tried to confirm the existence of hydroxides from the spectra of Co 2p_{3/2}, Ni 2p_{3/2}, Cu 2p_{3/2}, and Cu LMM, the spectra of Co 2p_{3/2}, Ni 2p_{3/2}, Cu 2p_{3/2}, Cu LMM were similar to those reported in our previous study.¹⁵ Hydroxides were not clearly detected from these spectra. On the other hand, the oxygen content analyzed by XPS was relatively high as 5.7 at. % that is twice as high as previously reported CoNiCu MEA without hydroxide precipitation. We think this increase in the oxygen content originates from the contribution of hydroxides of cobalt and/or nickel. It should be noted that the hydroxide layer did not form entirely parallel to the substrate surface like the case of native oxide/hydroxide; therefore, the hydroxide region is expected to expose slightly and zonally after Ar etching. This is the reason why the intensity of hydroxides by XPS was low.

In order to fabricate high-quality MEA films, it is necessary to increase the Ni composition and suppress the hydroxide precipitation. Although the reduction of Ni^{2+} cation at a more negative potential is one of the strategies to achieve the diffusion limitation for the reduction of Ni^{2+} cation, this approach is not appropriate because water decomposition occurs more intensely and the amount of hydroxide is

expected to increase. Alternatively, we tried to increase the viscosity of the aqueous solution in the droplet, making both the reduction of Ni^{2+} and the reduction of Co^{2+} and Cu^{2+} diffusion-limited. The addition of glycerol to an aqueous solution has been reported to change the reaction of PtCl_6^{2-} in a droplet from electron transfer-limited to diffusion-limited.^[21] We therefore examined the effect of glycerol on our deposition of the CoNiCu MEA using a dispersed phase in which the concentration of metal ions was the same as in the previously discussed experiments but with the aqueous phase composed of water and glycerol mixed 50/50 by volume. In addition, the mixture of glycerol is expected to reduce the activity of water and suppress the hydrogen evolution.

Figure 2.6 shows the STEM-EDS mapping images of the film deposited in the presence of both AOT in the oil phase and glycerol in the aqueous phase. Considering that oxygen is almost not detected in the film, the addition of glycerol suppresses the hydroxide precipitation. Each component is uniformly distributed throughout the film, and the average atomic ratio in the entire mapping area is Co:Ni:Cu = 36:35:29, being approximately the equiatomic ratio. Figure 2.7 shows the STEM-EDS depth profile of each component, indicating that no substantial deviation from the equiatomic ratio was observed and the addition of glycerol made the reduction of Ni^{2+} as well as Co^{2+} and Cu^{2+} diffusion-limited. Consequently, an approximately equiatomic ratio was achieved. We carried out the measurement of composition several times. The results showed that the dispersions in compositions of Co, Ni, and Cu were within 5.5 at%.

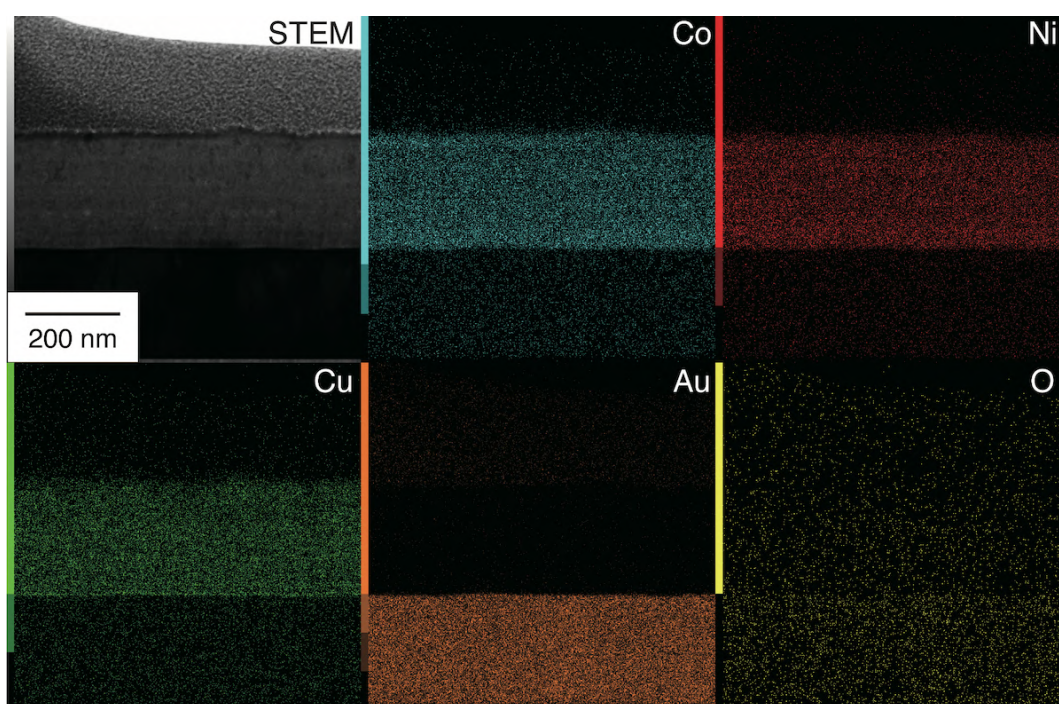


Figure 2.6. STEM image and corresponding EDS mappings of Co, Ni, Cu, Au, and O elements for the sample deposited in a water-in-oil emulsion containing both AOT in the oil phase and glycerol in the aqueous phase.

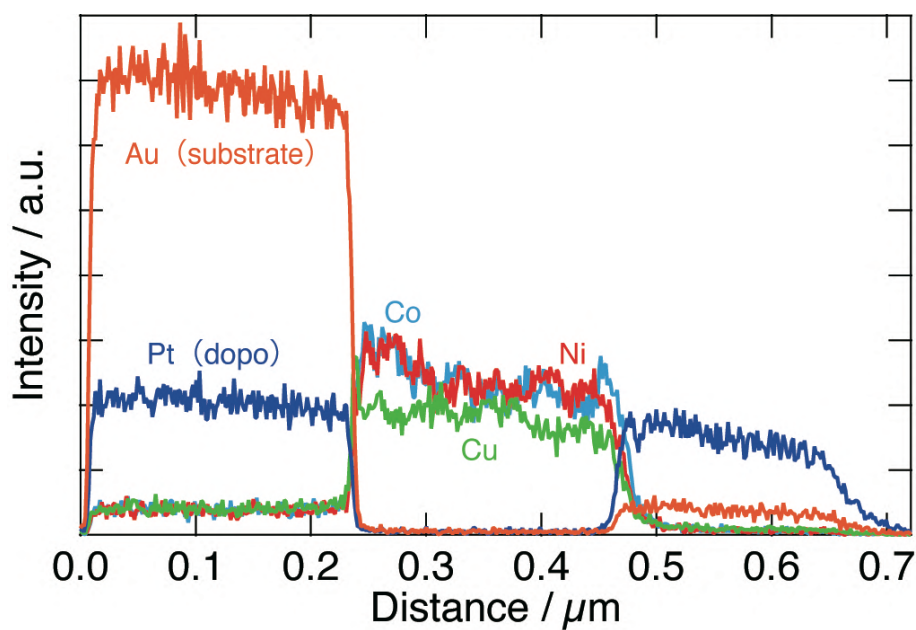


Figure 2.7. STEM-EDS depth profiles of a deposit from the emulsion with the mixture of water and glycerol as the dispersed phase.

As a simple comparison, cathodic linear sweep voltammograms of the bulk solutions, not emulsion, containing only the copper salt with and without glycerol are shown in Figure 2.8. The diffusion-limited current density when glycerol is present decreases to approximately one-tenth of that when glycerol is absent, indicating that the diffusion coefficients of the metal ions become approximately one-tenth of those in continuous aqueous phases as a result of the addition of glycerol. Figure 2.9 shows the results of the semi-quantitative calculation for the diffusion of a metal ion in a droplet by using COMSOL MULTIPHYSICS. The upper results are calculated with a diffusion coefficient similar to Ni^{2+} cation in a bulk aqueous solution ($D = 0.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), while the lower one is obtained with a smaller diffusion coefficient in a mixture of water and glycerol ($D = 0.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The horizontal axis shows the time development of the concentration of metal ion in the droplet after the droplet collides with the electrode. With the diffusion coefficient in the aqueous solution, the change of the concentration proceeds almost uniformly. On the other hand, the distribution of the concentration was clearly observed with the decreased diffusion coefficient. This indicates that a thin diffusion layer forms near the electrode surface and that the reduction becomes diffusion-limited only when glycerol is added. Note that this discussion is hold only when the dynamics of the adsorption and desorption of water droplets is slower than that of the diffusion of metal ions in the droplets. Considering that the desorption of a water droplet is mainly caused by sonication, the adsorption and desorption occur in the time scale of several seconds. Our numerical simulation suggests that the diffusion dynamics of metal ions in a water droplet is in the time scale of several milliseconds; therefore, the discussion is reasonable.

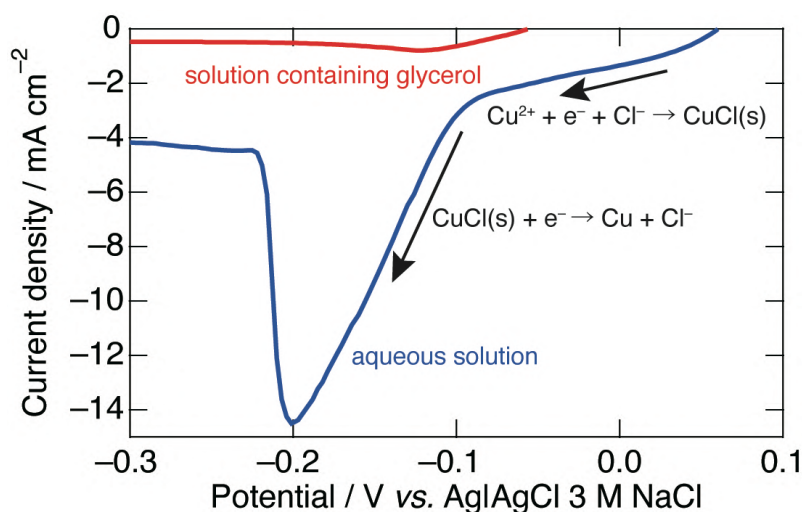


Figure 2.8. Cathodic linear sweep voltammograms measured in a bulk aqueous solution or a mixture of water and glycerol with the composition of 40 mM CuCl_2 + 0.4 M H_3BO_3 . Scan rate was set at 1 mV s^{-1} .

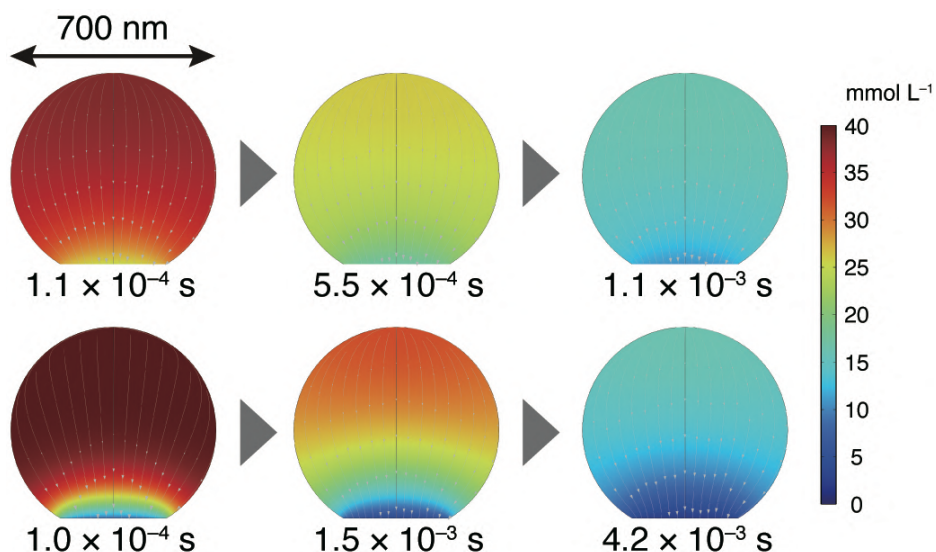


Figure 2.9. Numerical simulation showing how the spatial distribution of the concentration of a metal ion changes in a water droplet. The upper results are calculated with a diffusion coefficient similar to Ni^{2+} cation in a bulk aqueous solution ($D = 0.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), while the lower one is obtained with one order smaller diffusion coefficient in a mixture of water and glycerol ($D = 0.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). The simulation was carried out with 40 mM of a metal ion, the exchange current density of $4 \times 10^{-6} \text{ mA cm}^{-2}$, and the cathodic overpotential of 0.5 V.

Figure 2.10a shows the appearance of the film deposited in the presence of both AOT and glycerol. The deposited film exhibits a weak metallic luster, and the addition of glycerol results in a smoother film. As shown in Figure 2.10b, SEM observations of its cross-section show that the surface roughness is substantially lower than that of samples deposited without glycerol. Although the roughness was not quantitatively evaluated, the decrease in surface roughness was obvious only when using both AOT and glycerol. Figure 2.10c shows a cross-sectional TEM image of the deposited film. The average size of the crystal grains is ~ 5 nm, indicating that the crystal grains are finer than those in the film deposited without glycerol. One of the reasons for the smaller grains is smaller diffusion-limited current density due to the increase in viscosity in a droplet. As previously described, the diffusion-limited current density when glycerol is present decreases to approximately one-tenth of that when glycerol is absent (Figure 2.8). This result indicates that the amount of material deposited from the droplet with glycerol, when a single droplet collides with the electrode, is one-tenth of that deposited without glycerol. The other reason for the smaller grains is the change in droplet size in the emulsion due to the addition of glycerol. Figure 2.11 shows the results of the measurement of the droplet diameter by dynamic light scattering (DLS) using the emulsions without both AOT in the oil phase and glycerol in the aqueous phase (Figure 2.11a), only with AOT (Figure 2.11b), and with both AOT and glycerol (Figure 2.11c). The results indicate that the droplet diameter of the emulsion with both AOT and glycerol is slightly smaller than those of the emulsions without glycerol, which is one of the reasons for the smaller grains. As previously demonstrated, the difference in grain size with and without glycerol is substantial; thus, the smoothing of the surface is due to the deposition of these fine crystal grains.

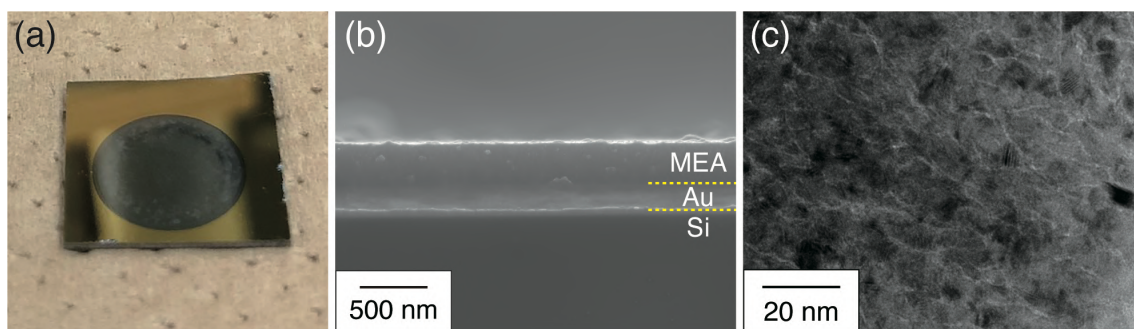


Figure 2.10. Images (a), (b), and (c) show the appearance, the cross-sectional FE-SEM, and TEM of the sample deposited in a water-in-oil emulsion containing both AOT and glycerol, respectively.

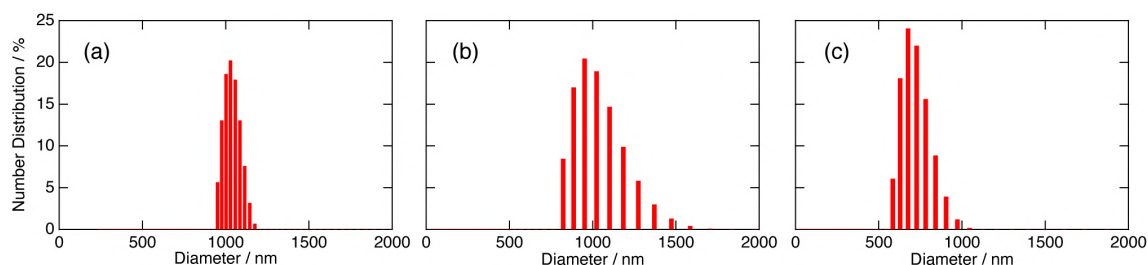


Figure 2.11. Histograms of droplet size of the emulsions (a) without both AOT and glycerol, (b) with AOT in the oil phase and (c) with both AOT in the oil phase and glycerol in the aqueous phase. These were measured by using DLS immediately after the preparation of the emulsions.

Figure 2.3c shows the electron diffraction pattern of the film deposited in the presence of both AOT and glycerol. Debye rings are assigned to the lattice spacings of 2.08 Å, 1.83 Å, 1.27 Å, and 1.10 Å, corresponding to 111, 200, 220, and 311 reflections of a FCC structure, as well as the film deposited in the absence of glycerol. Figure 2.12 shows the X-ray diffraction (XRD) pattern for the gold substrate and the film deposited in the presence of glycerol; specifically, the figure shows the angular range where the 111 reflections of elemental Co, Ni, and Cu having FCC structures appear. Only one symmetric diffraction peak is detected at 44.18° and is highly symmetric, indicating that phase

separation into pure metals or their binary alloys does not occur over the entire film.

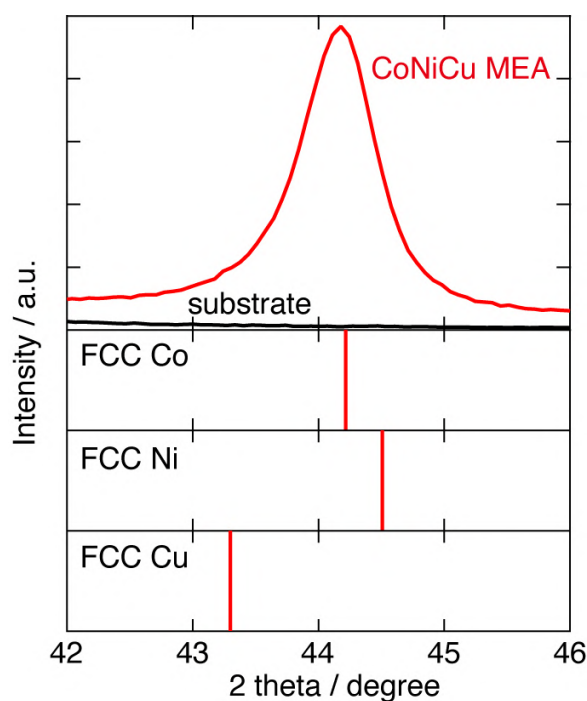


Figure 2.12. XRD pattern of a sample electrochemically deposited from a mixture of water and glycerol as the dispersed phase. The 2 theta range where 111 diffraction is detected is shown. Diffractions of metallic Co, Ni, and Cu with FCC structures are shown as well for comparison. Although a 200 diffraction of metallic Au should be in the same region, 200 diffraction of metallic Au as the substrate was not detected since the deposit is highly oriented to {111} parallel to the surface of Si wafer.

Controlling composition is critical to forming MEAs and HEAs by electrodeposition. The ratio among the concentrations of metal ions in a solution directly transfers to the ratio of the components in a deposited alloy only when the electrodeposition occurs under the perfect diffusion-limited condition. This behavior is attributed to the difference

in overpotential for electrodeposition affecting the composition under the electron transfer–limited condition; thus, under the electron-transfer–limited condition, the composition of alloys does not directly correlate with the concentration ratio of metal ions in a solution. Consequently, the first requirement for obtaining thin films of MEAs and HEAs is that the electrodeposition must be under the diffusion-limited condition. In general, electrodeposition under diffusion-limited conditions is unwelcome because the deposition tends to occur at accidental convex sites on an electrode, resulting in rough surfaces such as dendrite formation (Figure 2.2)^[22–24]. This general insight strongly suggests that electrodeposition under diffusion-limited conditions must be avoided to form smooth thin films; therefore, a paradox is encountered when attempting to achieve the formation of smooth MEA and HEA thin films by electrodeposition.

As demonstrated, the utilization of a water-in-oil emulsion promotes the formation of a smooth thin film of an MEA by electrodeposition. In the electrodeposition using an emulsion, metal ions are encapsulated within a water droplet. Without this encapsulation, such as in a bulk aqueous solution, the concentration of each metal ion distributes in the entire solution continuously. Under such a condition, a diffusion layer forms at the electrode/solution interface during electrolysis, and its thickness reaches ~ 0.1 mm, resulting in the formation of a quite rough surface due to the diffusion-limitation. In contrast, when the encapsulation occurs, each metal ion distributes within each submicron droplet. Consequently, the thickness of the diffusion layer must be smaller than the droplet size (Figure 2.11) and the instability due to diffusion is localized, resulting in a smooth surface; therefore, the second requirement is the confinement of the concentration distribution in a droplet.

2.4. Conclusions

We attained a smooth thin film of a CoNiCu MEA by electrodeposition. Although controlling the composition of alloys electrochemically deposited from bulk aqueous and nonaqueous solutions is generally difficult, the utilization of an emulsion promotes the formation of a smooth MEA thin film with controlled composition. Electrodeposition in an emulsion satisfies the two important requirements to produce the MEA thin film: *electrodeposition under a diffusion-limited condition* and *the confinement of the concentration distribution in a droplet*. This study provides a general strategy to produce thin films of MEAs and HEAs. We expect the results of this study to spur further fundamental and applied research on MEAs and HEAs.

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Chapter 3

Electrodeposition of a CoNiCu medium-entropy alloy: promotion of the electrodeposition rate and composite deposition with carbon nanotubes

3.1. Introduction

Multicomponent alloys generally refer to alloys composed of three or more elements. Due to their superior properties compared to pure metals or binary alloys, they have long been widely used as functional structural materials, such as nickel-based superalloys^[1] and stainless steels^[2]. In these alloys, the appropriate selection and precise control of constituent elements and their compositions enable various functional properties, such as high-temperature strength and corrosion resistance. Recently, high-entropy alloys (HEAs), a novel concept of multicomponent alloys composed of five or more elements with their compositions controlled to nearly equiatomic ratios, have gained significant attention. HEAs are reported to achieve an unprecedented combination of high strength and ductility through mechanisms such as distorted crystal lattices caused by atomic size mismatches and high work hardening rates due to deformation twinning^[3,4]. When the number of constituent elements is three or four, the alloys are referred to as medium-entropy alloys (MEAs), some of which exhibit superior mechanical properties exceeding those of HEAs. Generally, these alloys are classified based on the configurational entropy change, ΔS , which is calculated when the constituent metals are randomly distributed, as expressed by the following equation:

$$\Delta S = -R \sum_i c_i \ln c_i \quad (3.1)$$

Here, R represents the gas constant, and c_i denotes the molar fraction of component i . Based on a quantitative classification using ΔS , high-entropy alloys (HEAs) correspond to cases where $\Delta S > 1.5R$, and medium-entropy alloys (MEAs) correspond to cases where $1.0R < \Delta S < 1.5R$. Currently, the predominant fabrication method for HEAs and MEAs is casting, and their applications are primarily limited to bulk materials. Recently, novel reports have emerged on the use of these alloys as coating materials through techniques such as laser cladding^[5]. However, challenges remain, including the difficulty of forming uniform films on substrates with complex geometries and the requirement for large-scale equipment. As a promising method to address these challenges, electrodeposition has been proposed. If multicomponent alloys with arbitrary constituent elements and compositions can be fabricated through electrodeposition, new applications of HEAs, such as surface coatings, are anticipated.

To achieve superior properties in multicomponent alloys, the appropriate selection of constituent elements and precise control of their compositions are indispensable. In the case of alloy fabrication via electrodeposition, a critical issue arises from the differences in the equilibrium potentials of individual metals, resulting in varying overpotentials for deposition among the elements. When a certain potential is applied during electrodeposition, the composition of the deposited alloy does not necessarily match the ratio of metal ion concentrations in the solution. Moreover, as the number of constituent elements increases, specific combinations may lead to the preferential deposition of less noble metals over noble metals, a phenomenon known as anomalous codeposition^[6]. These factors make precise control of composition extremely challenging in the electrodeposition of multicomponent alloys.

To address these issues and achieve controlled composition in multicomponent alloy electrodeposition, the author focused on

electrodeposition using water-in-oil emulsions. A water-in-oil emulsion is a system in which immiscible organic solvents and water are forced to mix, resulting in tiny water droplets dispersed within the organic continuous phase. Recent studies have revealed that water-in-oil emulsions can serve as unique electrochemical reaction fields. Applications such as electrochemical measurements using emulsions as electrolytic solutions^[7] and the electrodeposition of Pt nanoparticles^[8] have been reported.

Electrodeposition of multicomponent alloys using emulsions involves confining metal ions within microscopic droplets. When these droplets collide with the electrode surface, the metal ions inside are instantly reduced, allowing the composition of the resulting alloy to be controlled by the ratio of metal ion concentrations within the droplets. The author has successfully achieved thin-film formation of a CoNiCu MEA via electrodeposition using a water-in-oil emulsion^[9]. In addition, it was found that introducing a suitable surfactant into the organic phase and adding a thickening agent to the aqueous phase enable the electrodeposition of the smooth MEA film^[10].

A key challenge of this system is that the supply of metal ions to the electrode surface occurs only through the collision of small water droplets with the electrode. As a result, the electrodeposition occurs discontinuously, leading to a slower deposition rate compared to conventional electrodeposition using aqueous solutions.

In this study, the electrodeposition of the CoNiCu MEA was selected as a model case to investigate methods for improving the deposition rate. Specifically, the effect of the concentration of metal ions within the water droplets on the deposition rate was examined. Furthermore, to enhance the deposition rate from the perspective of increasing nucleation sites for electrodeposition, the author also explored composite electroplating with multi-walled carbon nanotubes.

3.2. Experimental

For the preparation of the aqueous phase, cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99% purity, Wako), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 98% purity, Wako), copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 99% purity, Nacalai Tesque), boric acid (H_3BO_3 , 98.5% purity, Aldrich), and hydrochloric acid (HCl , 35%, Nacalai Tesque) were used. Ultrapure water (Millipore Co., Milli-Q Reference A+: $18.2 \text{ M}\Omega \cdot \text{cm}$) was employed for dissolving the reagents. Four types of mixed aqueous solutions were prepared, each containing $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at concentrations of 10 mM, 20 mM, 40 mM, and 80 mM, respectively, along with 0.4 M H_3BO_3 and adjusted to $\text{pH} = 1$. Boric acid was added as a buffer to suppress the pH increase of the aqueous phase due to hydrogen evolution.

For the preparation of the 1,2-dichloroethane (DCE) solution (organic phase), 1,2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$, 99.5% purity, Nacalai Tesque, hereafter referred to as DCE), 0.1 M tetrabutylammonium perchlorate ($(\text{C}_4\text{H}_9)_4\text{NClO}_4$, 98% purity, Nacalai Tesque, hereafter referred to as TBAP) as an amphiphilic supporting electrolyte, and 50 mM sodium bis(2-ethylhexyl) sulfosuccinate ($\text{C}_{20}\text{H}_{37}\text{NaO}_7\text{S}$, 95.0% purity, Tokyo Chemical Industry, hereafter referred to as AOT) as a surfactant to stabilize the emulsion were used. To produce the emulsion, 100 μL of the aqueous solution was added to the DCE solution using a micropipette, and sonication was performed using an ultrasonic homogenizer (VCX-130, SONICS) in a pulse mode of 140 W output for 18 cycles (5 seconds on and 5 seconds off).

In experiments involving composite plating with multi-walled carbon nanotubes (Showa Denko, hereafter referred to as MWCNT), MWCNTs were dispersed in the above DCE solution at a concentration of $0.4 \text{ g} \cdot \text{L}^{-1}$ by ultrasonic treatment for 2 hours. Subsequently, 140 μL of the aqueous solution was added to the DCE solution, and emulsion

formation was achieved by additional sonication. Since the dispersion of MWCNTs altered the hydrophobicity of the DCE solution, the amount of aqueous solution added was adjusted accordingly.

Au thin film is used for the working electrode (WE), which is formed by electron beam deposition of Au on a single-crystal Si substrate with Ti as an intermediate buffer layer (hereinafter referred to as Au substrate). Electrochemical measurements were conducted using a three-electrode system, with a platinum rod (2 mm diameter) as the counter electrode (CE) and an Ag|AgCl (1 M NaCl) electrode as the reference electrode (RE). All potentials are reported relative to this reference electrode. The Au substrate was cleaned by ultrasonic treatment in acetone and ultrapure water for 10 minutes respectively, followed by immersion in a heated cleaning solution of ultrapure water, hydrogen peroxide (H₂O₂, 35.5%, Wako), and concentrated nitric acid (HNO₃, 60%, Nacalai Tesque) mixed at a volume ratio of 4:1:1 on a 140 °C hot plate for over 20 minutes.

Electrodeposition experiments were carried out using a custom-made polytetrafluoroethylene (PTFE) electrochemical cell. The WE electrode surface area was 0.785 cm² (10 mm diameter). Current density values were calculated based on the measured current and this surface area. For electrodeposition using emulsions without dispersed MWCNTs, a potential of -1.5 V *vs.* RE was applied while operating the ultrasonic homogenizer in pulse mode. In contrast, when emulsions containing dispersed MWCNTs were used, a potential of -1.8 V *vs.* RE was applied to compensate for the reduced conductivity of the emulsion due to the dispersion of MWCNTs. Electrodeposition was conducted for a total of 2 hours, with the electrolytic solution replaced every 30 minutes. Additionally, to compensate for the reduction of the aqueous phase in the emulsion due to water decomposition, 40 µL of aqueous solution was added every 10 minutes.

After electrodeposition, the samples were thoroughly rinsed with

ethanol and ultrapure water and then dried. Surface morphology was observed using an SEM (TM4000Plus, Hitachi High-Technologies), and cross-sections were examined by cleaving the single-crystal Si to expose the deposited material, which was then observed using a FE-SEM (JSM-6500F, JEOL). The microstructure of the deposited films was analyzed using TEM (JEM-2100F, JEOL) after processing the sample into thin slices using FIB (Quanta 200 3DS, FEI). The droplet size in the emulsions was measured using dynamic light scattering (DLS) with an ELSZ-2000ZS (Otsuka Electronics). Droplet sizes were measured 70 times immediately after sonication, and the results were summarized into histograms. Since ultrasonication was also applied during potentiostatic electrodeposition, it was assumed that changes in droplet size during deposition were minimal. Therefore, the droplet sizes measured immediately after ultrasonication were considered representative of the droplet sizes during electrodeposition.

3.3. Results and discussion

3.3.1. Control of electrodeposition rate by metal ion concentration in water droplets of water-in-oil emulsions

The effect of metal ion concentration in the aqueous phase on the deposited material was investigated. The appearance of the deposits obtained under different metal ion concentrations is shown in Figure 3.1. When the concentrations of Co^{2+} , Ni^{2+} , and Cu^{2+} were set to 10 mM, 20 mM, and 40 mM each, the deposits appeared increasingly white as the concentration increased. However, when the concentration was further increased to 80 mM, the appearance of the deposits turned completely black. The surface SEM images of these deposits are shown in Figure 3.2. For deposits obtained with 10 mM of each metal ion, a

rough surface was observed. With 20 mM and 40 mM of each metal ion, the surface roughness transitioned to granular structures with diameters of several hundred nanometers. Although granular structures were present, the surface smoothness improved slightly as the concentration increased, which likely explains the white appearance of the surface. Particularly, deposits obtained with 40 mM of each metal ion exhibited fine and uniform particles.

On the other hand, deposits obtained with 80 mM of each metal ion showed numerous protrusions with sizes in the tens of micrometers, resulting in the black surface appearance. The elemental compositions of the deposits were analyzed by SEM-EDS at five points on each sample, and the average compositions and variations are summarized in Table 3.1. For deposits obtained from emulsions containing 10 mM, 20 mM, or 40 mM of each metal ion, the compositions showed little difference, with Co and Cu being approximately equal, while the Ni content was slightly lower. The similar levels of Co and Cu were attributed to diffusion-limited reduction reactions in the droplets, whereas the lower Ni content was likely due to its smaller exchange current density and the anomalous codeposition with Co, preventing electrodeposition of Ni from reaching the diffusion-limited condition under the applied potential^[10].

Linear sweep voltammetry (LSV) measurements were conducted using emulsions as electrolytes to verify the deposition process, as shown in Figure 3.3. The red voltammogram represents emulsions containing Co^{2+} , Ni^{2+} , and Cu^{2+} , while the black voltammogram represents emulsions without metal ions. The current rise observed at potentials of -0.4 V and -1.9 V in both cases corresponds to the decomposition of water and DCE, respectively. However, the current rises observed at -0.8 V and -1.3 V only in the red voltammogram were attributed to metal deposition. This metal deposition reached a diffusion-limited condition around -1.8 V, but at -1.5 V (the potential

used for potentiostatic deposition), not all metals deposited under diffusion-limited condition, consistent with the earlier discussion.

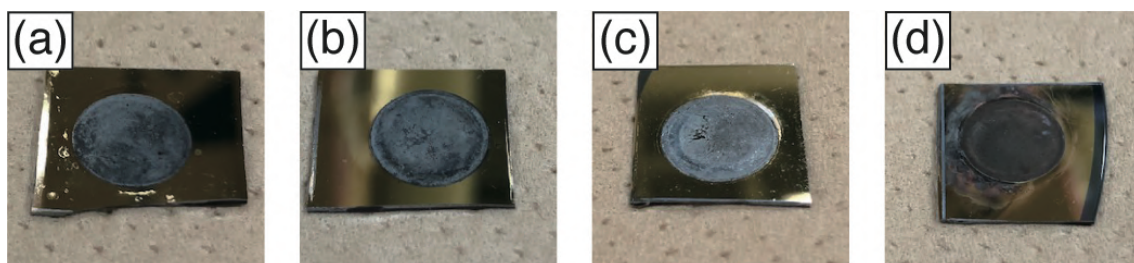


Figure 3.1. Photographs of CoNiCu MEA deposits formed using water-in-oil emulsions using aqueous solutions containing (a) 10 mM, (b) 20 mM, (c) 40 mM, and (d) 80 mM of each metal ion. Electrodeposition took place on the circular areas (10 mm ϕ) on the electrodes.

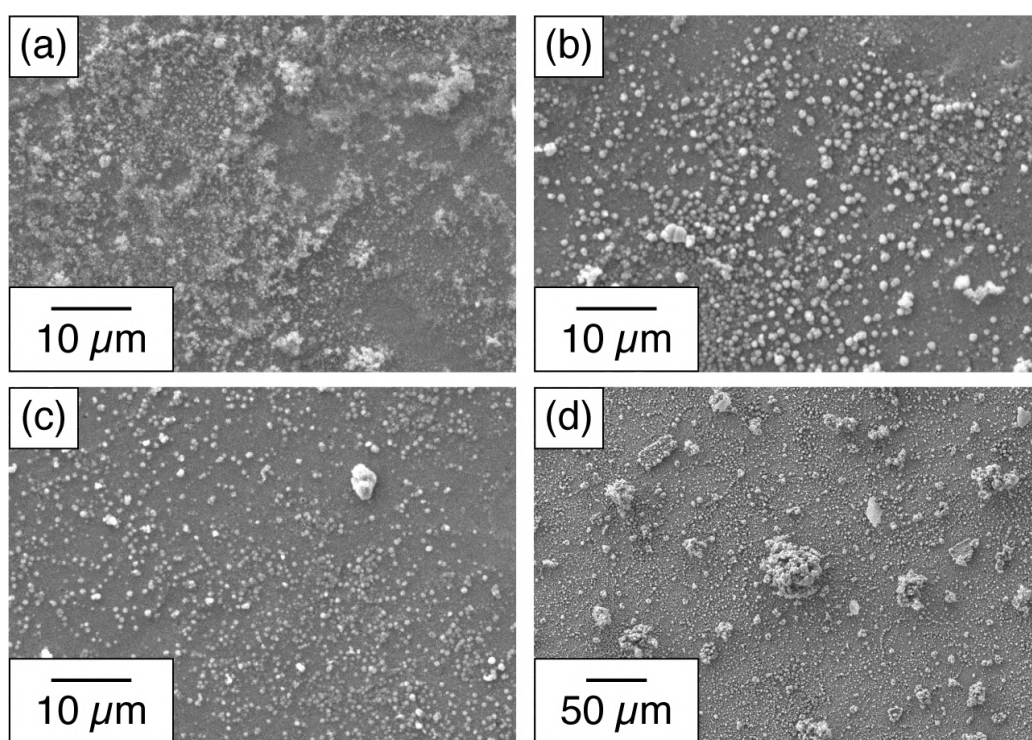


Figure 3.2. Top view SEM images of CoNiCu MEA deposits formed using water-in-oil emulsions using aqueous solutions containing (a) 10 mM, (b) 20 mM, (c) 40 mM, and (d) 80 mM of each metal ion.

Table 3.1. Compositions (at.%) of CoNiCu MEA deposits formed in water-in-oil emulsions using aqueous solutions containing different concentrations of metal ions.

	Co	Ni	Cu
10 mM	34±3	27±3	39±6
20 mM	37±3	24±4	39±7
40 mM	38±4	26±3	36±6
80 mM	28±3	24±1	48±3

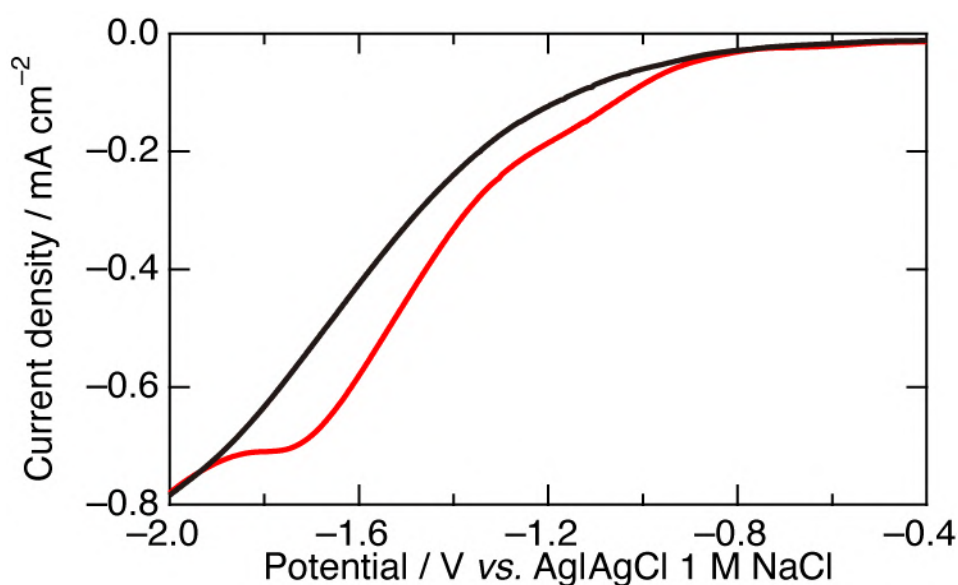


Figure 3.3. LSVs measured in water-in-oil emulsions without metal salts (black) and with metal salts (red). Scan rate was 50 mV s⁻¹.

From the perspective of composition control, it would be ideal to perform electrodeposition at potentials where all metals deposit under diffusion-limited condition. However, under such conditions, the decomposition of DCE and the excessive hydrogen evolution causing pH increase in the droplets would lead to hydroxide codeposition.

Therefore, a potential of -1.5 V was selected. For deposits obtained from emulsions with 80 mM of each metal ion, the compositions deviated significantly from equiatomic ratios. Nevertheless, all alloys obtained using the four tested concentrations satisfied the requirement of $\Delta S > 1.0R$.

As previously reported^[9,10], X-ray photoelectron spectroscopy (XPS) confirmed that Co, Ni, and Cu were deposited in metallic states within the films, STEM-EDS mapping showed a uniform distribution of these elements, and X-ray diffraction patterns indicated a single-phase face-centered cubic solid solution. These findings confirm successful electrodeposition of medium-entropy alloys under all conditions listed in Table 3.1. TEM images in Figure 3.4 reveal that these deposits are composed of fine crystalline grains, approximately 10 – 20 nm in size.

For deposits obtained with 80 mM of each metal ion, the Cu content was significantly higher compared to other concentrations, as shown in Table 3.1. To investigate this, the droplet sizes in the emulsions were measured using dynamic light scattering (DLS), as shown in Figure 3.5. Droplet sizes increased with higher metal ion concentrations. In electrodeposition using emulsions as electrolytic solutions, metal ions are confined in a microscopic space to obtain electrodeposits that cannot be obtained from bulk aqueous solutions. Up to 40 mM of each metal ion, the alloy composition showed minimal dependence on droplet size, indicating that the electrochemical reactions occurring within the droplet are independent of the droplet size. However, at 80 mM, the electrochemical reactions within the larger droplets resembled bulk aqueous behavior^[10], leading to the preferential deposition of the noblest metal, Cu. This suggests a threshold droplet size, beyond which droplets behave as bulk aqueous phases. Moreover, as the reactions approach the electrodeposition behavior observed in bulk aqueous solutions and a large overpotential is applied for Cu deposition, the formation of deposits with significant surface roughness becomes more

likely^[10]. Consequently, this resulted in the loss of surface smoothness at 80 mM of each metal ion concentration, as seen at 40 mM of each metal ion concentration.

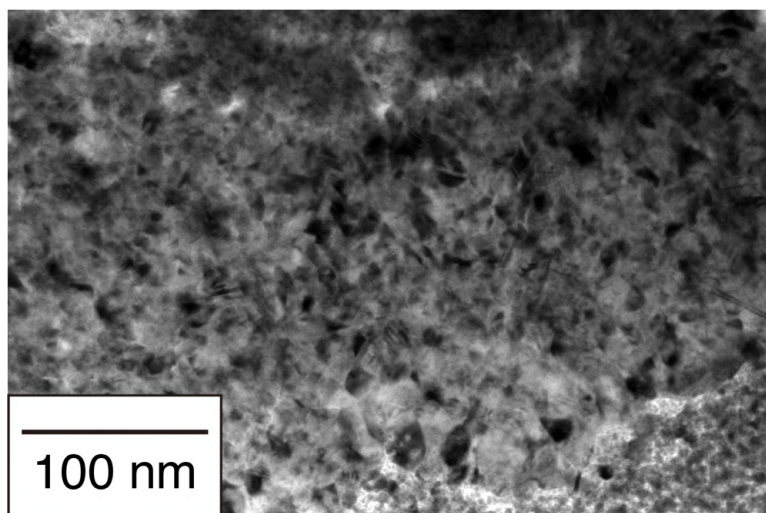


Figure 3.4. Cross-sectional TEM image of a CoNiCu MEA deposited from a water-in-oil emulsion using an aqueous solution containing 40 mM of each metal ion.

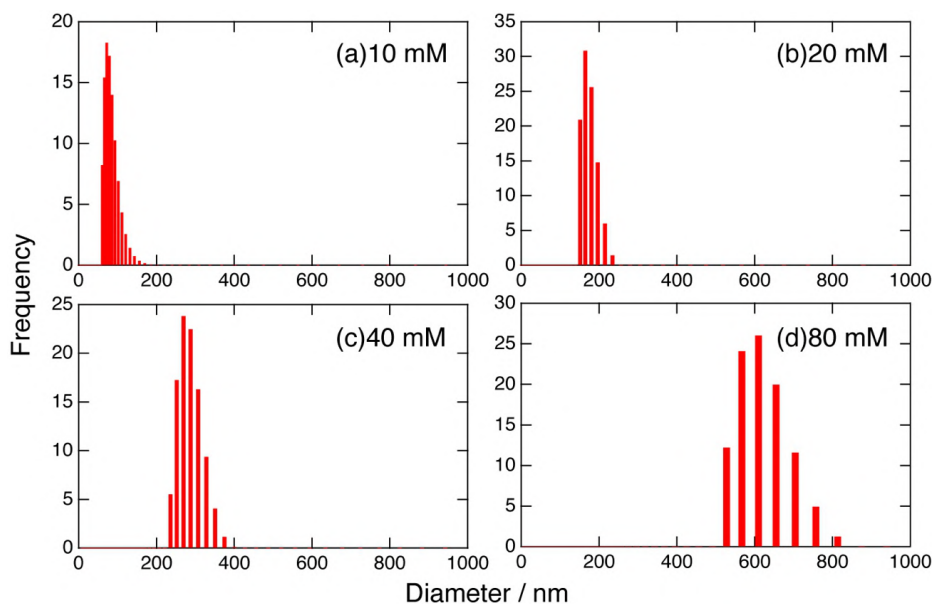


Figure 3.5. Histograms of droplet size in water-in-oil emulsions using aqueous solutions containing (a) 10 mM, (b) 20 mM, (c) 40 mM, and (d) 80 mM of each metal ion. These histograms were measured immediately after the preparation of emulsions.

Next, cross-sectional FE-SEM images and thickness measurements of the deposits obtained with emulsions at various concentrations are shown in Figure 3.6. The deposition rates calculated from the thicknesses were 115 nm h^{-1} , 230 nm h^{-1} , 400 nm h^{-1} , and 1025 nm h^{-1} for metal ion concentrations of 10 mM, 20 mM, 40 mM, and 80 mM, respectively. Deposition rates increased proportionally with the concentration, except for the 80 mM condition, which exhibited a higher-than-expected rate due to voids observed in the deposits (Figure 3.6d). In contrast, deposits obtained with 10 mM to 40 mM of each metal ion were dense and void-free. The formation of voids at 80 mM was likely due to the bulk aqueous behavior of larger droplets, as discussed earlier.

In summary, increasing metal ion concentrations enhances the deposition rate; however, there is a threshold (40 mM in this study) beyond which further increase leads to bulk-like behavior and loss of control over deposit smoothness. While current efficiency must also be considered, ultrasonic treatment during electrodeposition causes detachment of protrusions, making accurate measurement of efficiency challenging. Addressing this issue remains a topic for future research.

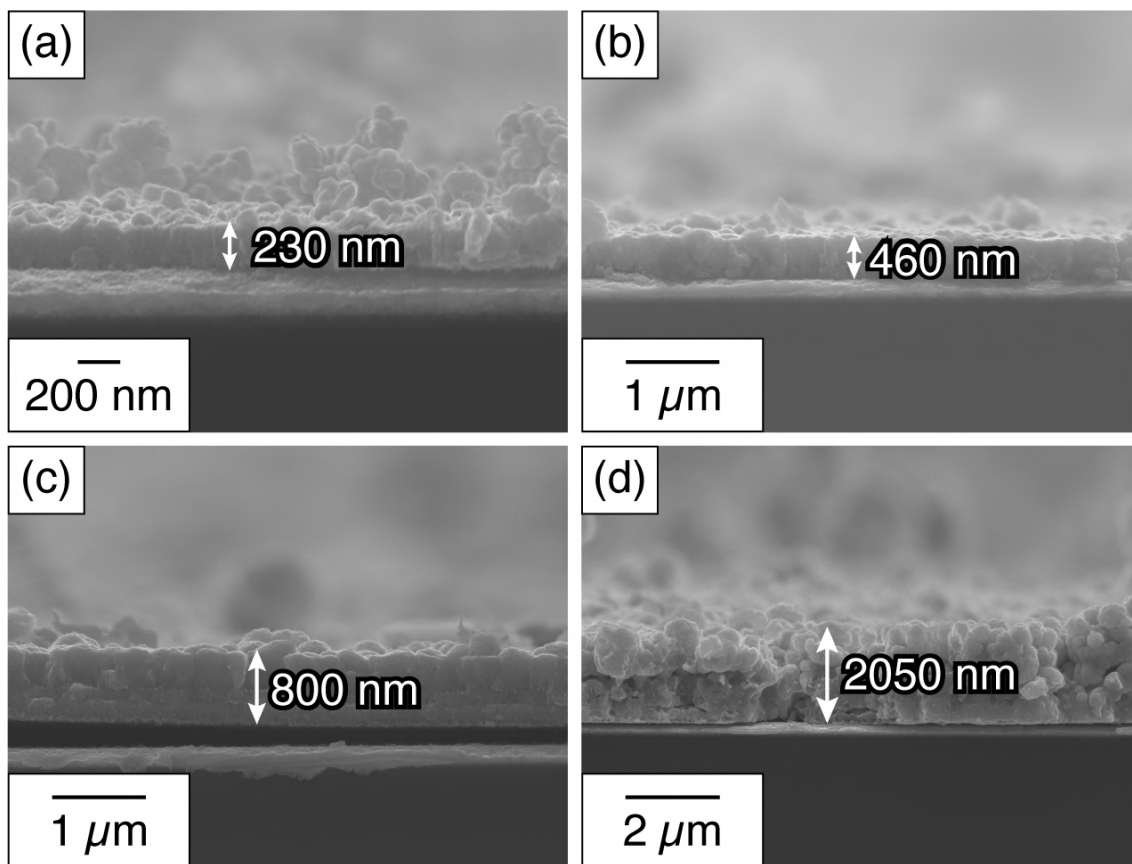


Figure 3.6. Cross-sectional FE-SEM images of CoNiCu MEA deposits formed using water-in-oil emulsions using aqueous solutions containing (a) 10 mM, (b) 20 mM, (c) 40 mM, and (d) 80 mM of each metal ion.

3.3.2. Control of electrodeposition rate via carbon nanotube composite electroplating

Carbon nanotubes (CNTs) are lightweight materials with high thermal conductivity, electrical conductivity, mechanical strength, and aspect ratio. These properties have led to the development of CNT composite materials with polymers, ceramics, and metals, which are known for their lightweight and superior mechanical properties^[11]. However, reports on CNT-metal composites are relatively limited due to the challenges of dispersing CNTs uniformly in metal matrices, as CNTs tend to aggregate. Furthermore, since CNTs cannot tolerate high temperatures in some processing environments, their use with metals is limited to composites using low-melting-point metals such as Al as the matrix^[12].

In conventional electrodeposition from aqueous solutions, it is difficult to disperse hydrophobic CNTs in the solution. Methods such as adding dispersants like polyacrylic acid have been employed to facilitate CNT composite electrodeposition in such systems^[13]. In this study, DCE (1,2-dichloroethane), used as the continuous phase of the emulsion, was identified as a solvent capable of dispersing CNTs. It is also known that when bulk water is added to DCE containing dispersed MWCNTs, the MWCNTs aggregate at the water/DCE interface^[14]. Using emulsions in which CNTs are dispersed in the continuous phase and metal ions are contained in the aqueous phase, it is hypothesized that MWCNTs adsorb at the water/DCE interface and are incorporated into the deposits when the droplets collide with the electrode. This enables the electrodeposition of CNT-metal composite materials. Additionally, this study investigates whether conductive CNTs function as nucleation sites for electrodeposition, thereby enhancing the deposition rate.

The surface SEM image of the deposit is shown in Figure 3.7a.

Similar to deposits without MWCNTs, the surface is covered with spherical particles, but numerous rod-shaped structures can also be observed. These structures are the MWCNTs incorporated from the electrolyte, along with the alloy deposited on them. Figure 3.7b highlights the rod-shaped structures observed in Figure 3.7a by overlaying red lines to emphasize the MWCNTs. Elemental analysis using SEM-EDS was performed at four points on these structures to evaluate the average alloy composition and its variation. The average composition was found to be Co:Ni:Cu = 35:25:40 (at.%), with a variation of $\pm 2\%$. The Ni content was slightly lower than Co and Cu, similar to the compositions obtained with metal ion concentrations of 10 mM to 40 mM. Since this alloy also satisfies the requirement of $\Delta S > 1.0R$, it can be classified as a CoNiCu medium-entropy alloy.

Attempts were made to quantitatively evaluate the amount of codeposited MWCNTs based on the carbon content detected by SEM-EDS. However, due to the low quantifiability of light elements like carbon and the inability to distinguish between codeposited MWCNTs and impurity carbon, the codeposition amount could not be estimated. Cross-sectional observations of the deposit are shown in Figure 3.7c. Figure 3.7d highlights the rod-shaped MWCNTs observed in Figure 3.7c by overlaying red lines. These images demonstrate that the incorporated MWCNTs are uniformly dispersed within the alloy without aggregation, indicating the successful fabrication of a composite material.

Although the significant surface roughness of the deposits makes it difficult to determine an accurate deposition rate, an estimated rate of approximately $1.6 \mu\text{m h}^{-1}$ was obtained. This represents about a fourfold increase compared to previous results. This enhancement is attributed to the large aspect ratio and high conductivity of MWCNTs, which increase the frequency of droplet collisions with the electrode. Furthermore, once incorporated into the alloy, MWCNTs act as

protrusions, promoting further collisions with other droplets and increasing the nucleation frequency of deposits.

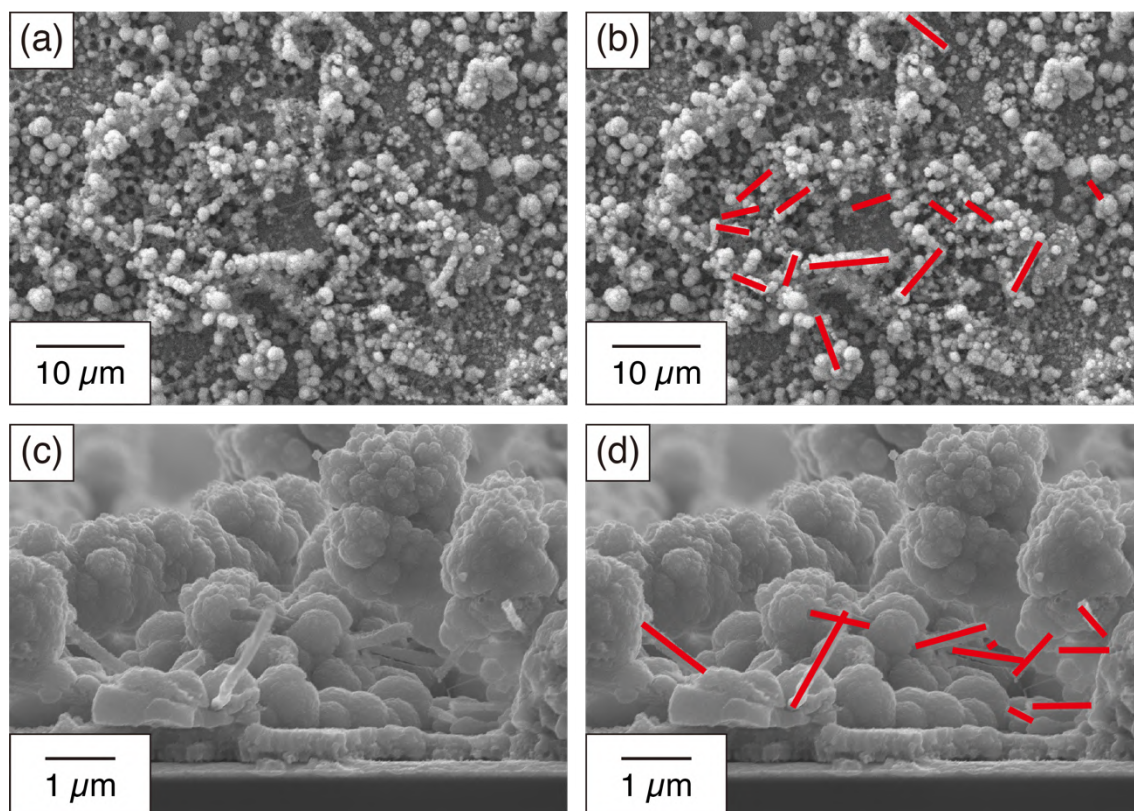


Figure 3.7. Top (a, b) and cross-sectional (c, d) views of a CoNiCu MEA deposit formed in a water-in-oil emulsion in which MWCNTs were dispersed in the oil phase. MWCNTs are emphasized by red lines in the images (b, d).

3.4. Conclusions

In this study, two approaches were explored to improve the deposition rate of CoNiCu medium-entropy alloy electrodeposition using water-in-oil emulsions as the electrolytic solutions: increasing the metal ion concentration within the droplets and composite electroplating with multi-walled carbon nanotubes (MWCNTs). While higher concentrations of metal ions in the water droplets resulted in higher deposition rates, there was a threshold value for this technique, above which the compositional uniformity of the alloys worsened. After optimizing the metal ion concentration, composite electroplating with MWCNTs was shown to be an effective method for further increasing the deposition rate.

Through these studies, the reproducible electrodeposition of medium-entropy alloys was successfully achieved using water-in-oil emulsions. In the future, this approach is expected to enable the development of coatings based on high-entropy alloys and medium-entropy alloys with various combinations of constituent elements, offering unprecedented mechanical properties and superior corrosion resistance.

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“Electrodeposition of a CoNiCu Medium-Entropy Alloy: Promotion of the Electrodeposition Rate and Composite Deposition with Carbon Nanotubes,”

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Chapter 4

Electroplating of wear and corrosion resistant CrCoNi medium-entropy alloys beyond hard chromium coatings

4.1. Introduction

High-entropy alloys (HEAs) are multicomponent solid solutions composed of five or more elements with a nearly equiatomic ratio and have been shown to exhibit excellent strength and toughness^[1,2]. The HEA composed of Cr, Mn, Fe, Co, and Ni with an equiatomic ratio is known as the Cantor alloy and has been intensively investigated as a model material for HEAs^[3,4]. Solid solutions composed of fewer than five elements with a nearly equiatomic ratio are called medium-entropy alloys (MEAs). In particular, derivative MEAs of the Cantor alloy, composed of Cr, Mn, Fe, Co, and Ni with one or two elements excluded, have been studied intensively^[5] and the CrCoNi MEA has been reported to exhibit strength^[6], toughness^[7,8], and corrosion resistance^[9] superior to those of the Cantor alloy at both room and cryogenic temperatures.

The production of such HEAs and MEAs has been based on casting. Recently, other production methods such as carbothermal shock^[10,11] and laser cladding^[12,13] have been used; however, the number of production technologies remains limited. Electrodeposition has played a central role in metallurgy and has opened a wide range of processes such as large-scale electrorefining, uniform surface coatings, charging/discharging of batteries, and production of ultra-large-scale-integration circuits at the nanoscale. These achievements demonstrate that electrodeposition is a key technology for further development of HEAs and MEAs. Despite such potential, the electrodeposition of HEAs and MEAs has not been studied intensively because of the

difficulty in controlling the alloys' composition. This difficulty originates from controlling the overpotentials for all the components simultaneously and from the necessity to avoid, for example, anomalous codeposition, which promotes the deposition of less-noble metal components rather than noble ones^[14]. In addition, although Cr is a necessary component to achieve high strength and corrosion resistance^[5], its electrodeposition as a crystalline phase is known to be difficult because of contamination by carbon^[15]. Consequently, the electrodeposition of single-phase CrCoNi MEA and HEAs containing Cr, Co, and Ni has not yet been achieved despite their potential as high wear- and corrosion-resistant coatings. In our previous studies, the electrodeposition of an MEA composed of Co, Ni, and Cu—elements with substantially different equilibrium potentials—was achieved using a water-in-oil emulsion as an electrolytic solution^[16,17]. However, the electrodeposition of HEAs and MEAs containing Cr has yet to be realized even using emulsions as electrolytic solutions.

Here, we report the electrodeposition of a crystalline CrCoNi MEA with uniform distribution of components using a mixture of 1-butyl-3-methylimidazolium chloride (C₄mimCl) and an aqueous solution. There are two reasons to choose the mixture of the ionic liquid and the aqueous solution for the electrodeposition of CrCoNi MEA. The first reason is that the mixture used for electrodeposition was reported to enable the electrodeposition of metallic chromium using Cr(III) cation. The second reason is that C₄mimCl and C₆mimCl are known to exhibit mesoscale phase separation into the polar and nonpolar domains. According to the previous reports^[18,19], the utilization of phase-separated solutions such as emulsions is necessary for the electrodeposition of multicomponent alloys. These two reasons suggest that MEAs containing Cr are deposited using the mixture. The CrCoNi coating obtained by electrodeposition has a smooth surface with metallic luster and exhibits superior wear and anticorrosion properties

compared with the conventional hard Cr coating prepared by plating using a toxic solution containing Cr(VI) ions. We also discuss the mechanism of CrCoNi electrodeposition, which is based on the mesoscopic phase separation of the solution used.

4.2. Results and Discussion

4.2.1. Exploring the optimum electrochemical condition for the CrCoNi electrodeposition

To identify the conditions under which the electrodeposition of CrCoNi MEA is likely, we recorded linear-sweep voltammograms (Figure 4.1a). In the case of a bath with pure C₄mimCl (black dotted line overlapped with the horizontal axis), no noticeable increase is observed in the cathodic current density within the measured potential region, indicating that the potential window of C₄mimCl is sufficiently wide. In the case of the C₄mimCl–H₂O mixture without metal salts (blue line), the reduction current increases from –1.0 V, which corresponds to water decomposition. When metal ions are present (red line), remarkable increases are observed in the reduction current density at –0.4 V, –0.7 V, and –1.0 V. Because the standard electrode potential for the reduction from Cr³⁺ to Cr⁰ is –0.943 V^[20], the increase in the current density at –1.0 V is attributed to the simultaneous reduction of water and Cr³⁺ ions. Given the standard electrode potentials of Co and Ni electrodeposition, the electrodeposition of Co and Ni occurs at much more negative potentials than –0.4 V; therefore, the increase in cathodic current from –0.4 V is assigned to the reduction of protons released by the ionization of H₂O molecules as a result of their coordination with Cr³⁺ cations. Accordingly, the increase in cathodic current from –0.7 V originates from the simultaneous electrodeposition of Co and Ni.

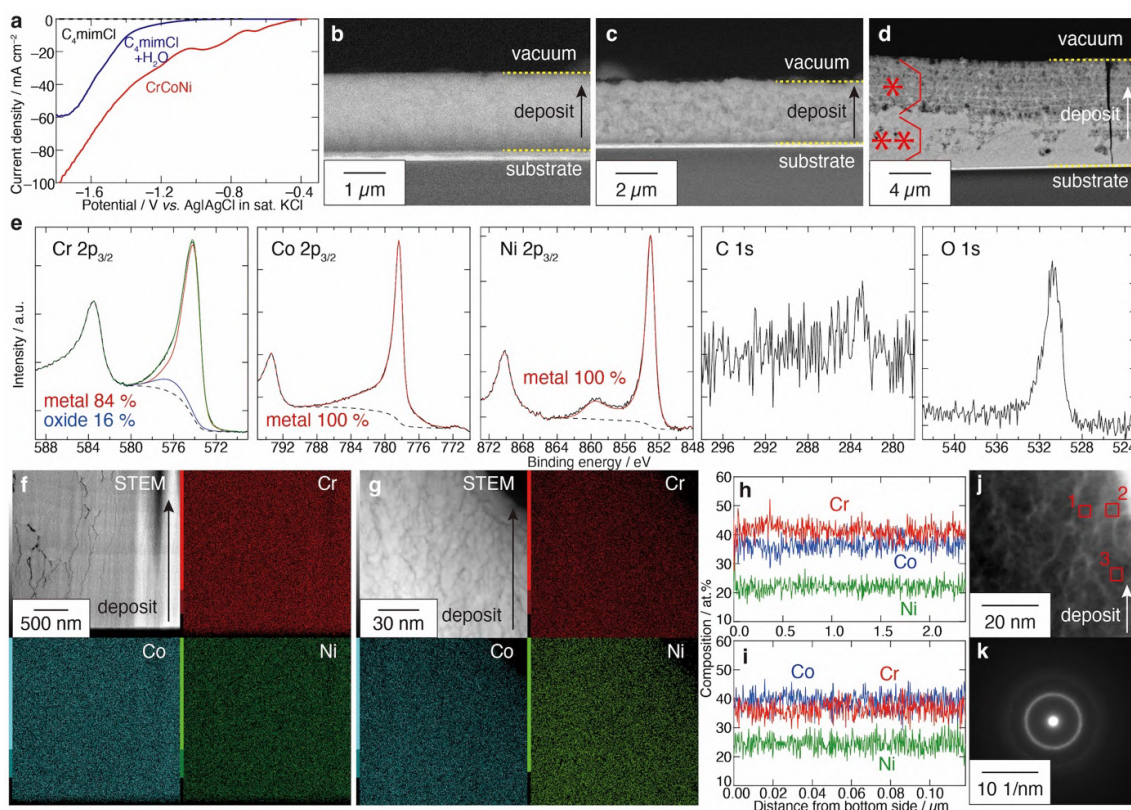


Figure 4.1. (a) Cathodic linear-sweep voltammograms for the mixture of C₄mimCl and an aqueous solution containing metal salts (red solid line), the mixture of C₄mimCl and an aqueous solution without metal salts (blue solid line), and pure C₄mimCl (black dotted line). The scan rate was 20 mV s⁻¹. The pure ionic liquid was measured at 100 °C; the other two samples were measured at 50 °C. (b-d) Cross-sectional backscattered electron images of samples obtained from (b) the mixture with a HCl ratio of 0.06 at -1.3 V, (c) the mixture with a HCl ratio of 0.60 at -1.2 V, and (d) the mixture with a HCl ratio of 0.06 at -1.6 V. (e) XPS spectra of Cr 2p_{3/2}, Co 2p_{3/2}, Ni 2p_{3/2}, C 1s, and O 1s for the same sample shown in (b) after Ar etching for 12 min. Black solid, red solid, blue solid, green solid, and black dotted curves in the spectra indicate the raw data, fitted curves with a bulk CrCoNi alloy as a reference for the metallic state, fitted curves with oxidized states, the total of fitted curves, and the background, respectively. (f, g) Cross-sectional STEM images and corresponding EDS mappings of Cr, Co,

and Ni for the same sample as (b) at (f) low and (g) high magnification. (h, i) STEM–EDS depth profiles of the same sample shown in (b) at (h) low magnification and (i) high magnification. (j) STEM-BF image at higher magnification. (k) Electron diffraction pattern of the same sample shown in (b).

To explore the best conditions for the electrodeposition of CrCoNi MEAs, we conducted a series of experiments in which the applied potential as well as the ratio of HCl in the mixture was varied (Table 4.S1, Supporting Information). The appearance of the deposits is classified into three types: with metallic luster, matte, and black. The deposit with metallic luster exhibits almost no contrast in the cross-sectional backscattered electron image (Figure 1b). Considering that a backscattered electron image generates a contrast corresponding to the atomic number, this image demonstrates that the film is uniform with no clear phase segregation and/or precipitates observable at this magnification. The average composition obtained by scanning electron microscopy–energy-dispersive X-ray spectroscopy (SEM–EDS) and the value of mixing entropy ΔS of the deposit, as calculated from the composition, are Cr/Co/Ni = 43:37:20 and $1.05R$, respectively, indicating that the composition is nearly equiatomic. Notably, $\Delta S > 1.5R$ for HEAs and $1.0R < \Delta S < 1.5R$ for MEAs hold according to the classical definition. The deposit with a matte appearance shows some contrast attributable to voids (Figure 4.1c) created during the electrodeposition. The average composition of this film is Cr/Co/Ni = 1:33:66, indicating that this coating does not satisfy the requirements for an MEA. In the case of the deposit with a black appearance, the cross-sectional image (Figure 4.1d) shows phase segregation into dark and bright areas (marked by * and **, respectively). The compositions obtained by SEM–EDS for these areas are summarized in Table 4.S2

(Supporting Information); they reveal that the dark areas contain more oxygen. This result indicates that the contrast is attributable to differences in the amount of codeposited hydroxide and/or oxide, which is undesirable for a surface coating. Notably, deposits obtained under certain conditions resulted in exfoliation (Table 4.S1, Supporting Information). The average composition of such an exfoliated film was Cr/Co/Ni = 2:59:39, showing that the principal element of the coating was Co. Therefore, the high Co ratio causes high internal stress in the film, resulting in exfoliation^[21].

The chemical state of the sample with metallic luster was characterized by X-ray photoelectron spectroscopy (XPS) (Figure 4.1e). The measurements were performed after Ar etching to remove the surface oxide layer. The Co 2p_{3/2} and Ni 2p_{3/2} spectra are fitted completely with each reference peak of metallic Co and Ni, respectively; however, the spectrum of Cr 2p_{3/2} does not match the reference peak and another peak related to an oxidized state appears at a higher binding energy. The ratio between the metallic and oxidized states of Cr determined from the peak areas is 84:16. The C 1s spectrum indicates that no carbon contamination exists in the film; therefore, the oxidized Cr is attributed to oxides and/or hydroxides codeposited as a result of the local pH increase induced by hydrogen evolution. This result indicates that a small amount of oxide precipitation during electrodeposition is inevitable. The electrodeposition of crystalline Cr in a concentrated aqueous solution has been reported to result in such codeposition of a similar amount of oxidized Cr^[22]. The molar fractions of the constituent elements in the metallic state and its ΔS are Cr/Co/Ni = 39:40:21 and 1.06*R*, which satisfy the requirement for an MEA.

Cross-sectional scanning transmission electron microscopy (STEM) images and the corresponding EDS mappings of Cr, Co, and Ni elements with low and high magnifications are shown in Figures 4.1f and 1g. These results at both magnifications show that the elements are

uniformly distributed in the deposit. The depth profiles at both magnifications (Figures 4.1h and 4.1i) indicate the components are homogeneously distributed. Although a difference in the composition is found by comparing the high and low magnification analyses, it originates from a local deviation of composition since the analyzed areas are not totally the same position. The composition at high magnification is Cr/Co/Ni = 38:41:21, which is consistent with the results obtained from the SEM–EDS. A STEM bright-field (BF) image at higher magnification (Figure 4.1j) clarifies that this deposit is composed of nanocrystals smaller than 10 nm. Table 4.S3 (Supporting Information) summarizes the results of the EDS analyses of the three grains marked in the STEM-BF image. The compositional differences are small, indicating that Cr, Co, and Ni are soluble in each other at the nanoscale. The selected-area electron diffraction (SAED) pattern of the deposit (Figure 4.1k) shows relatively broad Debye rings, and the plane spacing of the most intense ring is 2.001 Å, corresponding to the 111 or 200 planes of a face-centered cubic (FCC) structure and/or the 0002 planes of a hexagonal close-packed structure (HCP). Indeed, the nanobeam diffraction (NBD) patterns of this deposit (Figure 4.S1, Supporting Information) indicate that FCC and HCP structures coexist, which is attributed to the CrCoNi MEAs with FCC and HCP structures exhibiting similar thermodynamic stability (i.e., a low stacking fault energy on the 111 planes)^[23–25].

4.2.2. Annealing effect on the metallographic structures of the CrCoNi MEA

To investigate whether annealing causes the phase segregation and precipitation of chromium carbide as a result of carbon contamination, we further annealed the deposit prepared at -1.3 V in the bath with an HCl ratio of 0.06 at 400 °C or 550 °C for 30 min under vacuum. The STEM images and the corresponding EDS mappings for the sample annealed at 400 °C are shown in Figures 4.2a and 4.2b, respectively. The EDS mappings show little elemental segregation. The depth profiles at two different magnifications (Figures 4.2c and 4.2d) indicate that the components are homogeneously distributed even after annealing. The depth profile at low magnification (Figure 4.2c) shows that the composition of Cr in the vicinity of the surface decreases while that of Co increases. This difference is as small as $\sim 5\%$, and a layered distribution of composition is not observed; therefore, a clear phase separation does not occur in this sample. Since the crystalline structure of Cr (BCC) is different from that of Co (HCP and FCC) and Ni (FCC), the deposition of Cr is slightly suppressed when the deposition of Co tends to be promoted. The composition at high magnification is Cr/Co/Ni = 35:41:24, consistent with the ratio of the as-deposited film (Figure 4.1i). The STEM-BF image at higher magnification (Figure 4.2e) indicates that, compared with the crystal grains in the as-deposited film, those in the annealed film grew larger than 10 nm and their grain boundaries became more apparent. Table 4.S4 summarizes the results of two individual grains and two spot analyses of grain boundaries shown in Figure 4.2e. The EDS analyses of these grains show that the compositional difference between the crystals in the annealed film is small and that Cr, Co, and Ni form a near-equiatomic solid solution, similar to the EDS analysis results for the as-deposited film (Table 4.S3, Supporting Information). However, the results of the

point analyses qualitatively show that Cr, O, and Cl are more concentrated at the grain boundaries than in the interior of the grains. Although oxidized Cr would be concentrated at the grain boundaries even before annealing, the grain size of the as-deposited film is too small for the composition at the grain boundaries to be measured. The SAED pattern of the film (Figure 4.2f) shows clear spots compared with the pattern of the as-deposited film, indicating that they are composed of relatively large crystals with HCP and FCC structures. The XRD pattern in Figure 4.S2 (Supporting Information) is also consistent with this result. The STEM images and corresponding EDS mappings after the annealing at 550 °C (Figure 4.S3, Supporting Information) are similar to those of the film annealed at 400 °C, except that the grain size increased slightly. Note that the composition at high magnification is Cr/Co/Ni = 36:42:22, indicating that the composition and elemental distributions do not change even after high-temperature annealing.

The Ar-etched films were analyzed by XPS; the results for the films annealed at 400 °C and 550 °C are shown in Figures 4.2g and 4.S4 (Supporting Information), respectively. The Co 2p_{3/2} and Ni 2p_{3/2} XPS spectra of the annealed samples are completely fitted by the respective metallic peaks, whereas the peak shape of Cr 2p_{3/2} at high binding energies does not match the metallic peak, indicating the presence of oxidized Cr. By contrast, the C 1s spectrum shows that no carbon contamination is present inside the film. These results are similar to those for the as-deposited film. However, the ratio of oxidized Cr increases after annealing and further increases at higher annealing temperatures, indicating that a small amount of oxygen likely diffuses into the film during annealing.

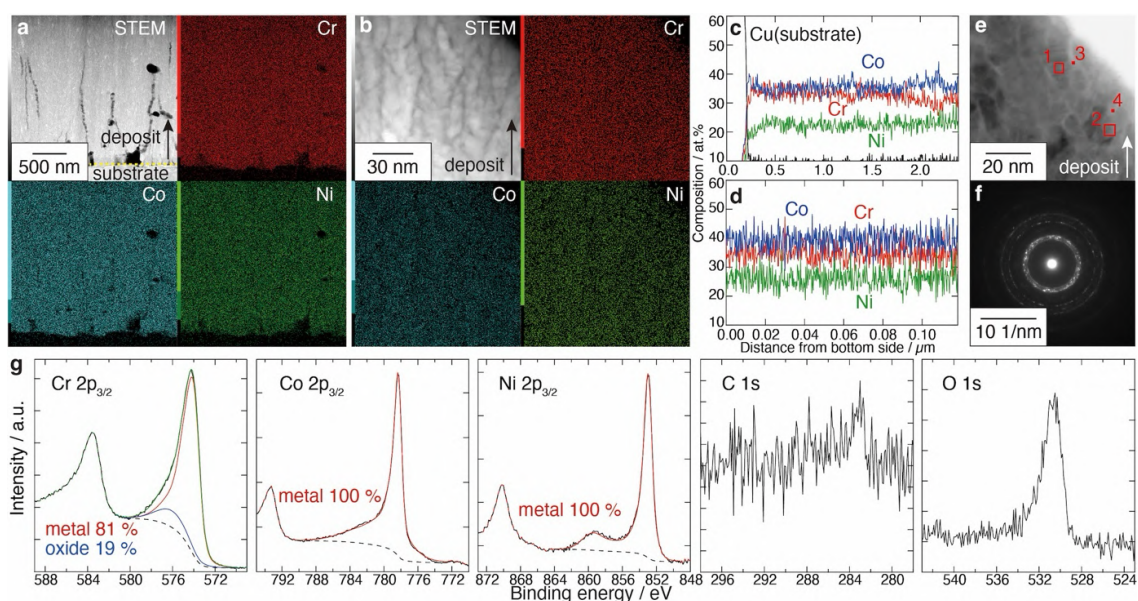


Figure 4.2. (a, b) Cross-sectional STEM images at (a) low and (b) high magnification and the corresponding EDS mappings of Cr, Co, and Ni for the sample deposited from the C₄mimCl mixture with HCl ratio of 0.06 at -1.3 V and annealed at 400 °C for 30 min under vacuum. Black areas observed in the image are voids created during annealing. (c, d) STEM–EDS depth profiles of the same annealed sample at (c) low and (d) high magnification. (e) STEM-BF image at higher magnification. (f) Electron diffraction pattern of the same sample. (g) XPS spectra of Cr 2p_{3/2}, Co 2p_{3/2}, Ni 2p_{3/2}, C 1s, and O 1s obtained after Ar etching for 12 min with the same sample. Black solid, red solid, blue solid, green solid, and black dotted curves in the spectra indicate the raw data, fitted curves with a bulk CrCoNi alloy as a reference of the metallic state, fitted curves with oxidized states, the total of fitted curves, and the background, respectively.

4.2.3. Mechanical and anticorrosion properties of the CrCoNi MEA

Mechanical properties were evaluated by nanoindentation of three MEA samples: the as-deposited CrCoNi MEA film and the CrCoNi MEA films annealed at 400 °C and 550 °C. A conventional hard Cr coating deposited electrochemically from a Cr(VI) bath was also evaluated for comparison. Both the reduced elastic modulus and hardness increased after annealing, with higher values observed for the film annealed at 550 °C (Figure 4.3a). In conventional polycrystals with coarse grains, the elastic modulus originates from the atomic bonding of elements with a periodic arrangement within a grain. While, the arrangement of atoms is irregular at grain boundaries, where the situation is similar to the atoms in amorphous phases with a lower elastic modulus than that in crystalline phases, in general. This suggests that the elastic modulus decreased in the as-deposited sample since it had a high density of grain boundaries. Annealing grows the film into dense crystals, and its modulus approaches that of the bulk CrCoNi MEA (226 GPa)^[5]. The hardness of the as-deposited film is 6 GPa, which is lower than that of the hard Cr film (10 GPa); however, the hardness after annealing reaches 11 GPa at 400 °C and 13.5 GPa at 550 °C, which is superior to that of the hard Cr film. This hardening is attributed to three phenomena. First, the yield strength increases because of annealing hardening, which is common in many metallic materials^[26–28]. Second, annealing annihilates the lattice defects often present in the as-deposited film, resulting in an increase in the work-hardening rate. Figure 4.S5 (Supporting Information) shows the load–displacement curves obtained from the nanoindentation tests. The slope at the beginning of loading is larger after annealing, confirming that annealing improved the work-hardening rate. Third, the grain growth during annealing affects the strength. When crystal grains are large, the

yield stress increases in inverse proportion to the square root of the grain diameter, which is called the Hall–Petch relation^[29–31]. Notably, this relation holds for hardness instead of stress. However, the Hall–Petch relation is no longer valid when the grain size is less than a few hundreds or tens of nanometers, in which case the hardness decreases with decreasing grain size, which is called the inverse Hall–Petch rule^[32,33]. The grain size that shows the maximum hardness determined by the Hall–Petch and inverse Hall–Petch relations is on the order of a few tens of nanometers in transition metals and their alloys^[33], although it varies depending on the materials and their fabrication method. From the STEM images of the annealed films (Figures 4.2e and S3f, Supporting Information), the grain size is ~20 nm, which is comparable to the grain size corresponding to maximum hardness. The hardness of hard Cr films deposited from a conventional Cr(VI) bath decreases after annealing because of crystalline growth^[34]. Thus, no further mechanical improvement of the hard Cr coating is expected through annealing. Leyland and Matthews have claimed that the hardness value normalized by the elastic modulus (H/E) is an excellent indicator of wear resistance^[35,36]. The as-deposited CrCoNi MEA film shows an H/E value close to that of the hard Cr, and the CrCoNi films after annealing exhibit higher values; therefore, the wear resistance of the as-deposited CrCoNi MEA is equivalent to that of conventional hard Cr coatings and the annealed MEA exhibits much higher wear resistance.

The wear resistance of the samples was evaluated by a scratch test using the nanoindenter (Figure 4.S6, Supporting Information). The sample surface was scratched with a constant load of 2000 μN for a length of 6 μm , and the difference in the height of the sample surface before and after scratching was examined by scanning probe microscopy (SPM). While the annealed CrCoNi MEA (Figure 4.S6b, Supporting Information) and the hard Cr coating (Figure 4.S6c,

Supporting Information) showed a similar degree of height change before and after scratching, the as-deposited CrCoNi MEA (Figure 4.S6a, Supporting Information) showed ~ 1.5 times larger height change. Figure 4.S6d (Supporting Information) shows the friction coefficient during the scratching test, and the values for the three samples were similar. It should be noted that the scratch test using the nanoindenter does not allow highly quantitative comparisons in the following two respects. First, the height measurement by SPM cannot distinguish between changes in height due to plastic deformation and wear; therefore, changes in height cannot be attributed solely to wear. The plastic deformation is more likely to occur compared to the wear in the as-deposited CrCoNi MEA, which has a lower hardness and reduced elastic modulus than those of hard chromium coating, resulting in an overestimation of the wear volume when calculated from the height change. Second, the results of wear tests vary greatly depending on the surface condition and the film thickness after electrochemical polishing. Even though the electropolishing was conducted under the same condition, the surface of the CrCoNi MEAs was rough compared to that of the hard chromium coating since it was not the optimum condition for the CrCoNi MEAs. Thus, it was difficult to achieve a flat surface of the CrCoNi MEA with the same thickness as the hard chromium sample. Based on these concerns, the scratch test is suitable for semi-quantitative comparisons.

Although macroscopic tribological tests and weight change methods are preferable to nano-scratch tests for evaluating wear resistance, they require a large area coating such as 100 mm x 100 mm. To obtain such large area coatings, the design of a large electrochemical cell is necessary to achieve uniform current distribution, temperature, and purge control. The scale-up required for practical electroplating is our future work.

Table 4.S5 (Supporting Information) summarizes the results of this work and previous studies that measured the hardness of the CrCoNi MEAs prepared by methods other than electrodeposition. These studies measured the Vickers hardness, which can be converted to the hardness of the nanoindenter by multiplying the value by 1/94.547 according to ISO 14577-1 Annex F. It should be noted, however, that the converted values are not quantitatively comparable. The converted hardness of the CrCoNi MEA fabricated by laser cladding is 2.8 GPa, and the CrCoNi MEA composites with TiC and SiC have hardnesses of 3.3 GPa and 3.4 GPa, respectively. The CrCoNi MEAs fabricated by laser cladding have larger crystal grains, and their hardness is lower than that of the CrCoNi MEAs in this study because they follow the Hall-Petch relation. The converted hardness of CrCoNiTi MEAs fabricated by laser cladding with two-phase separation and bulk CrCoNi MEAs fabricated by arc melting is 8.1 GPa and 3.6 GPa, respectively. The hardness of the CrCoNi MEAs annealed at 550 °C and reported in this study (13 GPa) is higher than those of the CrCoNi MEAs fabricated using other methods, indicating that the electrodeposition enables a unique microstructure composed of nanocrystals, resulting in higher hardness.

Since the electrodeposition of CrCoNi MEAs has not been achieved, there are no publications that discuss the wear and corrosion resistance of CrCoNi MEA films. The hardness and elastic modulus of other MEAs and HEAs produced using electrodeposition together with our present result are summarized in Table 4.S6 (Supporting Information). The highest hardness and H/E values obtained other than this study are 8.5 GPa and 0.063 for CrFeNi alloys annealed at 550 °C. However, the authors of the study mentioned that annealing caused the precipitation of Cr₂O₃ and α -Cr (BCC) from the FCC phase and that the precipitation of Cr₂O₃ is due to the oxygen contamination in the coating. A phase-separated microstructure is undesirable for coatings because it causes galvanic corrosion, resulting in lower corrosion resistance. On the other

hand, the CrCoNi MEA fabricated in this study is an MEA with no precipitation of single component metals or oxides even after annealing due to the small amount of impurity contamination. This leads to the hardness and H/E ratio of 13.3 GPa and 0.072 for the annealed CrCoNi MEA, resulting in the more excellent mechanical property than the other MEAs and HEAs fabricated so far by electrodeposition.

In general, the yield strength increases with increasing Cr content, while the work hardening is expected to be enhanced due to the twinning and the formation of the hcp phase when the content of Co and Cr is high^[37–39]. Based on the aforementioned trends observed in bulk materials, one can expect higher wear resistance with high Cr and/or Co contents.

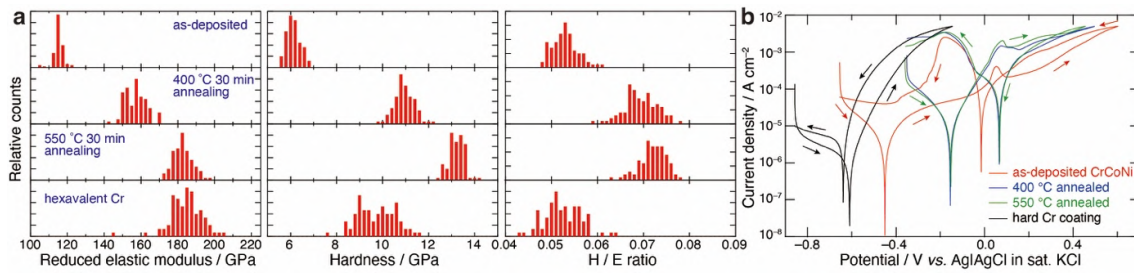


Figure 4.3. (a) Histograms of the reduced elastic modulus and hardness measured at 100 points for an as-deposited CrCoNi film, CrCoNi films annealed at 400 °C and 550 °C, and a hard Cr coating deposited from a Cr(VI) bath; hardness values were normalized by the elastic modulus. (b) Polarization curves under corrosion tests using 0.1 M NaCl aqueous solution for an as-deposited CrCoNi film, CrCoNi films annealed at 400 °C and 550 °C, and the hard Cr coating from the conventional Cr(VI) bath. The measurements were performed after deaeration by Ar bubbling. The scan rate was 1 mV s⁻¹.

The corrosion resistance of the deposits obtained from the C₄mimCl mixture at -1.3 V was evaluated. The corrosion resistance of bulk CrCoNi MEAs has been extensively studied and found to be superior

to that of CrMnFeCoNi HEAs and stainless steels^[9]. However, the corrosion resistance of coatings prepared by electrodeposition generally differs from that of the corresponding bulk materials because of the presence of impurities and differences in the microstructure. We here compare the corrosion resistance of a CrCoNi MEA prepared by electrodeposition with that of a conventional hard Cr coating. The corrosion potential E_{corr} and corrosion current I_{corr} of each coating, as determined from the Tafel plots (Figure 4.3b), are summarized in Table 4.S7 (Supporting Information). The corrosion current is higher for the as-deposited CrCoNi MEA than for the hard Cr coating because the as-deposited CrCoNi MEA is composed of nanocrystals smaller than 10 nm, resulting in a higher density of grain boundaries that act as active reaction sites. Passivation is not measured at a positive potential during the potential scan using the hard Cr coating, whereas the as-deposited CrCoNi MEA has a relatively wide passivation region. This result suggests that passivation mechanism differs between the hard Cr coating and the CrCoNi MEA. Secondary electron images of the coating surface before and after the corrosion test are shown in Figure 4.S7 (Supporting Information). As is well known, hard Cr coating has many cracks on the surface, and if the cracks reach the substrate, dissolution of the substrate will occur, and corrosion resistance will decrease. On the other hand, the CrCoNi MEA electrochemically deposited has a completely crack-free surface before corrosion tests. Therefore, a passivation film derived from Cr and Ni is ideally formed, which prevents leaching of the substrate and thus provides excellent corrosion resistance. After the corrosion test, it is partially cracked, but the crack density is significantly lower than that of hard chromium coating. The additional corrosion experiments also reveal that the corrosion potentials of the CrCoNi MEAs are relatively unstable and the reproducibility was not good enough to discuss the anticorrosion property. On the contrary, the passivation behavior at the anodic

potentials showed a good reproducibility; therefore, the anticorrosion behavior is mainly due to the passivation of the surface. The polarization curves of the films annealed at 400 °C and 550 °C overlap each other, suggesting that the effect of annealing temperature on the corrosion resistance is small. Passivation is also observed for the annealed samples, meaning that the corrosion is suppressed compared with the hard Cr within the passivation region for practical uses.

The relationship between the short-range order and the mechanical properties of HEAs and MEAs has been discussed intensively^[25,40–52], but a general conclusion has not yet been reached due to the lack of reliable and systematic experimental evidence of short-range order. It was reported that the short-range order was detected by the selected area electron diffraction (SAED) analyses^[43]; however, it was denied later^[44]. As far as we concern, atom probe tomography (APT) is the most reliable experimental method to detect short-range order in solid solutions^[49]. To conduct APT, the crystal grain size at the tip of a CrCoNi MEA sample is several tens of nanometers. As shown in Figure 4.1j, the size of the grain was smaller than 10 nm in our electroplated sample. With such a sample, the APT is not possible to characterize the short-range order of the deposit, and thus it is difficult to draw a clear conclusion about the impact of short-range order on the mechanical properties in the present study alone. The increase of the grain size by electroplating for the enhancement of mechanical properties is our future work. Our future work on the increase of the grain size by electroplating will enable the APT and it is expected to give a clear view of the relation between the short-range order and the mechanical properties. With respect to corrosion resistance, the distribution of the electric double layer, which drives the corrosion reaction, is not discontinuous at the atomic scale. Thus, the short-range order of the CrCoNi MEA is not crucial for its corrosion resistance.

4.2.4. Impact of the type of ionic liquid for the electrodeposition of the CrCoNi MEA

As summarized in Table 4.S8 (Supporting Information), the potential dependence of the appearance in the case where 1-hexyl-3-methylimidazolium chloride ($C_6\text{mimCl}$) was used showed the same trend as that in the case where $C_4\text{mimCl}$ was used. By contrast, the use of 1-ethyl-3-methylimidazolium chloride ($C_2\text{mimCl}$) resulted in films with a matte appearance without metallic luster. The cross-sectional backscattered electron images and the average composition for these deposits are summarized in Figures 4.4a–c and Table 4.S9 (Supporting Information), respectively. In Figure 4.4a, the matte film deposited at -1.2 V from the $C_2\text{mimCl}$ mixture shows no apparent contrast; however, the principal element is Co (nonequiatomic). The chemical state of each metal element was determined by XPS analysis (Figure 4.4d). All the metal elements were present in their oxidized states; notably, 92% of the Cr was oxidized. Given that some of the Cr_2O_3 might have been reduced during the Ar-etching process before the XPS measurement, little metallic Cr was deposited. Thus, the alloy composition of the metallic-state components is Cr/Co/Ni = 2:79:19 ($\Delta S = 0.58R$). Given that Cr is the least noble of the three metals and that Co deposits preferentially over Ni because of anomalous codeposition^[14], this compositional tendency is consistent with that expected for a film deposited from a bulk aqueous solution. The films deposited at -1.3 V and -1.4 V from the $C_2\text{mimCl}$ mixture, both of which have a matte appearance, show a compositional tendency similar to that of the film deposited at -1.2 V. In the case of the film deposited at -1.4 V, the greater cathodic overpotential leads to an increase in the Cr ratio. However, the corresponding XPS spectra (Figure 4.S8, Supporting Information) indicate that a high proportion of Cr is oxidized and that the alloy composition of the metallic-state components is Cr/Co/Ni =

18:66:16 ($\Delta S = 0.88 R$). These results clearly indicate that the MEAs are difficult to deposit from the C₂mimCl mixture.

Figure 4.4b shows a cross-sectional SEM image of the metallic-luster film deposited at -1.3 V using C₆mimCl. The image shows that the film is ~ 400 nm thick, or one-fourth the thickness of the film deposited using C₄mimCl at the same potential. The film deposited using C₆mimCl was too thin for its contrast to be identified. The average composition of the film deposited at -1.3 V using C₆mimCl (Table 4.S9, Supporting Information) is near-equiatomic; however, the variation in composition among different measurement positions is greater than that observed for the film deposited at -1.3 V using C₄mimCl (Table 4.S4, Supporting Information). XPS spectra of this film indicate that this alloy is composed of a small amount of oxidized Co and Ni (Figure 4.4e) and one-third to one-half oxidized Cr. The composition of this alloy in the metallic state is 27:46:27 ($\Delta S = 1.06R$), satisfying the criterion for an MEA. Cross-sectional STEM images and corresponding EDS mappings of this film are shown in Figures 4.4f and 4.4g. At both magnifications, the components are uniformly distributed, and no phase segregation is observed. The composition at high magnification is Cr/Co/Ni = 35:44:20, consistent with the SEM-EDS results. The STEM-BF image at higher magnification (Figure 4.S9a, Supporting Information) shows that the size of the crystalline grains with a black appearance is smaller than 2 nm and much finer than that of the as-deposited film prepared using C₄mimCl. Such a smaller grain size leads to a high proportion of grain boundaries in the deposited film, resulting in a high ratio of oxidized Cr observed by XPS. The SAED pattern of the film deposited at -1.3 V from the C₆mimCl mixture (Figure 4.S9b, Supporting Information) indicates a relatively broad Debye ring corresponding to the 111 diffraction of the FCC structure with a plane spacing of 2.002 Å, consistent with the pattern of the film deposited at -1.3 V from the C₄mimCl mixture. These results confirm

that, unlike the C₂mimCl mixture, the C₆mimCl mixture enables the electrodeposition of the CrCoNi MEA. The cross-sectional backscattered electron image of the film deposited at -1.4 V from the C₆mimCl mixture (Figure 4.4c) shows a clear contrast within the film, suggesting the codeposition of hydroxides and/or oxides. Figure 4.S10 (Supporting Information) shows the XRD results of the films deposited at -1.4 V from the C₂mimCl, at -1.3 V from the C₄mimCl mixture, and at -1.3 V from the C₆mimCl mixture. The diffraction patterns of all three samples show a peak at approximately the same diffraction angles; however, the peak shapes differ substantially. In the pattern of the film deposited from the C₂mimCl mixture, the peak is noisy and broad because of the high Co ratio in the alloy and the fine grains. In the pattern of the film deposited from the C₆mimCl mixture, the peak intensity is weaker because of the thinner film and much finer grain size.

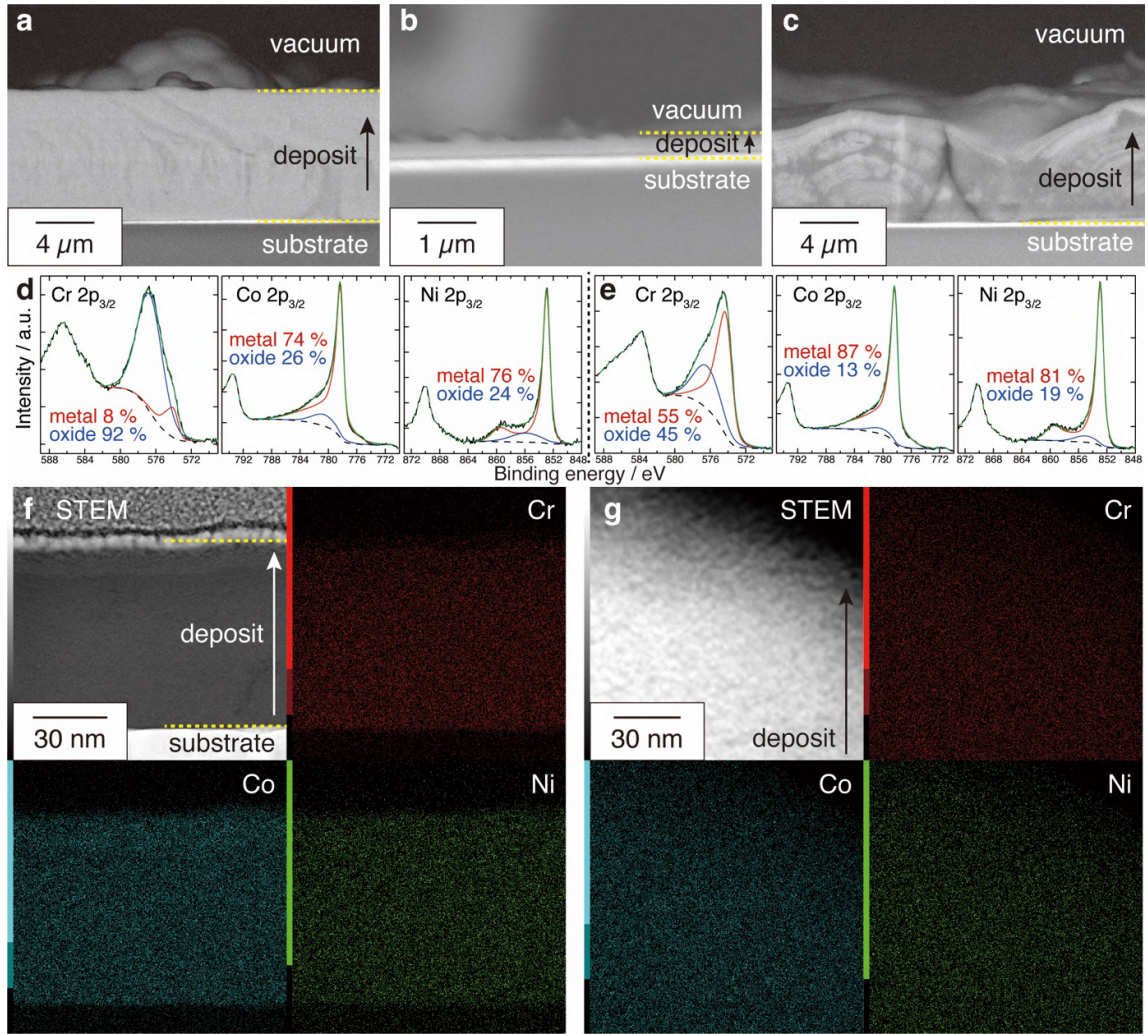


Figure 4.4. (a-c) Cross-sectional backscattered electron images of the samples from (a) C₂mimCl mixture with a HCl ratio of 0.06 at -1.2 V, (b) C₆mimCl mixture with a HCl ratio of 0.06 at -1.3 V, and (c) a C₆mimCl mixture with a HCl ratio of 0.06 at -1.4 V. (d, e) XPS spectra of Cr 2p_{3/2}, Co 2p_{3/2}, and Ni 2p_{3/2} obtained after Ar etching for 12 min with the same samples as (a) and (b). Black solid, red solid, blue solid, green solid, and black dotted curves in the spectra indicate the raw data, fitted curves with a bulk CrCoNi alloy as a reference for the metallic state, fitted curves with oxidized states, the total of fitted curves, and the background, respectively. (f, g) Cross-sectional STEM images and corresponding EDS mappings of Cr, Co, and Ni for the sample shown in (b) at (f) low and (g) high magnifications.

4.2.5. Role of the solution in the electrodeposition of the CrCoNi MEA

Here, we attempt to explain the effect of the length of the alkyl chain attached to the imidazolium ring of the cation on the electrodeposition of MEA in terms of mesoscopic heterogeneity in the electrolytic solution. Molecular dynamics (MD) simulation is a powerful tool that enables visualization of phase-separated structure at the atomic scale. Figure 4.5a shows the snapshots of the production simulations after equilibration, indicating that the volume ratio occupied by the nonpolar domains (green) increases with increasing length of the alkyl chain attached to the imidazolium ring. As the alkyl chain length increases, the nonpolar interactions between the alkyl chains become stronger and the alkyl chains tend to self-assemble with each other to form large nonpolar domains. Domain analyses were carried out to quantitatively evaluate the characteristics of these domains. Table 4.S10 (Supporting Information) summarizes the domain counts, average volume of one domain, and average, minimum, and maximum values of isoperimetric quotient Q (described later). In addition, Figures 4.S11–4.S13 (Supporting Information) depict the time evolution of these values for the nonpolar domain in five production MD simulations of $C_n\text{mimCl}$ ($n = 2, 4, 6$) mixtures, each starting from a randomly generated initial configuration. The stability of these values over time indicates that the system reached equilibrium. Furthermore, the small standard deviations shown in Table 4.S10 (Supporting Information) confirm that the equilibrium structure is independent of the initial configuration. These results also reveal that, as the alkyl chain length attached to the imidazolium ring increases, the number of nonpolar domains decreases, and the domains tend to connect with each other. However, in the case of the $C_2\text{mimCl}$ mixture, the average number of nonpolar domains is 1202. Given that the number of

imidazolium cations in the box is 2262 (Table 4.S11, Supporting Information), the average number of cations constituting one nonpolar domain is ~ 2 . This domain is more like a dimer than a nonpolar domain formed by the aggregation of some alkyl chains, and the nonpolar groups are uniformly distributed throughout the solution. In this case, the nonpolar groups cannot suppress the diffusion of metal ions through the polar domain; therefore, this C₂mimCl mixture is similar to a homogeneous solvent, such as a bulk aqueous solution. However, the C₄mimCl and C₆mimCl baths form nonpolar domains consisting of ~ 5 and ~ 12 cations on average (Tables 4.S10 and 4.S11, Supporting Information), which are sufficiently large to disturb the diffusion of metal ions. This idea is similar to that of tortuosity^[53,54], which also slows diffusion in porous materials. Figure 4.5b shows the diffusion coefficients of metal cations in aqueous solution and in mixtures with ionic liquids having various lengths of alkyl chains determined from MD simulations. It is obvious that these diffusion coefficients in the aqueous solution are higher than those in the mixtures with ionic liquids. The absence of ionic liquids reduces the concentration of ionic species, resulting in faster diffusion of metal ions. In addition, Figure 4.5b shows that all diffusion coefficients of metal ions decrease uniformly as the alkyl chain length increases. In our previous paper, we reported that the electrodeposition of an equiatomic CoNiCu medium-entropy alloy was successful when the reduction of all the components took place under the diffusion-limited condition^[17]. Since the equilibrium potential of the Cr electrodeposition is less-noble, the Cr reduction is generally difficult to be diffusion-limited compared to the other Co and Ni reduction. The decrease of their diffusion coefficients is an alternative control other than the control of the applied potential to achieve the diffusion-limitation. The present result suggests that the diffusion coefficients using C₄mimCl and C₆mimCl are small enough to achieve the diffusion-limited reduction of all the components and to

result in the nearly equiatomic CrCoNi MEA deposition. Note that the difference in the diffusion coefficients of metal ions obtained by the MD simulation is mainly due to the difference in the valence of the metal ions. In the case of Cr(III), the higher valence compared to those of Co(II) and Ni(II) induces stronger interactions with water and Cl⁻, resulting in a lower diffusion coefficient. The diffusion coefficients of Co(II) and Ni(II) are relatively similar, but their difference is likely due to the solvation structure of the water molecules.

It is important to experimentally evaluate the diffusion coefficients of metal ions and compare with results of MD simulation. The metal elements used in the present study are electrochemically deposited under the hydrogen evolution as a side reaction; therefore, it is difficult to electrochemically determine the diffusion coefficients of their cations using a rotating disc electrode. Copper is an ideal element that can be electrochemically deposited without hydrogen evolution. Thus, in this study, the diffusion coefficient of Cu(II) ion with changing the alkyl chain length was electrochemically measured as a model case. The mixture was prepared with the same ratio as the experiment of the alloy deposition, i.e., C_nmimCl (*n* = 2, 4, 6) : H₂O : HCl = 6 : 45 : 0.06. Note that the metal ion concentration should be low for the reaction to become diffusion-limited condition so that the concentration of Cu(II) ions was set to 5 mM in all solutions. The diffusion-limited current density was measured by changing the rotating rate of the electrode to 100, 250, 500, 750, and 1000 rpm. By measuring the viscosity and density of the solutions, the diffusion coefficient of Cu(II) ion was obtained based on the Levich plot (Figure 4.S14, Supporting Information), and the results are summarized in Table 4.S12 and Figure 4.S15 (Supporting Information). The diffusion coefficient of Cu(II) ion in aqueous solution was close to the reference value ($7.13 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) at infinite dilution^[55]. The diffusion of Cu(II) ion is fastest in aqueous solution and slows down in the order of C₂mimCl mixture,

C₄mimCl mixture, and C₆mimCl mixture. This trend exactly matches the result obtained by the MD simulation, suggesting that the MD simulation reproduces the experimental result well.

The validity of the MD simulation of the mixture solution is crucial for the present study. To evaluate the accuracy of the MD simulation, we additionally carried out small angle X-ray scattering (SAXS) to discuss whether a mesoscopic structure formation takes place or not. It is not possible to measure SAXS using the mixture containing 3d metal cations due to the significant absorption of the X-ray. Instead of the mixture with metal ions, the SAXS from the mixture of the ionic liquid and the aqueous solution without the metal salts was measured (Figure 4.S16a, Supporting Information). The mixture using C₂mimCl does not show peaks on the scattering profile, while that using C₆mimCl clearly shows a scattering peak at $q = 3 \text{ nm}^{-1}$. Similar results without the addition of the aqueous solution were reported in the literature^[56]. We have carried out the MD simulations without the metal ions, and compared the structure factors of the C_nmimCl mixtures with those converted from the experimental SAXS profiles (Figures 4.S16b-d, Supporting Information). These results are in good agreement with the experimental structure factors. In the case of C₆mimCl mixture, although the maximum values of the peaks differ from each other, the peak shape and the q value at the peak top are consistent. Comparing the structure factors obtained from MD simulations with each other (Figure 4.S16e, Supporting Information), the structure factor of the C₄mimCl mixture is increased compared to that of the C₂mimCl mixture in the low q range; however, the increase is not high enough to be detected as a peak. This trend is same with the experimental SAXS results (Figure 4.S16a, Supporting Information), indicating that the MD simulations in the present work are sufficiently accurate.

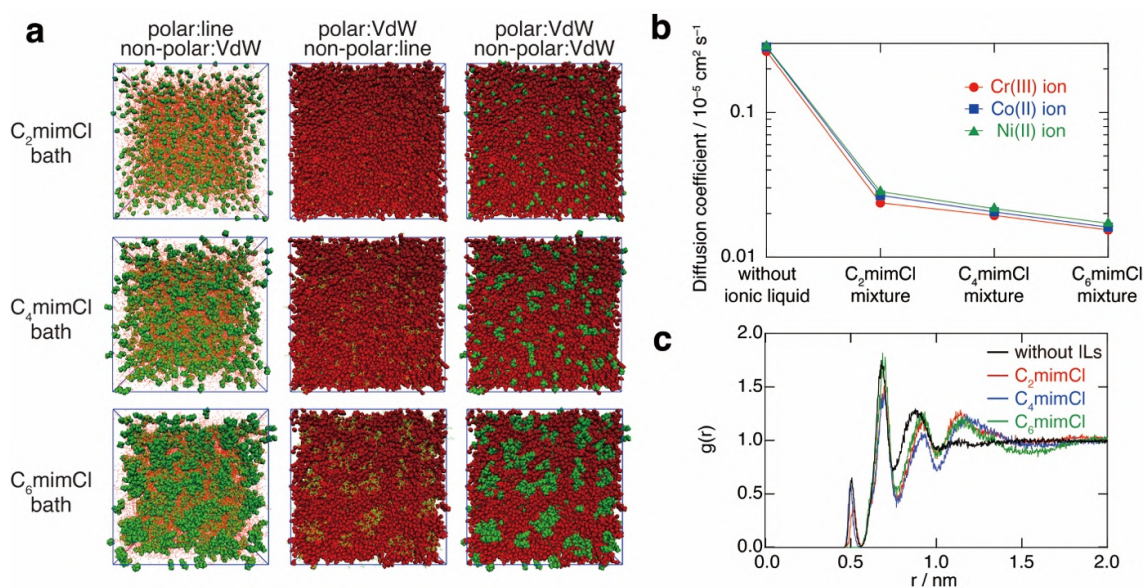


Figure 4.5. (a) Snapshots of the three mixtures containing ionic liquids with different alkyl chain lengths, showing polar domains in red and nonpolar domains in green. Here, the metal ions, water molecules, and chloride ions exist within the polar domain. For the cations of the ionic liquids, the imidazolium ring and the methyl group attached to the ring exist within the polar domain, whereas the rest of the alkyl chain exists within the nonpolar domain. Figures 4.5a show three different types of snapshots in columns. The left snapshots use the van der Waals (VdW) radii model in green to describe nonpolar molecules and the line model in red to describe polar molecules to emphasize the nonpolar domains. The snapshots in the middle use the VdW radii model to describe polar molecules and the line model to describe nonpolar molecules. The right snapshots use the VdW radii model to describe both polar and nonpolar molecules. The length of one side of these simulation boxes is approximately 10 nm. (b) Effect of alkyl chain length of ionic liquids on the diffusion coefficients of metal ions, as obtained by MD simulation. (c) Radial distribution functions between Cr(III) ions obtained by MD simulation for a single-phase aqueous solution (without ionic liquids) and mixtures of aqueous solutions and ionic liquids having different alkyl chain lengths.

In addition, Figure 4.S16f (Supporting Information) shows the calculated structure factors of the mixtures with metal ions. The peak shapes of the structure factors for the C₂mimCl and C₆mimCl mixtures are not significantly different with and without metal ions, whereas the structure factor for the C₄mimCl mixture shows a more distinct and broad peak when metal ions are added. This is because the number of free water molecules decreases due to coordination to metal ions and the mesoscale structure formation is promoted. Although the quantitative accuracy of the MD simulation using Lennard-Jones potentials is not high, the results of the MD simulation as well as the experimental SAXS measurement give satisfactory evidence of the mesoscale phase separation, which is of importance to achieve the electroplating of the CrCoNi MEA.

The isoperimetric quotient Q is an indicator of the domain shape (Table 4.S10, Supporting Information), and a Q value close to 1 indicates a spherical domain shape, whereas a small Q value corresponds to a domain structure with a large surface area, such as a three-dimensional network structure. The average Q value is weakly affected by the length of the alkyl chain attached to the imidazolium ring, whereas the minimum Q value for each snapshot (i.e., the Q value of the nonpolar domain farthest from the sphere) is large for the C₂mimCl mixture and similar for the C₄mimCl and C₆mimCl mixtures. Thus, the Q values indicate that the short alkyl chains of C₂mimCl can only form nearly spherical aggregates of a small number of nonpolar groups, whereas the relatively long alkyl chains of C₄mimCl and C₆mimCl can form highly ordered structures with complex shapes. The smaller grain size of the film deposited from the C₆mimCl mixture compared with that of the film deposited using C₄mimCl is likely due to the higher volume ratio of nonpolar domains in C₆mimCl, which disturbs the diffusion of metal ions. In general, the electrodeposition of a HEA or MEA should be conducted under the diffusion-limited

condition of metal ions to effectively control the composition of the HEA or MEA such that it is nearly equal to the ratio of metal ions in the aqueous solution. For instance, in the case of the FeCoNi MEA, its electrodeposition is possible by precisely controlling the ratio of the metal cations in the solution^[57,58]. This is because the equilibrium potentials of Fe, Co, and Ni are relatively close to each other; therefore, the electrodeposition is under the electron-transfer limited condition. On the contrary, the equilibrium potential of Cr is far more negative than those of Co and Ni. This means that the electrodeposition is diffusion-limited at least for Co and Ni. Under the diffusion-limited condition, the partial current density of each metal deposition is proportional to the concentration of metal cations in the solution. From the viewpoint of the control of composition in the alloy, the electrodeposition under the diffusion-limited condition is preferable since the composition is easily controlled by the concentration of metal salts; however, the electrodeposition under the diffusion-limited condition promotes the dendritic growth resulting in a rough surface. Fortunately, the utilization of the phase-separated mixture suppresses the concentration of current density at a certain site and suppresses the dendritic growth as well. We have solved this contradiction by using a water-in-oil emulsion as the bath for the electrodeposition of the CoNiCu MEA^[16]. Using a water-in-oil emulsion enables a high cathodic overpotential to be applied to easily achieve the diffusion-limited electrodeposition condition without depleting metal ions near the working electrode because water droplets containing a sufficient amount of metal ions are readily available near the working electrode. In the previous study, we proposed an important requirement that the electrodeposition of HEAs and MEAs is conducted under diffusion-limited conditions with a discontinuous supply of metal ions^[17]. Indeed, we used a large cathodic overpotential for electrodepositing the CrCoNi MEA; therefore, the electrodeposition of any metal is expected to occur

under diffusion-limited conditions. As shown in the MD simulations, the use of C₄mimCl and C₆mimCl in the mixture resulted in mesoscopic phase separation, whereas the use of C₂mimCl did not. The mixture with C₂mimCl was uniform; therefore, the electrodeposition is similar to the case of conventional single-phase aqueous solutions. On the contrary, because of the large nonpolar domains, the diffusion of metal ions is disturbed and discontinuous when a mixture with C₄mimCl or C₆mimCl is used. This situation is similar to the supply of metal ions using emulsions.

According to the aforementioned discussion, the use of an emulsion should enable the electrodeposition of CrCoNi MEAs; however, attempts to deposit the CrCoNi MEA using a water-in-oil emulsion were unsuccessful (results not shown). Cr(III) cations tend to cause olation that crosslinks many Cr(III) aqua complexes, resulting in structures that are inactive toward electrodeposition^[59,60]. Because the size of the aqueous phase in emulsions is as large as ~1 μm , the olation occurs with Cr(III). However, both experimental and calculated SAXS profiles shown in Figures 4.S16a-c (Supporting Information) indicate that the scale of the mesoscopic domain structure is ~2 nm. Olation in such a unique liquid with an inhomogeneous structure is expected to be difficult.

Figure 4.5c shows the radial distribution functions (RDFs) between Cr(III) ions for a simple aqueous solution as well as for the mixtures of aqueous solutions and ionic liquids. Although the effect of the alkyl chain length on the RDFs is small for the mixtures with ionic liquids, the oscillatory decay of the RDFs for the mixtures is distributed widely compared with that of the RDFs for the single-phase aqueous solution. Because the characteristic size of the phase-separated mixture solution is ~2 nm, the aqueous phase in the polar domain is totally filled with the volume of the structured distribution of Cr(III) ions. Thus, the olation, which is expected to occur in the homogeneous liquid state,

does not readily proceed in the polar domain. Indeed, $C_n\text{mimCl}$ ($n = 2, 4, 6$) mixtures have been reported to enable the electrodeposition of single Cr metal^[61], indicating that these mixtures suppress the oxidation, consistent with our MD results. When $C_4\text{mimCl}$ or $C_6\text{mimCl}$ is used, the deposition of Cr metal and the mesoscopic phase separation, which enable the deposition of multicomponent alloys, are simultaneously achieved, leading to the successful deposition of the CrCoNi MEA.

The RDFs of Co(II) ion and Ni(II) ion as well as Cr(III) ion in the mixtures with $C_n\text{mimCl}$ ($n = 2, 4, 6$) are shown in Figure 4.S17 (Supporting Information). The RDFs of Co(II) ion and Ni(II) ion show more intense peaks at 0.6 nm compared to Cr(III) ion. On the other hand, the RDFs of Co(II) ion and Ni(II) ion show similar profiles to each other in the same mixture, suggesting that the difference in the amplitudes of the oscillations appears to be due to the difference in the valence of the ions. Focusing on the oscillatory decay of RDFs for Co(II) and Ni(II) ions, they also oscillate over a longer distance in the mixtures with ionic liquids than in aqueous solutions, which is similar to the RDF for Cr(III) ions.

As summarized in Table 4.S9 (Supporting Information), the deviations in composition are reduced. To achieve it, it is important to control the temperature of the bath as uniformly as possible so that the current distribution becomes uniform since the partial reduction current densities of the component metals directly determine the composition of the MEA. As explained in the mechanism of corrosion, the existence of cracks strongly affects the corrosion behavior. As a result, the reproducibility of the corrosion potential is not high enough to be discussed quantitatively. After the corrosion test using the CrCoNi MEA, a small number of cracks was observed; therefore, exploring additives for the ionic liquid and aqueous solution mixture that perfectly suppress the formation of cracks is highly desired.

The most significant issue is the utilization of an ionic liquid.

C₄mimCl is one of the well-known and often used ionic liquids; therefore, it is relatively low cost when compared with other ionic liquids. Toxic Cr(VI) baths for hard chromium coatings are much cheaper than our system. Exploring another system which exhibits a similar mesoscale phase separation is necessary. We think that bicontinuous microemulsions are potential substitutes for the mixture solution proposed in this study. Regarding scalability, one can use conventional electroplating facilities once the cost issue is solved. However, note that the temperature control of deposition baths is necessary to enhance the conductivity of the mixture. The control of the grain size by electrodeposition conditions is also an important issue in achieving excellent mechanical properties without annealing. In addition, the scale-up of the process is the next issue as well. Since the conductivity of the solution is not as high as conventional aqueous solutions for metal electrodeposition, the current distribution is significant when one designs much larger electrodeposition cells.

It is important to discuss the sustainability of this technique in more detail. It is reported that the electroplating of hard chromium gives one-third of global warming potential compared to the production of chromium coating using magnetron sputtering^[62]. This difference mainly originates from the electricity used in the production. Thus, given energy consumption, electroplating is much more energy-saving. The emission of Cr(III) to the environment in dry processes such as magnetron sputtering is much less than the conventional hard chromium electroplating. Once the issue of Cr(III) emission to the environment is solved, electroplating becomes a more powerful technique. In addition, the natural resources of Cr exist as Cr(III); therefore, the electrodeposition can be conducted without changing the valence from Cr(III) to Cr(VI). Thus, we believe that our process is promising as a potential substitute for hard chromium electroplating.

4.3. Conclusion

We successfully electrodeposited a crystalline CrCoNi MEA. The as-deposited CrCoNi MEA was expected to exhibit high wear resistance equivalent to or even better than that of conventional hard Cr coatings. The CrCoNi MEA showed a higher corrosion resistance under conditions mimicking those encountered in practical applications. The key factor of successful electrodeposition was the mesoscale phase separation of the ionic liquid-water mixtures.

Hard Cr coatings have played a central role in the anticorrosion of materials; however, the technology requires the use of the toxic Cr(VI) ion as a Cr source for electrodeposition. Alternative Cr electrodeposition technologies that use environmentally friendly Cr(III) ions and alternative materials that exhibit excellent mechanical and anticorrosion properties are desired. The CrCoNi MEA coating demonstrated here overcomes such issues; therefore, from an industrial perspective, it is a potential substitute for conventional Cr coatings. From an academic viewpoint, it is important that we clarified the electrodeposition mechanism of the high-quality CrCoNi MEA from various aspects such as electrochemistry, solution chemistry, and metallography. Ionic liquid-water mixtures have a great potential as electrolytic solutions^[63,64], and thus the present study paves the way for the environmentally friendly and energy-saving production of HEA and MEA coatings by electrodeposition.

4.4. Method

4.4.1. Chemicals

Chromium(III) chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, FUJIFILM Wako Pure Chemicals, 93%), cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, FUJIFILM Wako Pure Chemicals, 99%), nickel(II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, FUJIFILM Wako Pure Chemicals, 98%), hydrochloric acid (HCl , Nacalai Tesque, 35.0–37.0 wt%), boric acid (H_3BO_3 , Sigma-Aldrich, 98.5%), 1-ethyl-3-methylimidazolium chloride ($\text{C}_6\text{N}_2\text{H}_{11}\text{Cl}$, C_2mimCl , Tokyo Chemical Industry, 98%), 1-butyl-3-methylimidazolium chloride ($\text{C}_8\text{N}_2\text{H}_{15}\text{Cl}$, C_4mimCl , Tokyo Chemical Industry, 98%), and 1-hexyl-3-methylimidazolium chloride ($\text{C}_{10}\text{N}_2\text{H}_{19}\text{Cl}$, C_6mimCl , Tokyo Chemical Industry, 98%) were used for the preparation of the electrolytic solutions without further purification.

4.4.2. Preparation of electrolytic solutions

Electrolytic solution was prepared by mixing C_nmimCl ($n = 2, 4, 6$), CrCl_3 , CoCl_2 , NiCl_2 , H_2O , and H_3BO_3 in a 6:1:1:1:45:2 molar ratio. When HCl was added to lower the pH, it was added at molar ratios of 0.06, 0.30, and 0.60 relative to the metal ions. A reference paper reported that C_2mimCl does not show the phase separation, while C_4mimCl and C_6mimCl are spontaneously phase separated into polar and nonpolar domains. By changing n being 2, 4, and 6, one can evaluate the effect of mesoscale phase separation of the mixture solution on the electrodeposition behavior of CrCoNi MEAs.

For the deposition bath, 5 g of the ionic liquid and the corresponding other chemicals were mixed so that the total amount of the mixture was ~10 mL. All of our experiments were carried out with the 10 mL mixture using a three-electrode setup as shown in Figure 4.S18 (Supporting Information). Ultra-pure water by Milli-Q water purification was used to prepare the mixture. The resultant solutions were mixed at 80 °C for more than 30 min at 700 rpm using a hotplate–stirrer.

4.4.3. Electrochemical measurements

Electrochemical measurements were carried out using a potentiostat (SP-150, Biologic). A three-electrode cell was used for the measurements (Figure 4.S18, Supporting Information). A Pt plate and an Ag|AgCl (in saturated KCl) electrode were used as the counter electrode (CE) and reference electrode (RE), respectively. All the potentials in this study are specified relative to the reference electrode. Electrodeposition was conducted on an Au substrate and a Cu sheet as the working electrode (WE). The Au substrate was a thin film (250 nm in thickness) prepared on a Si wafer by electron-beam deposition. Before using the Au substrate, it was ultrasonically cleaned with acetone and water. When the Cu sheet was used, it was cleaned by immersion in 15 wt% HNO₃ solution. Since the conductivity of the mixture solution is low compared to conventional aqueous baths, it is important to enhance the conductivity as much as possible. In the present case, the electrodeposition was carried out at a constant temperature of ~50 °C to increase the conductivity but to avoid the evaporation of water. Thanks to the enhancement of the conductivity, the concentration of current density at a certain position was suppressed, and the uniform current distribution resulted in the uniform composition of the CrCoNi MEA with less variability. During electrodeposition, electrolytic solutions were mixed at ~50 °C and 200 rpm using a hotplate–stirrer. The electrochemical cell was gently covered so that the decrease of water at the elevated temperature was avoided. Before or during the electrodeposition, the purge using N₂ or Ar gas was not performed. After the deposition, the sample was rinsed with ethanol, followed by water.

Hard Cr coating as a comparative object was fabricated by electrodeposition from an aqueous solution containing 250 g L⁻¹ of H₂CrO₄, 2.5 g L⁻¹ of H₂SO₄, 3 g L⁻¹ of Cr(III) ion, and 20 mL L⁻¹ of Cr electroplating additive (Top Hard Chrome HE-2, Okuno Chemical

Industries) onto an Fe sheet at 55 °C at a current density of 45 A dm⁻² for 15 min.

Corrosion tests were carried out after deaeration by Ar bubbling and open-circuit potential (OCP) measurement for 1 h. Polarization was started from an initial potential of -0.25 V *vs.* OCP to a final potential of 1.5 V *vs.* OCP. When the current density reached a value of 5 mA cm⁻² before the potential of 1.5 V *vs.* OCP was reached, the scan direction was reversed. Back scans were carried out to a potential of -0.25 V *vs.* OCP. The scan rate was 1 mV s⁻¹. Corrosion tests for CrCoNi samples were performed after electrochemical polishing at 30 V for 10 s using a mixture of ethanol 90 vol% and aqueous HClO₄ solution 10 vol% as the electrolytic solution. Electroplated hard Cr was cleaned by immersion in 0.1 M HCl solution.

Diffusion coefficients of metal ions were obtained by electrochemical measurements. Cathodic linear sweep voltammetry was performed using rotating disc electrode of Pt (diameter 5 mm) at 10 mV s⁻¹. In the electrochemistry of rotating disc electrodes, it is well known that the diffusion-limited current density $|i_L|$ is proportional to the square root of the angular velocity $\omega^{1/2}$ in accordance with the Levich equation^[65]:

$$|i_L| = 0.62zFcD^{2/3}\nu^{-1/6}\omega^{1/2} \quad (\text{Eq. 4.1})$$

with z being the number of electrons involved in the reaction, F being the Faraday constant, c being the bulk concentration of reactant, D being the diffusion coefficient, and ν being the kinematic viscosity. The diffusion-limited current density was measured by changing the rotating rate of the electrode to 100, 250, 500, 750, and 1000 rpm.

4.4.4. Characterization

Samples were characterized using scanning electron microscopy (SEM, Hitachi High Technologies TM4000Plus) in conjunction with energy-dispersive X-ray spectroscopy (EDS), field-emission transmission electron microscopy (TEM, JEOL JEM-2100F) in conjunction with EDS and bright/annular dark-field scanning TEM (STEM) detectors, X-ray diffraction (XRD, PANalytical, X'Pert PRO Alpha-1 with a Cu K α source ($\lambda = 0.1542$ nm)), and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, PHI VersaProbe4). To determine the average compositions of samples, SEM–EDS measurements were performed at five points separated by more than 1 mm, unless otherwise stated. Although the EDS analysis is semi-quantitative, it gives reliable data for the comparison among 3d-transition metals. On the contrary, the composition analyzed by XPS is not quantitative; therefore, the compositions reported in this study were obtained by EDS. Note that the spatial resolution of the surface analyses is not high enough to discuss the short-range order of alloying elements. The mixing entropy ΔS was calculated using the following equation: $\Delta S = -R\sum_i(x_i \ln x_i)$, with x_i being the molar ratio of component i . Note that the top and bottom of the STEM images correspond to the directions of the top surface of the deposit and the interface between the deposit and the substrate, respectively. The depth profile of the EDS was acquired by adding up the intensities of each pixel along the horizontal direction, meaning that the depth profiles were obtained from the whole areas of the images. Samples for TEM observation were prepared using a focused ion beam (FIB, Quanta 200 3DS). The SAED patterns were obtained from a sufficiently large area compared to the grain size. XPS was carried out after Ar etching to remove the surface oxide layer. A sheet of CrCoNi with equiatomic ratios (and an oxygen ratio less than 1%) was used as a reference of the metallic state for fitting. This CrCoNi sample was fabricated by the following steps. A 30 g CrCoNi

ingot was fabricated by vacuum arc-melting of pure Cr, Co, and Ni with a purity of 99.9 wt.%. Afterwards, the ingot was subjected to a homogenization treatment at 1200 °C for 24 h, followed by water quenching to eliminate elemental segregation that occurred during the casting process. The homogenized material was then cold rolled with 90% reduction in thickness (final thickness of 1.0 mm). Measurements of hardness and elastic modulus were carried out using a nanoindenter (Bruker, TI950 TriboIndenter) equipped with the Berkovich tip. Measurements were conducted at 100 points for each sample, with the maximum load varied from 2000 to 6000 μN . The holding time at maximum load was 2 s. The loading and unloading rates were determined such that the load would reach the preset values in 5 s. The hardness and reduced elastic modulus values were obtained by fitting nanoindentation load–displacement curves with the Oliver–Pharr model^[66]. Reduced elastic modulus E_r is defined by Eq. 4.2:

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s} \quad (\text{Eq. 4.2})$$

where E_i is the elastic modulus of the indenter, ν_i is the Poisson's ratio of the indenter, E_s is the elastic modulus of the sample, and ν_s is the Poisson's ratio of the sample. All the nanoindentation measurements were performed after surface smoothing by electrochemical polishing at 30 V for 15–30 s using a mixture of ethanol 90 vol.% and aqueous HClO_4 solution 10 vol.% as the electrolytic solution.

4.4.5. MD simulation

Classical MD simulations were performed using the GROMACS-2023 software^[67]. The selection of appropriate force fields is critical for obtaining the accurate solution structure of ionic liquids by MD simulations. We adopted the well-known and well-reliable force field: an all-atom nonpolarizable force field reported by Canongia Lopes and Pádua^[68] being chosen to model the imidazolium-based ionic liquid and

the extended simple point charge (SPC/E) model^[69] being applied for water molecules. The number of molecules in simulation boxes for the mixtures was determined such that the total number of atoms would be $\sim 100,000$. The number of molecules and the length of cubic boxes obtained after canonical ensemble (NVT) and isothermal–isobaric ensemble (NPT) equilibration are summarized in Table 4.S11 (Supporting Information). The results indicate that the box sizes of the three mixture solutions are nearly equivalent. The van der Waals (VdW) interactions were represented by the 12–6 Lennard–Jones potential, and the parameters for the metal ions referred to the values of the ion–oxygen distance (IOD) parameter sets reported by Merz et al.^[70,71]. The parameters used in the present study are summarized in Tables 4.S13–4.16 (Supporting Information). The cutoff distance of the Lennard–Jones and Coulomb was set to 12 Å. The electrostatic interaction was calculated by applying the smooth particle mesh ewald (SPME) method^[72]. The velocity Verlet method was used to calculate the equations of motion. The relative dielectric constant was set to 1. The time step was set to 1 fs for all of the simulations. It is commonly known that machine learning potentials are more accurate in simulating the structure of solid crystals. On the other hand, the number of the configurations of chemicals in a liquid state is huge. Therefore, the same quality of calculation is not possible with the state-of-the-art modeling technique of liquids. Because of such a background, MD simulations of ionic liquids as well as liquid water using Lennard-Jones potentials are still often conducted^[73–77]. In fact, from the historical viewpoint, MD simulations using Lennard-Jones potentials have predicted the emergence of mesoscale phase separations of ionic liquids^[74,75], and the emergence of phase separations has been supported by experimental SAXS measurements^[56,78]. In addition, both machine learning potentials and ab initio calculations of liquid water remain topics of ongoing scientific discussion, and no universally

accurate or definitive model currently exists for liquid water^[79]; therefore, for the systems in this study, using the machine-learning potential of liquid water instead of the Lennard-Jones potential may not be advantageous in terms of accuracy. Moreover, it is well-known that empirical potentials, which have been optimized over a long history, have remarkably succeeded in accurately capturing the properties of water when the purpose of the calculation is not related to chemical reactions or the dissociation of water into protons and hydroxide ions^[80]. In the present study, it is important to simulate whether the mesoscale phase separation of the mixture solution occurs or not. This is because the phase-separated solutions simply play roles as the diffusion field that enables the discontinuous supply of metal cations which is essential for the electrodeposition of the CrCoNi MEA. Thus, we believe that the results of SAXS together with the MD simulation using Lennard-Jones potentials support our proposed mechanism of successful electroplating.

The initial configuration for the MD simulation is shown in Figure 4.S19 (Supporting Information). This configuration is set so that the molecules are randomly distributed using PACKMOL^[81] and fftool^[82] in a sufficiently large box. Thus, the nonpolar groups are uniformly distributed and do not form aggregates. First, the mixtures were energy minimized using the steepest descent method^[83] and then equilibrated under NVT conditions for 2 ns at 423 K by the V-rescale thermostat^[84]. Next, the systems were equilibrated under NPT conditions for 4 ns at 423 K by the V-rescale thermostat and the C-rescale barostat^[85] regulated the constant pressure at 1 bar. Second, the following NPT equilibration for 4 ns at 343 K was carried out using Nosé–Hoover thermostat^[86] and C-rescale barostat. After confirming that the energy, density, pressure, and temperature reached equilibrium, we ran the production simulation for 20 ns under NVT conditions by using Nosé–Hoover thermostat. The trajectories were saved every 20 ps. The MD snapshot was created using Visual Molecular Dynamics (VMD)^[87]. To

evaluate the mesoscopic phase separation of mixtures quantitatively, we carried out domain analysis using the Travis software^[88,89]. The values of the isoperimetric quotient Q as an indicator of the shape of domains were obtained in Eq. 4.3, which takes values between 0 and 1.

$$Q = \left\{ \frac{r_{\text{sphere}}(V)}{r_{\text{sphere}}(A)} \right\}^6 \quad (\text{Eq. 4.3})$$

The values of $r_{\text{sphere}}(V)$ and $r_{\text{sphere}}(A)$ were the radius calculated assuming a spherical shape with the volume and area obtained from the domain analysis.

To ensure that the conditions of the MD simulation accurately replicate the experimental setup, it is crucial to confirm that the concentration of each chemical species in the experimental mixture solution matches that in the MD simulation box after equilibration. The concentration of each chemical species is summarized in Table S17 (Supporting Information). The experimental concentrations were calculated using the density measured from the experiment and the molar ratio used during solution preparation. The concentrations in the MD simulations were determined from the number of molecules in the simulation boxes and their volume. As described above, proton dissociation cannot be calculated in classical MD simulations; therefore, hydrochloric acid and boric acid were excluded from the calculations. A comparison of these concentrations shows that the discrepancy is within 3%, indicating that the MD simulation effectively models the experimental system.

4.4.6. Small-angle X-ray scattering (SAXS) measurements

The electrolytic solutions mixing $C_n\text{minCl}$ ($n = 2, 4$, and 6), H_2O , and HCl in $6 : 45 : 0.06$ molar ratio were used for SAXS measurements. The measurements were carried out on a NANO-Viewer (Rigaku) equipped with a HyPix-6000C silicon pixel detector and an X-ray source at a wavelength of 0.1542 nm ($\text{CuK}\alpha$). The sample-to-detector

distance was set to be 0.3 m and calibrated using the Bragg diffraction pattern of silver behenate. The position of the incident X-ray beam on the detector was also determined by the Bragg diffraction pattern. A 1 mm thickness aluminum cell with quartz windows was used as the solution holder for the measurements. The scattering intensities for the sample solutions, pure water, and the blank cell were recorded by the detector stopping the direct beam with a beam stopper. For each two-dimensional scattering intensity data, a circular-average procedure was employed to obtain the scattering intensity $I^{(\text{det})}(q)$ as a function of the magnitude q of the scattering vector. The direct beam intensities $I^{(\text{direct})}$ were measured for each sample by the detector without the beam stopper and with an attenuator. The scattering intensity $I(q)$ in absolute scale for each sample was determined by the following equation:

$$I(q) = \phi \left[\frac{I^{(\text{det})}(q) - I_{\text{dark}}^{(\text{det})}}{I^{(\text{direct})}} - \frac{I_{\text{blank}}^{(\text{det})}(q) - I_{\text{dark}}^{(\text{det})}}{I_{\text{blank}}^{(\text{direct})}} \right] \quad (\text{Eq. 4.4})$$

where the subscript “blank” represents the values for the blank cell, $I_{\text{dark}}^{(\text{det})}$ is the dark intensity recorded without X-rays, and ϕ is an apparatus constant, of which value was determined from the scattering data and the absolute scattering intensity of pure water at 25 °C [$I(0) = 1.643 \times 10^{-2} \text{ cm}^{-1}$, calculated from the density^[90] and isothermal compressibility^[91]. Note that the Eq. (4.4) includes the correction for the incident X-ray intensity and the transmittance of the sample solutions and the subtraction of parasitic scattering.

For the comparison of experimental and simulated X-ray scattering profiles, structure factors were calculated from 100 snapshots of the production simulations using trAVIS software^[88,89]. The structure factor $S(q)$ is expressed as follows^[92]:

$$S(q) = \frac{\sum_{i=1}^N \sum_{j=1}^N x_i x_j f_i(q) f_j(q) H_{ij}(q)}{\{\sum_{i=1}^N x_i f_i(q)\}^2} \quad (\text{Eq. 4.5})$$

with the indices i and j being the atom types, the number of which is from 1 to N . x_i is the molar ratio of the atom type i , and $f_i(q)$ is the atomic scattering factor of the atom i , the value of which was obtained from a reference paper^[93,94]. Note that $H_{ij}(q)$ is the partial structure factor.

$$H_{ij}(q) = 4\pi\rho_0 \int_0^{r_{\max}} r^2 (g_{ij}(r) - 1) \frac{\sin(qr)}{qr} dr \quad (\text{Eq. 4.6})$$

with r being the distance between the atoms. $g_{ij}(r)$ expresses the radial distribution functions of atom types i and j . ρ_0 and $r_{\max}$ respectively stand for the number density of the atoms and the maximum sampling distance. $r_{\max}$ was set as half of the box length.

The structure factor was extracted from the experimental SAXS profiles according to the following equation^[95,96]:

$$S(q) = \frac{\frac{I(q)}{a_e^2 \rho_0} - \sum_{i=1}^N x_i f_i^2(q)}{\{\sum_{i=1}^N x_i f_i(q)\}^2} \quad (\text{Eq. 4.7})$$

with $I(q)$ being the intensity from the experimental SAXS, and a_e being the classical radius of the electron, $a_e = 2.818 \times 10^{-13}$ cm.

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4.5. Supporting Information

Table 4.S1. Appearance of deposits obtained from C₄mimCl mixtures with HCl ratios of 0, 0.06, 0.30, and 0.60 at applied potentials of –1.1 V to –1.6 V in 100 mV increments.

Applied potential	HCl ratio			
	0	0.06	0.30	0.60
–1.1 V	metallic luster	passivation	matte	exfoliated
–1.2 V	metallic luster	metallic luster	matte	matte
–1.3 V	passivation	metallic luster	metallic luster	exfoliated
–1.4 V	matte & black	black	metallic luster	exfoliated
–1.5 V	black	black	black	metallic luster
–1.6 V	black	black	black	matte

Table 4.S2. Composition at the two areas marked by * and ** in Figure 1d, as determined by SEM–EDS. The sample was deposited at –1.2 V from a C₄mimCl mixture with a HCl ratio of 0.60.

Area	Composition (at.%)			
	Cr	Co	Ni	O
dark area (*)	27	9	10	54
bright area (**)	36	16	12	36

Table 4.S3. Composition at the three rectangular areas indicated in Figure 1j, as determined by STEM–EDS. The sample was deposited at –1.3 V from a C₄mimCl mixture with a HCl ratio of 0.06, without post-deposition annealing.

Area number	Composition (at.%)		
	Cr	Co	Ni
1	39	40	21
2	37	42	21
3	43	36	21

Table 4.S4. Composition at the two rectangular areas and two spots in Figure 2e, determined by STEM–EDS. The sample was deposited at –1.3 V from a C₄mimCl mixture with a HCl ratio of 0.06 and subsequently annealed at 400 °C.

Area number	Composition (at.%)				
	Cr	Co	Ni	O	Cl
1	27	42	22	9	0
2	26	41	25	8	0
3	39	27	17	14	3
4	36	30	15	17	2

Table 4.S5. Results of this work and previous studies that measured the hardness of the CrCoNi MEAs prepared by methods other than electrodeposition.

Sample	Method	Hardness (converted value)	Microstruc ture	Grain size	Ref.
as-deposited CrCoNi	electrodeposition	6.2 GPa	FCC	< 10 nm	this work
CrCoNi annealed at 550 °C for 30 min	electrodeposition	13.3 GPa	FCC+HCP	~20 nm	this work
CrCoNi	laser clading	265.3 HV (~2.8 GPa)	FCC	19.3 µm	[1]
CrCoNi-TiC	laser clading	315.9 HV (~3.3 GPa)	FCC+TiC	8.7 µm	[1]
CrCoNi-SiC	laser clading	321.8 HV (~3.4 GPa)	FCC+SiC	6.6 µm	[1]
CrCoNiTi	laser clading	762 HV (~8.1 GPa)	BCC + Cr ₂ Ti (Laves phase)	4.8 µm	[2]
CrCoNi	arc melting	340 HV (~3.6 GPa)	FCC	1.0 µm	[3]

Table 4.S6. Hardness and elastic modulus of other MEAs and HEAs produced using electrodeposition together with our present result.

Sample	Annealing	Hardness	Elastic modulus	H / E ratio	Microstructure	Ref.
CrCoNi	without	6.2 GPa	116 GPa	0.053	FCC	this work
CrCoNi	550 °C, 30 min	13.3 GPa	184 GPa	0.072	FCC+HCP	this work
FeCoNi	without	4.8 GPa	135 GPa	0.036	FCC	[4]
FeCoNi	300 °C, 1 h	5.5 GPa	140 GPa	0.039	FCC	[4]
CrFeNi	without	5.4 GPa	100 GPa	0.054	amorphous	[4]
CrFeNi	550 °C, 1 h	8.5 GPa	135 GPa	0.063	FCC+Cr ₂ O ₃ + α -Cr	[4]
FeCoNiMo	without	5.3 GPa	126 GPa	0.042	amorphous	[5]
FeCoNiW	without	5.3 GPa	113 GPa	0.047	amorphous	[5]
FeCoNiMo W	without	4.6 GPa	103 GPa	0.045	amorphous	[5]

Table 4.S7. Corrosion potential (E_{corr}) and corrosion current density (i_{corr}), as determined from the results of the corrosion tests using 0.1 M NaCl aqueous solution (Figure 3b).

Deposited material	$E_{\text{corr}} / \text{V}$	$i_{\text{corr}} / \text{A cm}^{-2}$
as-deposited CrCoNi	−0.45	4.40×10^{-6}
CrCoNi annealed at 400 °C	−0.16	1.87×10^{-5}
CrCoNi annealed at 550 °C	−0.15	2.02×10^{-5}
hard Cr coating	−0.61	1.38×10^{-6}

Table 4.S8. Appearance of deposits obtained from a C₂mimCl mixture, C₄mimCl mixture, and a C₆mimCl mixture with an HCl ratio of 0.06.

Applied potential	Ionic liquid component		
	C ₂ mimCl	C ₄ mimCl	C ₆ mimCl
−1.2 V	matte	metallic luster	metallic luster
−1.3 V	matte	metallic luster	metallic luster
−1.4 V	matte	black	black

Table 4.S9. Average composition of deposits obtained from a C₂mimCl mixture and a C₆mimCl mixture with a HCl ratio of 0.06, as determined by SEM–EDS. The result for the sample deposited from C₂mimCl mixture at –1.2 V is the averaged composition at three measurements.

Ionic liquid, applied potential	Composition (at.%)		
	Cr	Co	Ni
C ₂ mimCl, –1.2 V	16±7	68±5	16±3
C ₂ mimCl, –1.3 V	1±1	71±4	28±4
C ₂ mimCl, –1.4 V	35±5	52±6	13±1
C ₆ mimCl, –1.2 V	39±8	34±12	27±5
C ₆ mimCl, –1.3 V	37±6	39±6	24±5
C ₆ mimCl, –1.4 V	64±10	13±8	23±3

Table 4.S10. Domain counts, average volume of one domain, and values of isoperimetric quotient Q of the average, minimum, and maximum determined by domain analysis using production MD simulations of $C_n\text{mimCl}$ ($n = 2, 4, 6$) mixtures, each starting from five randomly generated initial configurations. Values are presented as mean $\pm$ standard deviation. We do not consider average volume per domain for the polar domains, since the size of the continuous polar domains is larger than the volume of the simulation box.

	Domain counts	Average volume per domain / $\text{\AA}^3$	Isoperimetric quotient		
			Minimum	Average	Maximum
$C_2\text{mimCl}$					
polar domain	1 $\pm$ 0	—	0.1963 ± 0.0007	0.1963 ± 0.0007	0.1963 ± 0.0007
$C_2\text{mimCl}$					
nonpolar domain	1202 ± 21	76.8 $\pm$ 1.4	0.250 ± 0.021	0.6618 ± 0.0031	0.8273 ± 0.0070
$C_4\text{mimCl}$					
polar domain	1.006 ± 0.079	—	0.0660 ± 0.0002	0.068 ± 0.020	0.069 ± 0.040
$C_4\text{mimCl}$					
nonpolar domain	436 ± 20	479 $\pm$ 22	0.0187 ± 0.0005	0.6710 ± 0.0079	0.8323 ± 0.0072
$C_6\text{mimCl}$					
polar domain	1.12 ± 0.35	—	0.0485 ± 0.0003	0.080 ± 0.090	0.11 ± 0.18
$C_6\text{mimCl}$					
nonpolar domain	150 ± 12	2010 $\pm$ 160	0.0195 ± 0.0002	0.5522 ± 0.0060	0.635 ± 0.015

Table 4.S11. Number of molecules/ions and length of MD simulation boxes containing ionic liquids with different alkyl lengths, metal salts, water molecules, and chloride ions after NVT and NPT equilibration processes. Systems containing metal salts were used to investigate the structure of solutions employed for alloy electrodeposition, while systems without metal salts were used to compare with experimental SAXS measurement results.

	Ionic liquid cation	Number of molecules/ions					Box length /nm
		Cr ³⁺	Co ²⁺	Ni ²⁺	H ₂ O	Cl ⁻	
C ₂ mimCl– CrCoNi	2262	377	377	377	16965	4901	10.472
C ₄ mimCl– CrCoNi	1992	322	322	322	14940	4316	10.404
C ₆ mimCl– CrCoNi	1776	296	296	296	13320	3848	10.369
C ₂ mimCl without metal salts	2352	–	–	–	17640	2352	10.154
C ₄ mimCl without metal salts	2058	–	–	–	15435	2058	10.094
C ₆ mimCl without metal salts	1830	–	–	–	13725	1830	10.070
single aqueous solution	–	322	322	322	14940	2324	8.141

Table 4.S12. Density, viscosity, slope of Levich plot and calculated diffusion coefficient of Cu(II) ion in C₂mimCl mixture, C₄mimCl mixture, C₆mimCl mixture, and aqueous solution without ionic liquid.

Solution	Viscosity / mPa s	Density / g cm ⁻³	Slope of Levich plot	Diffusion coefficient of Cu(II) ion / cm ² s ⁻¹
C ₂ mimCl mixture	4.59	1.084	0.0846	2.16×10^{-6}
C ₄ mimCl mixture	6.89	1.062	0.0630	1.54×10^{-6}
C ₆ mimCl mixture	11.46	1.037	0.0447	1.05×10^{-6}
Aqueous solution	1.11	1.008	0.2513	7.89×10^{-6}

Table 4.S13. Nonbonded force field parameters of ionic liquid C₂mimCl. The van der Waals potential is described by the Lennard–Jones potential, $4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}$. The numbers indicating each atom are referred to as those shown in the molecular structure shown below.

Atom	Atom type	Mass / u	Charge / e	Sigma / Å	Epsilon / kJ mol ⁻¹
N1	NA	14.007	0.15	0.325	0.71128
C1	CR	12.011	-0.11	0.355	0.29288
N2	NA	14.007	0.15	0.325	0.71128
C2	CW	12.011	-0.13	0.355	0.29288
C3	CW	12.011	-0.13	0.355	0.29288
C4	C1	12.011	-0.17	0.35	0.27614
H1	HCR	1.008	0.21	0.242	0.12552
C5	C1A	12.011	-0.17	0.35	0.27614
H2	HCW	1.008	0.21	0.242	0.12552
H3	HCW	1.008	0.21	0.242	0.12552
H4	H1	1.008	0.13	0.25	0.12552
H5	H1	1.008	0.13	0.25	0.12552
H6	H1	1.008	0.13	0.25	0.12552
C6	CE	12.011	-0.05	0.35	0.27614
H7	H1	1.008	0.13	0.25	0.12552
H8	H1	1.008	0.13	0.25	0.12552
H9	HC	1.008	0.06	0.25	0.12552
H10	HC	1.008	0.06	0.25	0.12552
H11	HC	1.008	0.06	0.25	0.12552

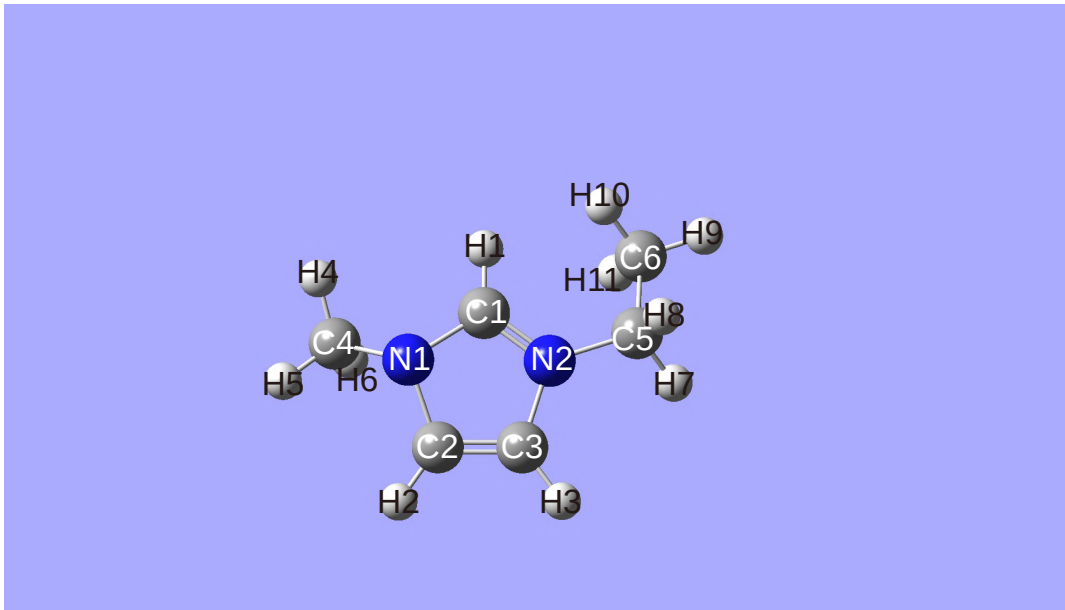


Table 4.S14. Nonbonded force field parameters of ionic liquids C₄mimCl. The van der Waals potential is described by the Lennard–Jones potential, $4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}$. The numbers indicating each atom are referred to as those shown in the molecular structure shown below.

Atom	Atom type	Mass / u	Charge / e	Sigma / Å	Epsilon / kJ mol ⁻¹
N1	NA	14.007	0.15	0.325	0.71128
C1	CR	12.011	−0.11	0.355	0.29288
N2	NA	14.007	0.15	0.325	0.71128
C2	CW	12.011	−0.13	0.355	0.29288
C3	CW	12.011	−0.13	0.355	0.29288
C4	C1	12.011	−0.17	0.35	0.27614
H1	HCR	1.008	0.21	0.242	0.12552
C5	C1A	12.011	−0.17	0.35	0.27614
H2	HCW	1.008	0.21	0.242	0.12552
H3	HCW	1.008	0.21	0.242	0.12552
H4	H1	1.008	0.13	0.25	0.12552
H5	H1	1.008	0.13	0.25	0.12552
H6	H1	1.008	0.13	0.25	0.12552
C6	C2	12.011	0.01	0.35	0.27614
H7	H1	1.008	0.13	0.25	0.12552
H8	H1	1.008	0.13	0.25	0.12552
C7	CS	12.011	−0.12	0.35	0.27614
H9	HC	1.008	0.06	0.25	0.12552
H10	HC	1.008	0.06	0.25	0.12552
C8	CT	12.011	−0.18	0.35	0.27614
H11	HC	1.008	0.06	0.25	0.12552
H12	HC	1.008	0.06	0.25	0.12552
H13	HC	1.008	0.06	0.25	0.12552
H14	HC	1.008	0.06	0.25	0.12552

H15	HC	1.008	0.06	0.25	0.12552
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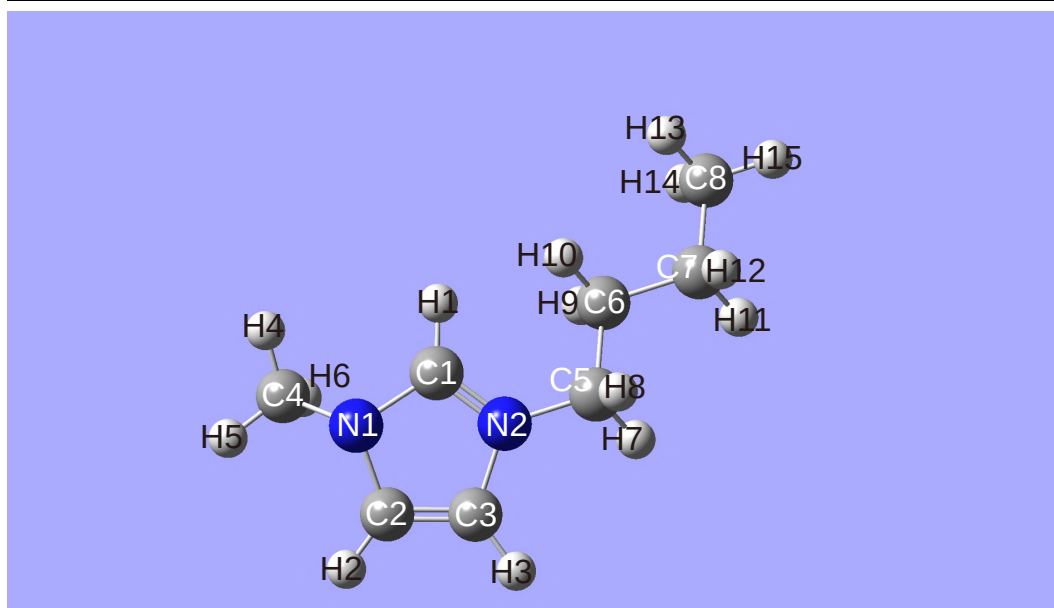


Table 4.S15. Nonbonded force field parameters of ionic liquid C₆mimCl. The van der Waals potential is described by the Lennard–Jones potential, $4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}$. The numbers indicating each atom are referred to as those shown in the molecular structure shown below.

Atom	Atom type	Mass / u	Charge / e	Sigma / Å	Epsilon / kJ mol ⁻¹
N1	NA	14.007	0.15	0.325	0.71128
C1	CR	12.011	−0.11	0.355	0.29288
N2	NA	14.007	0.15	0.325	0.71128
C2	CW	12.011	−0.13	0.355	0.29288
C3	CW	12.011	−0.13	0.355	0.29288
C4	C1	12.011	−0.17	0.35	0.27614
H1	HCR	1.008	0.21	0.242	0.12552
C5	C1A	12.011	−0.17	0.35	0.27614
H2	HCW	1.008	0.21	0.242	0.12552
H3	HCW	1.008	0.21	0.242	0.12552
H4	H1	1.008	0.13	0.25	0.12552
H5	H1	1.008	0.13	0.25	0.12552
H6	H1	1.008	0.13	0.25	0.12552
C6	C2	12.011	0.01	0.35	0.27614
H7	H1	1.008	0.13	0.25	0.12552

H8	H1	1.008	0.13	0.25	0.12552
C7	CS	12.011	−0.12	0.35	0.27614
H9	HC	1.008	0.06	0.25	0.12552
H10	HC	1.008	0.06	0.25	0.12552
C8	CS	12.011	−0.12	0.35	0.27614
H11	HC	1.008	0.06	0.25	0.12552
H12	HC	1.008	0.06	0.25	0.12552
C9	CS	12.011	−0.12	0.35	0.27614
H13	HC	1.008	0.06	0.25	0.12552
H14	HC	1.008	0.06	0.25	0.12552
C10	CT	12.011	−0.18	0.35	0.27614
H15	HC	1.008	0.06	0.25	0.12552
H16	HC	1.008	0.06	0.25	0.12552
H17	HC	1.008	0.06	0.25	0.12552
H18	HC	1.008	0.06	0.25	0.12552
H19	HC	1.008	0.06	0.25	0.12552

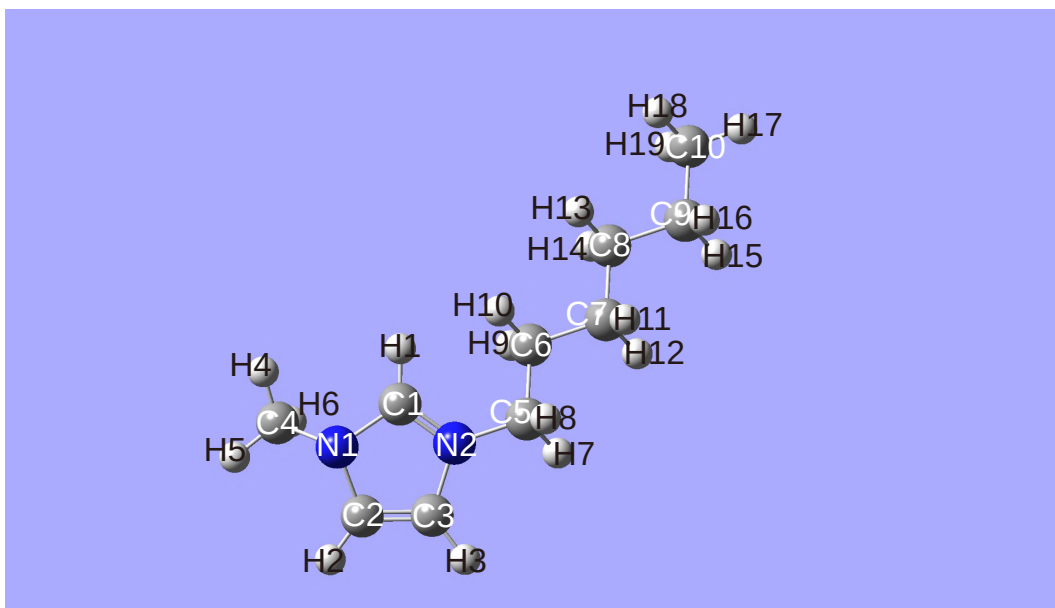


Table 4.S16. Nonbonded force field parameters of metal ions, chloride anion, and water molecule. The van der Waals potential is described by the Lennard–Jones potential, $4\varepsilon\{(\sigma/r)^{12} - (\sigma/r)^6\}$.

Atom	Atom type	Mass / u	Charge / e	Sigma / Å	Epsilon / kJ mol ⁻¹
Cr ³⁺	CRM	51.996	3	0.2393	0.0351
Co ²⁺	COM	58.933	2	0.25016	0.0685
Ni ²⁺	NIM	58.693	2	0.24464	0.0493
Cl ⁻	Cl	35.453	-1	0.441724	0.492833
Hw	Hw	1.008	0.4238	0	0
Ow	Ow	15.999	-0.8476	0.31655	0.6503

Table 4.S17. Comparison of concentration of each chemical species between the experimental mixture solution and the MD simulation box after equilibration. Experimental concentrations were calculated based on the measured density and the molar ratios during solution preparation, while the concentrations in the MD simulation were determined from the number of molecules in the simulation box and its volume. A comparison of these concentrations shows that the discrepancy is within 3%, indicating that the MD simulation effectively models the experimental system.

Concentration / mol·L ⁻¹							
	Ionic liquid	CrCl ₃	CoCl ₂	NiCl ₂	H ₂ O	HCl	H ₃ BO ₃
Experiment							
C ₂ mimCl–CrCoNi	3.33	0.56	0.56	0.56	25.00	0.03	1.11
C ₄ mimCl–CrCoNi	2.97	0.50	0.50	0.50	22.29	0.03	0.99
C ₆ mimCl–CrCoNi	2.69	0.45	0.45	0.45	20.18	0.03	0.90
C ₂ mimCl without metal salts	3.84	–	–	–	28.82	0.04	–
C ₄ mimCl without metal salts	3.42	–	–	–	25.68	0.03	–
C ₆ mimCl without metal salts	3.07	–	–	–	23.00	0.03	–
Simulation							
C ₂ mimCl–CrCoNi	3.27	0.55	0.55	0.55	24.53	–	–

C ₄ mimCl– CrCoNi	2.94	0.49	0.49	0.49	22.03	–	–
C ₆ mimCl– CrCoNi	2.65	0.44	0.44	0.44	19.84	–	–
C ₂ mimCl without metal salts	3.73	–	–	–	27.98	–	–
C ₄ mimCl without metal salts	3.32	–	–	–	24.92	–	–
C ₆ mimCl without metal salts	2.98	–	–	–	22.32	–	–

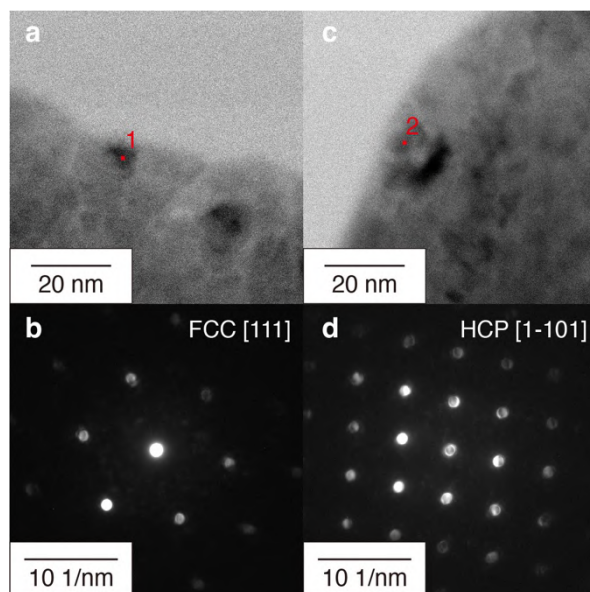


Figure 4.S1. (a, c) STEM-BF images of an as-deposited sample obtained at -1.3 V from the C_4mimCl mixture with HCl ratio of 0.06. (b, d) Nanobeam diffraction (NBD) patterns obtained at (b) point 1 and (d) point 2.

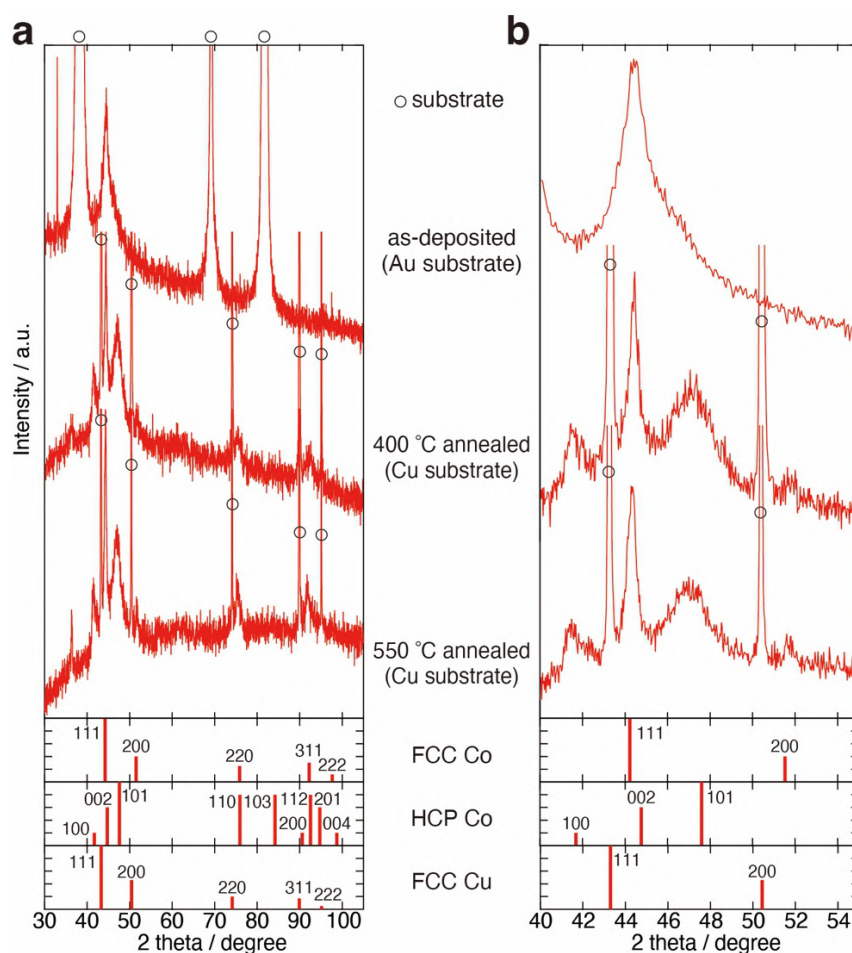


Figure 4.S2. XRD patterns of samples deposited at -1.3 V from a C_4mimCl mixture with a HCl ratio of 0.06 (top) without post-deposition annealing, (middle) with annealing at 400 °C for 30 min, and (bottom) with annealing at 550 °C for 30 min for (a) a wide angular range and (b) a narrow angular range. The as-deposited sample was obtained on a thin Au film prepared on a Si wafer. The annealed samples were deposited onto Cu sheets to avoid interdiffusion.

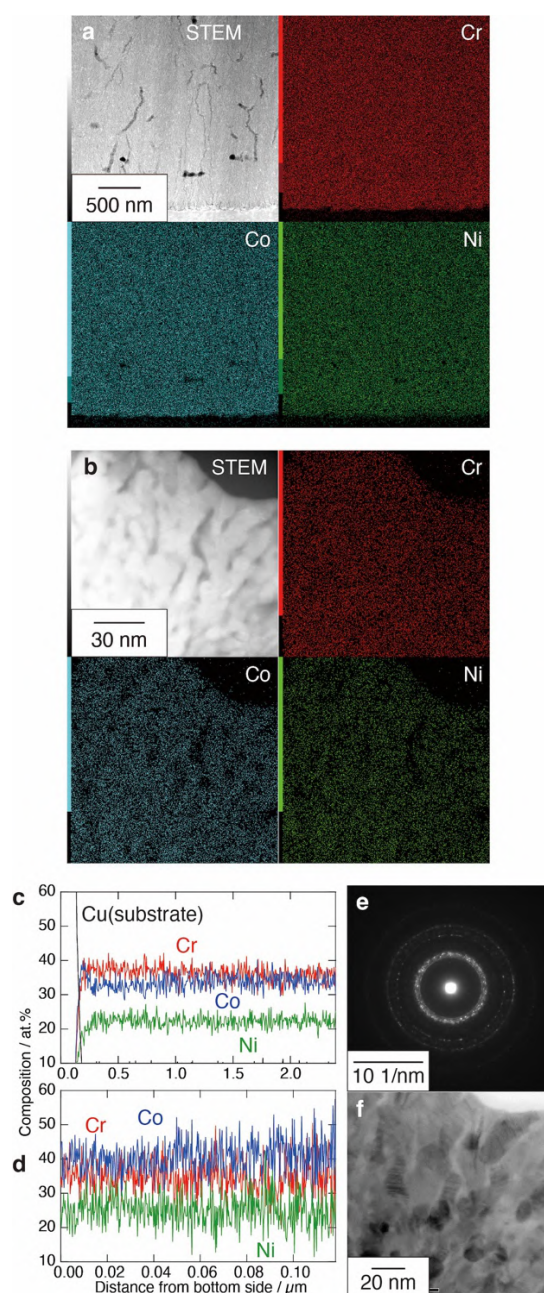


Figure 4.S3. (a, b) Cross-sectional STEM images at (a) low and (b) high magnification and the corresponding EDS mappings of Cr, Co, and Ni for a sample deposited at -1.3 V from the C_4mimCl mixture with a HCl ratio of 0.06 and annealed at 550 °C for 30 min under vacuum. (c, d) STEM–EDS depth profile of the sample annealed at 550 °C for 30 min at (c) low and (d) high magnifications. (e) Electron diffraction pattern. (f) STEM-BF image at higher magnification.

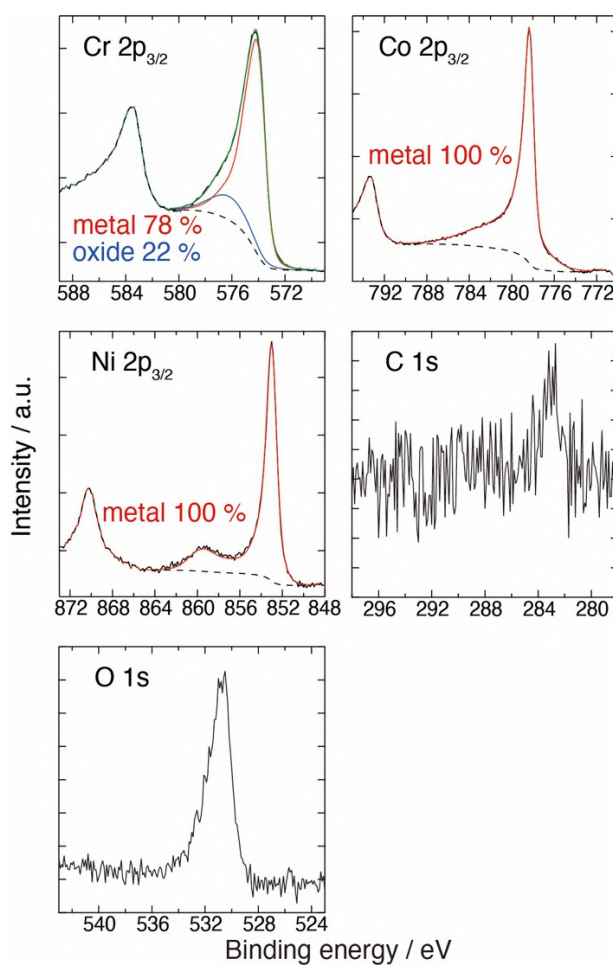


Figure 4.S4. XPS spectra of Cr 2p_{3/2}, Co 2p_{3/2}, Ni 2p_{3/2}, C 1s, and O 1s measured after 12 min of Ar etching of a CrCoNi MEA sample annealed at 550 °C. Black solid, red solid, blue solid, green solid, and black dotted curves in the spectra indicate the experimental data, fitted curves with bulk CrCoNi alloy as a reference for the metallic state, fitted curves with the oxidized states, the total of the fitted curves, and the background, respectively.

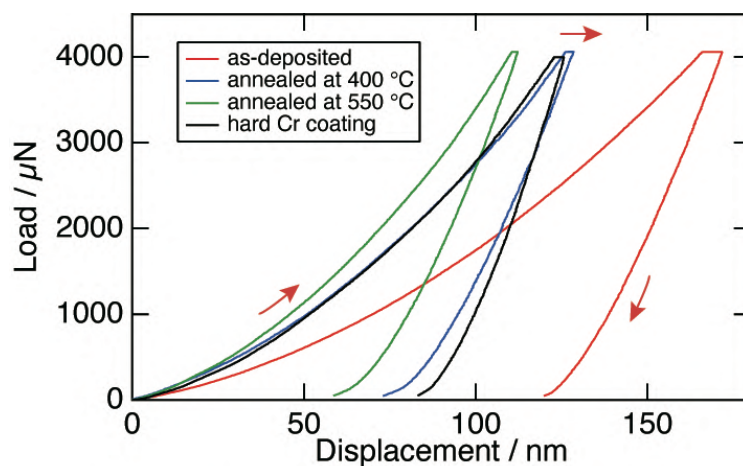


Figure 4.S5. Load–displacement curves obtained from nanoindentation tests for a sample of an as-deposited CrCoNi MEA prepared at -1.3 V using the C_4mimCl mixture with a HCl ratio of 0.06 and for samples deposited under the same conditions but with post-annealing for 30 min at 400 °C or 550 °C. The curve obtained for a hard Cr coating deposited from a Cr(VI) bath is shown for comparison.

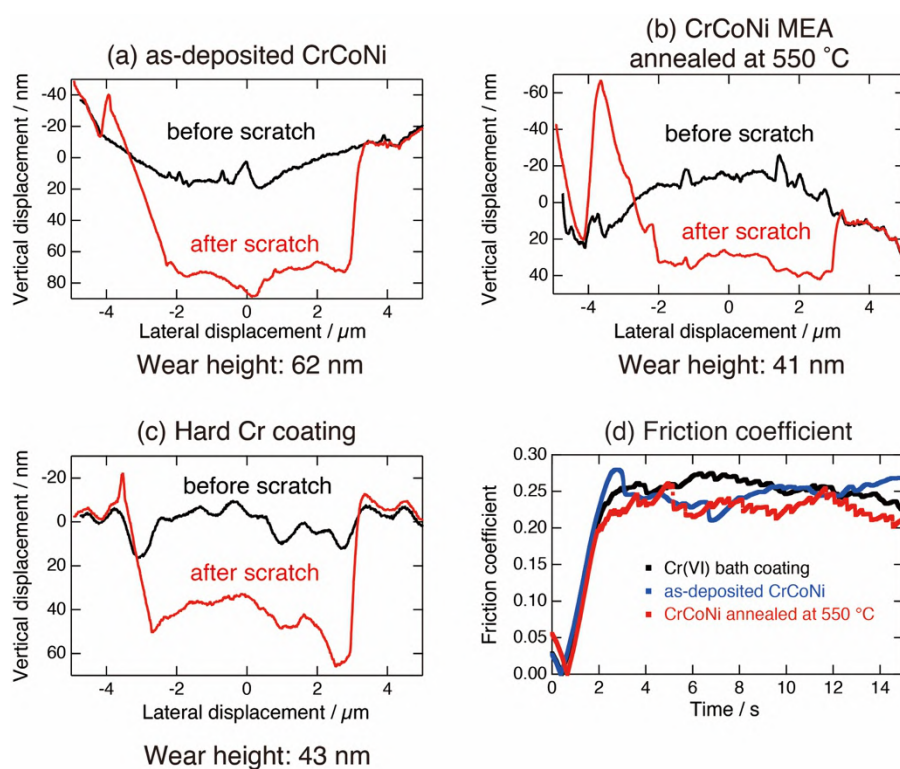


Figure 4.S6. (a-c) Scratch test results using the as-deposited CrCoNi MEA (a), the CrCoNi MEA film after annealing at 550°C (b), and a conventional hard chromium film (c). The scratch was performed within $\pm 3 \mu\text{m}$ of lateral displacement. Friction coefficients are also shown in (d).

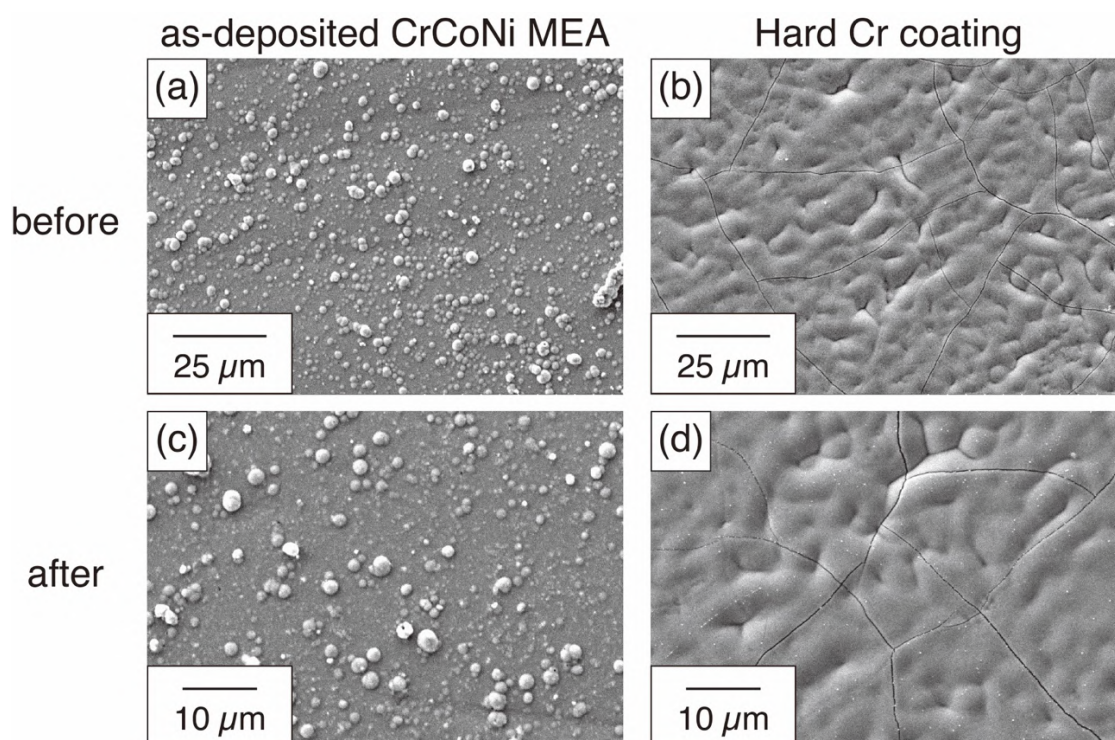


Figure 4.S7. Secondary electron images of surface of as-deposited CrCoNi MEA and hard Cr coating before and after corrosion test. Cracks are clearly observed on the surface of hard chromium coatings before and after the corrosion test, while such cracks are not observed on the surface of the CrCoNi MEA.

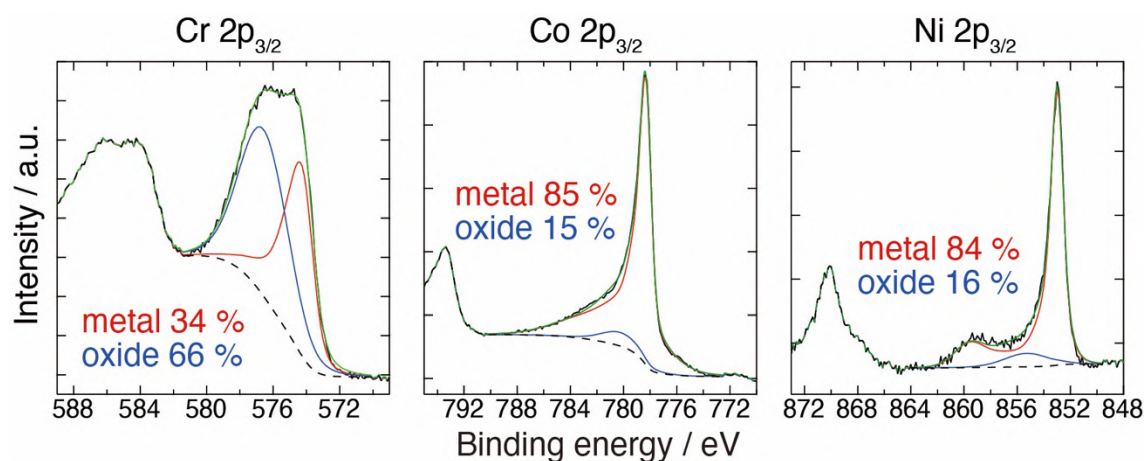


Figure 4.S8. XPS spectra of Cr $2p_{3/2}$, Co $2p_{3/2}$, and Ni $2p_{3/2}$ obtained after Ar etching for 12 min with the sample deposited at -1.4 V from the C₂mimCl mixture with a HCl ratio of 0.06. Black solid, red solid, blue solid, green solid, and black dotted curves in the spectra indicate the raw data, fitted curves with a bulk CrCoNi alloy as a reference for the metallic state, fitted curves with oxidized states, the total of fitted curves, and the background, respectively.

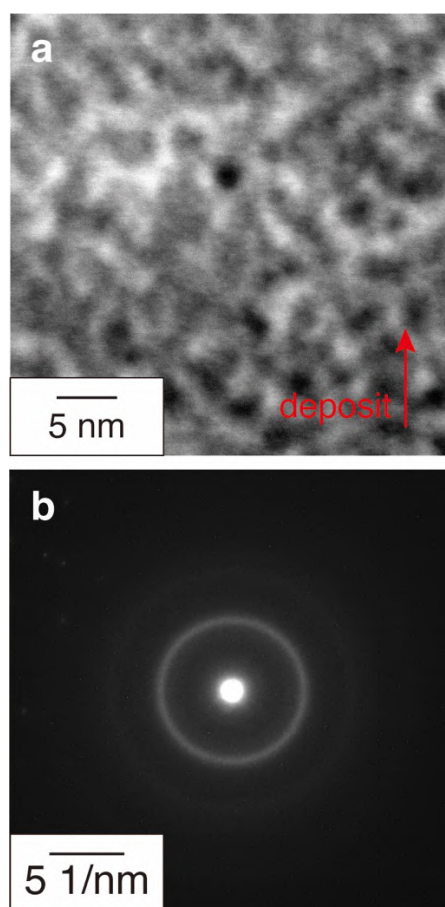


Figure 4.S9. (a, b) STEM-BF image of the sample shown in Figure 4b, together with the corresponding SAED pattern.

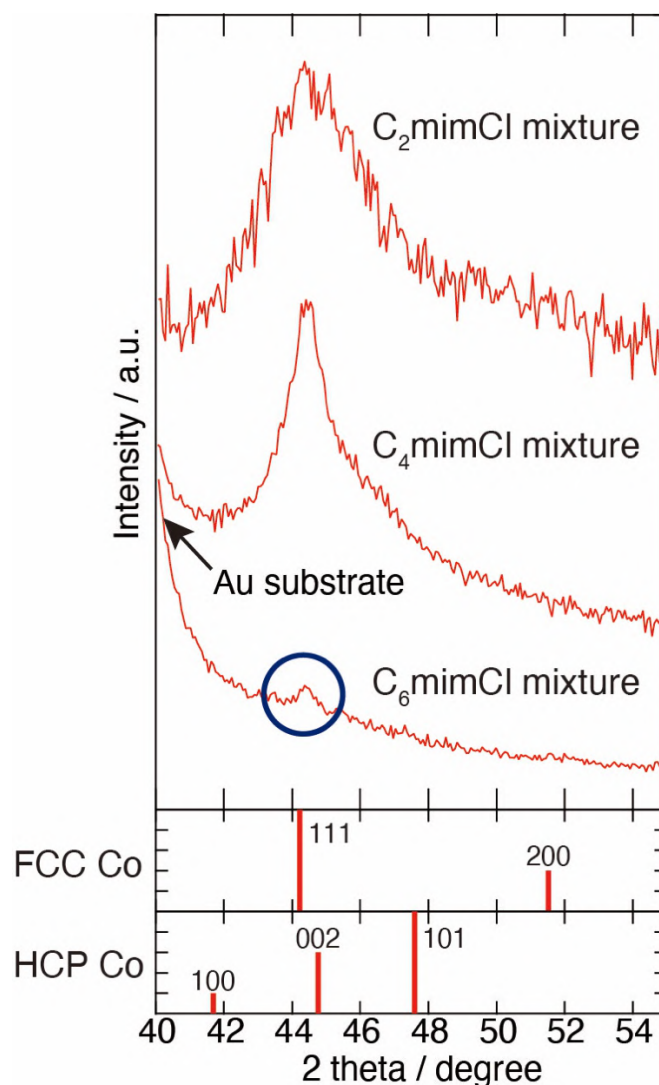


Figure 4.S10. XRD patterns of the as-deposited samples obtained from (top) the $C_2\text{mimCl}$ mixture with a HCl ratio of 0.06 at -1.4 V, (middle) the $C_4\text{mimCl}$ mixture with a HCl ratio of 0.06 at -1.3 V, and (bottom) the $C_6\text{mimCl}$ mixture with a HCl ratio of 0.06 at -1.3 V. All the samples were deposited onto a thin Au film prepared on a Si wafer. Diffraction attributable to the substrates occurs at degrees smaller than 40° and does not appear in the figure. For the bottom sample, diffraction attributed to the deposited film is highlighted by a circle.

C₂mimCl mixture

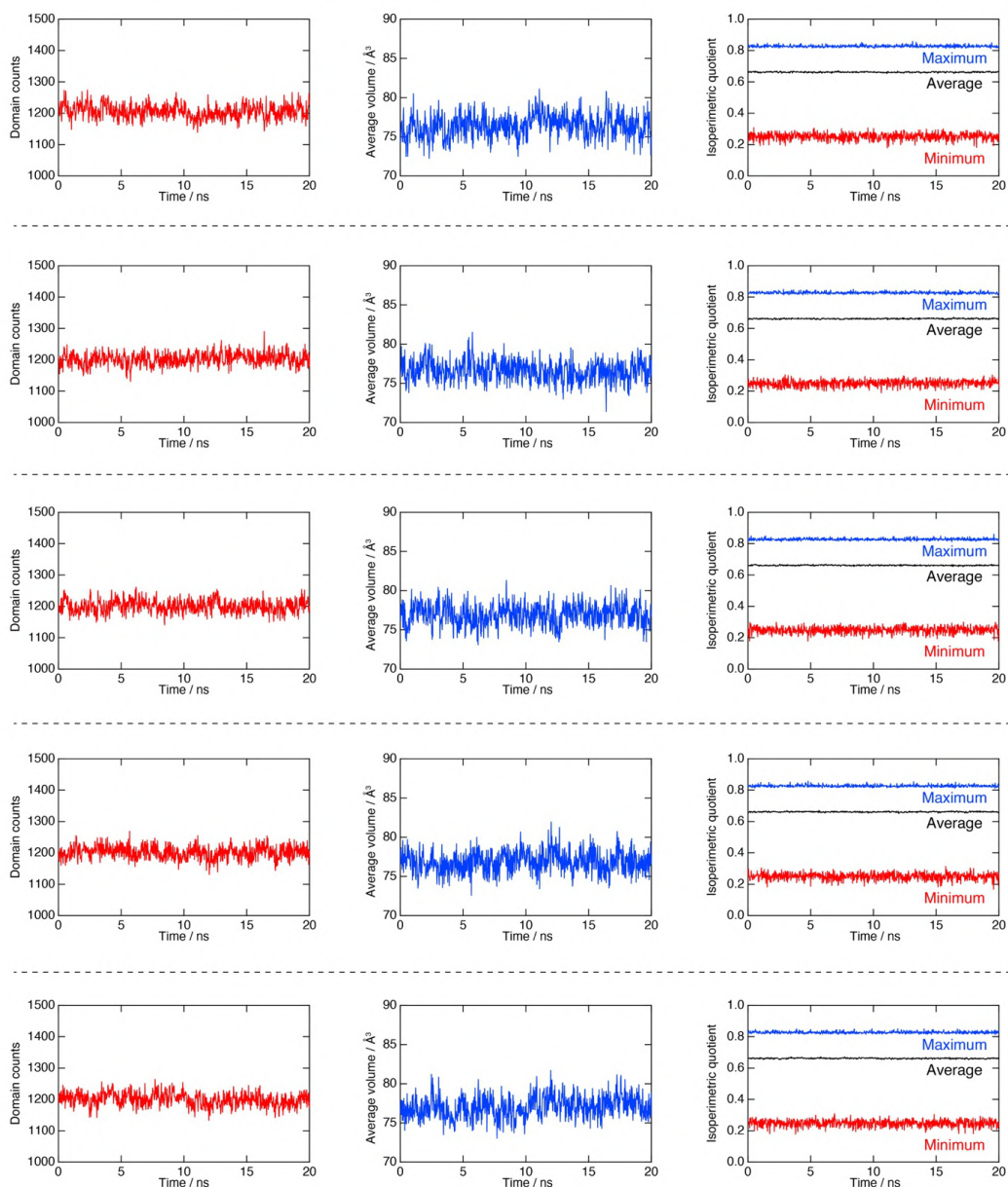


Figure 4.S11. Time evolution of domain counts, average volume of one domain, and values of isoperimetric quotient Q of the average, minimum, and maximum in five production MD simulations of C₂mimCl mixtures, each starting from a randomly generated initial configuration, based on the domain analyses of the nonpolar domain. The phase-separated structure serves as a diffusion field that enables the discontinuous supply of metal cations, making the analysis of the nonpolar domain more significant than that of the polar domain.

C₄mimCl mixture

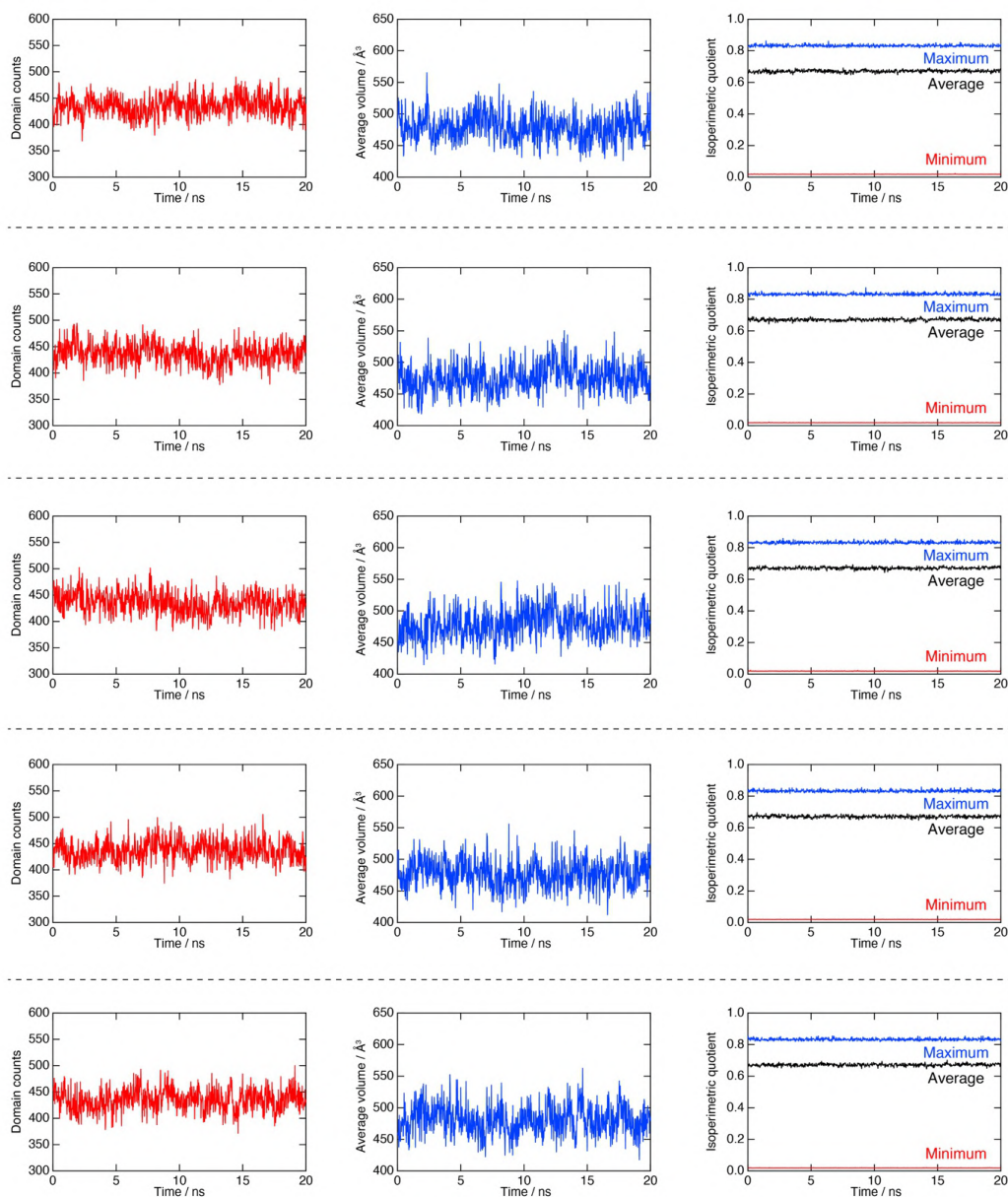


Figure 4.S12. Time evolution of domain counts, average volume of one domain, and values of isoperimetric quotient Q of the average, minimum, and maximum in five production MD simulations of C₄mimCl mixtures, each starting from a randomly generated initial configuration, based on the domain analyses of the nonpolar domain. The phase-separated structure serves as a diffusion field that enables the discontinuous supply of metal cations, making the analysis of the nonpolar domain more significant than that of the polar domain.

C₆mimCl mixture

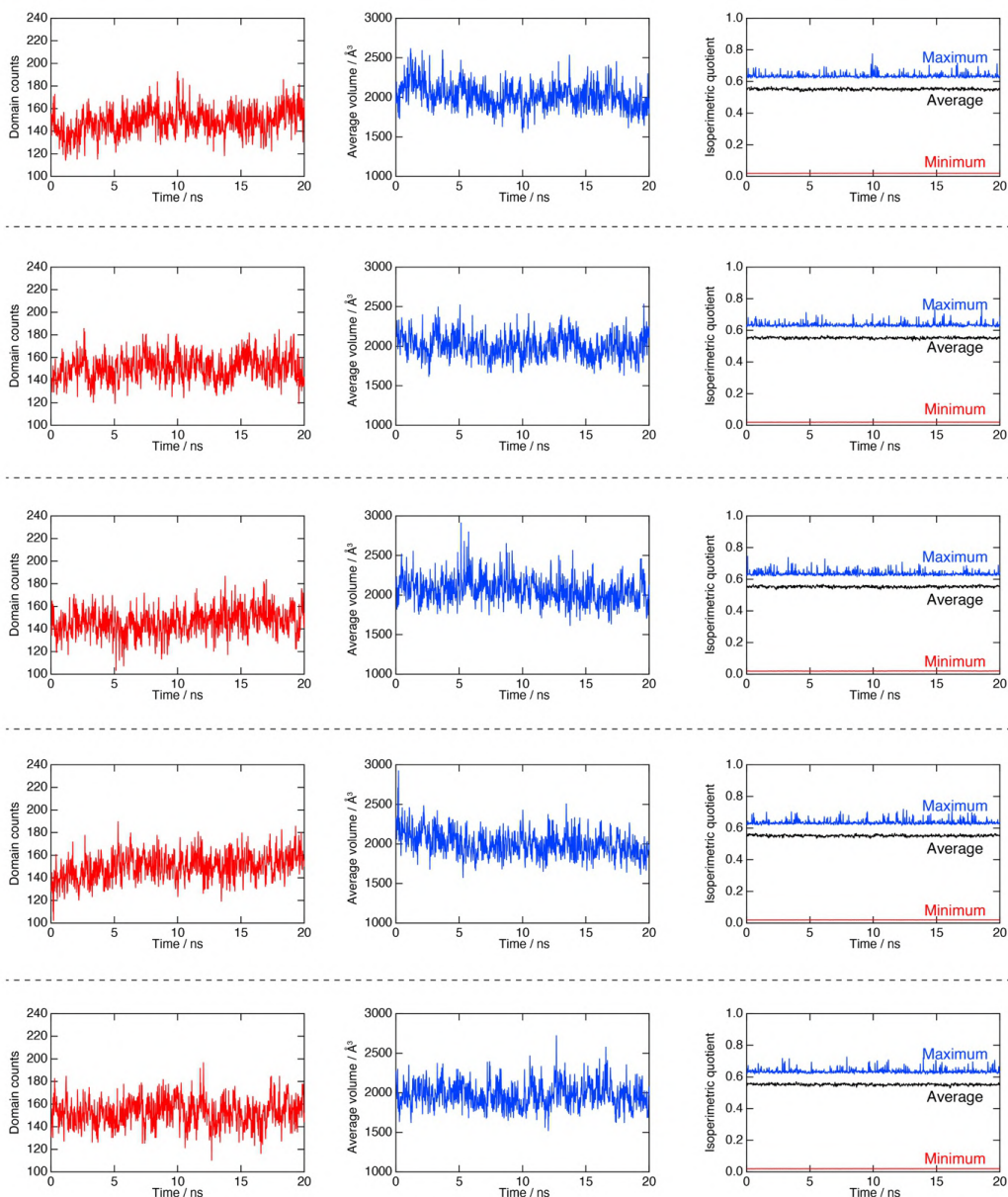


Figure 4.S13. Time evolution of domain counts, average volume of one domain, and values of isoperimetric quotient Q of the average, minimum, and maximum in five production MD simulations of C₆mimCl mixtures, each starting from a randomly generated initial configuration, based on the domain analyses of the nonpolar domain. The phase-separated structure serves as a diffusion field that enables the discontinuous supply of metal cations, making the analysis of the nonpolar domain more significant than that of the polar domain.

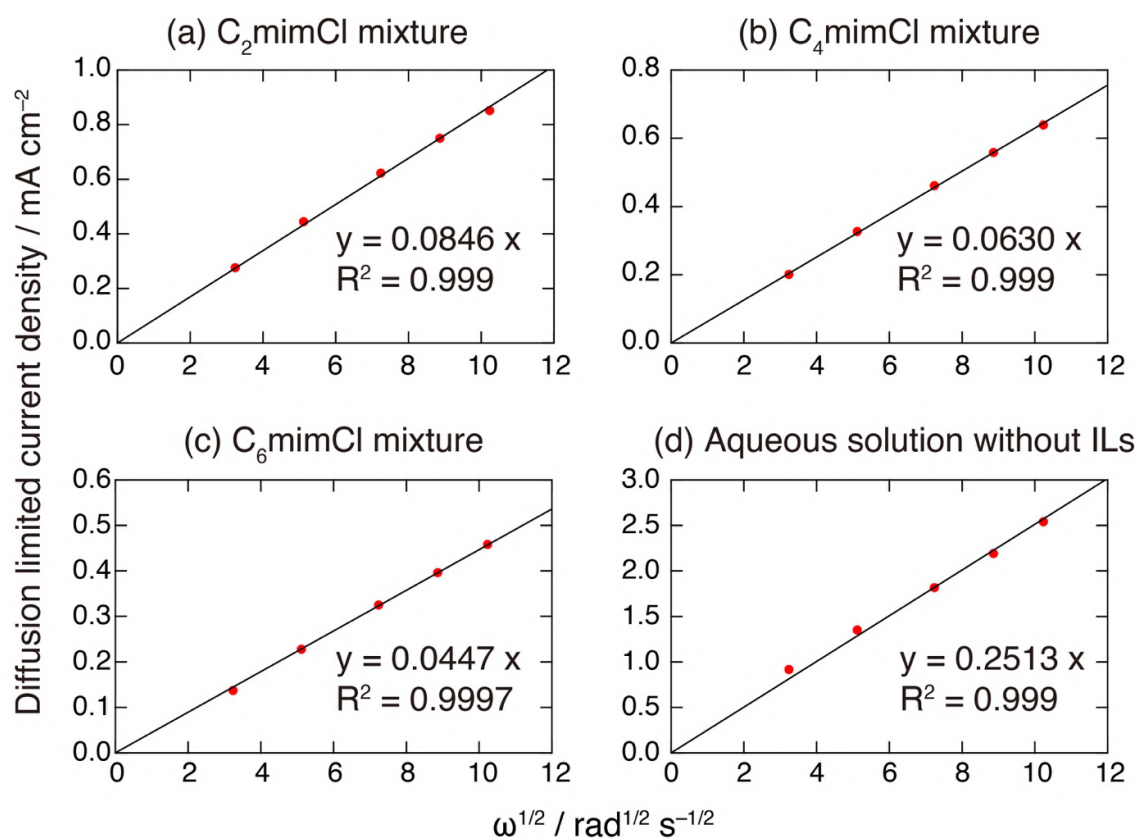


Figure 4.S14. Levich plot for (a) C₂mimCl mixture, (b) C₄mimCl mixture, (c) C₆mimCl mixture, and (d) aqueous solution without ionic liquid.

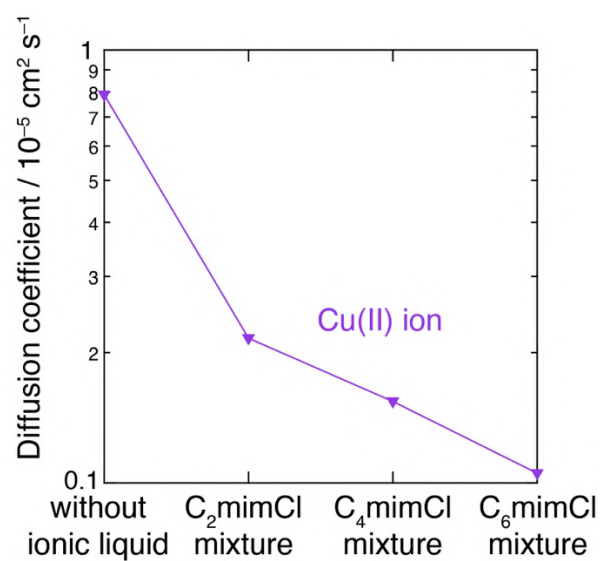


Figure 4.S15. Diffusion coefficient of Cu(II) ion in aqueous solution without ionic liquid, C_2mimCl mixture, C_4mimCl mixture, and C_6mimCl mixture obtained from Levich slope.

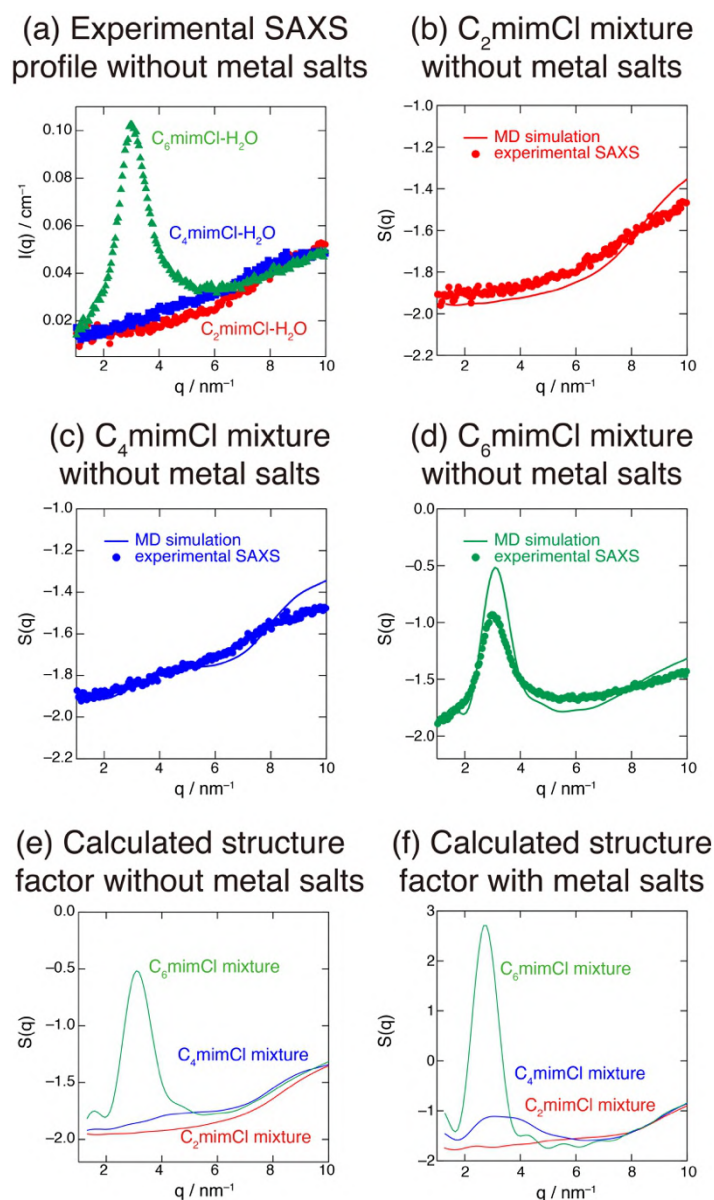


Figure 4.S16. (a) Experimental SAXS profiles measured with the mixtures of $C_n\text{mimCl}$ ($n = 2, 4$, and 6) and aqueous solutions without the metal salts. (b) Structure factors of the $C_2\text{mimCl}$ mixture without the metal salts obtained from experimental SAXS and MD simulation. (c) Structure factors of the $C_4\text{mimCl}$ mixture without the metal salts obtained from experimental SAXS and MD simulation. (d) Structure factors of the $C_6\text{mimCl}$ mixture without the metal salts obtained from experimental SAXS and MD simulation. (e) Structure factors of the mixtures of $C_n\text{mimCl}$ ($n = 2, 4$, and 6) and aqueous solutions without

the metal salts calculated from MD simulations. (f) Structure factors of the mixtures of $C_n\text{mimCl}$ ($n = 2, 4$, and 6) and aqueous solutions with the metal salts calculated from MD simulations.

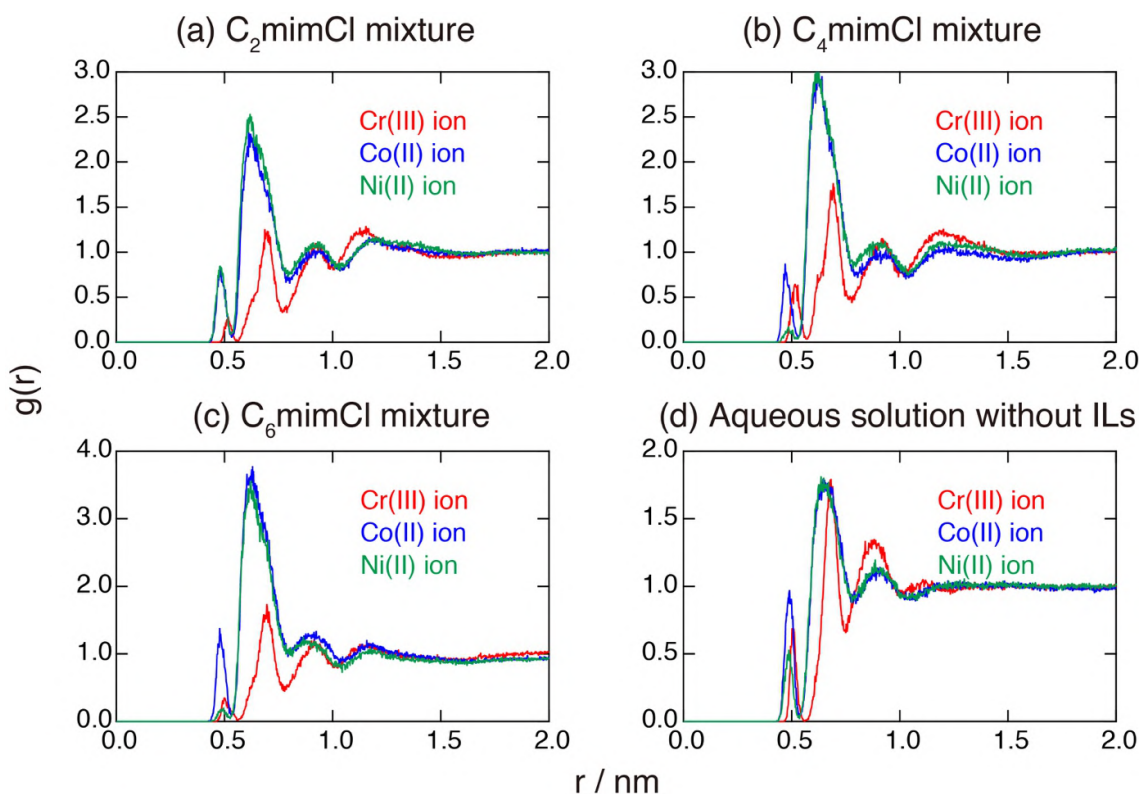


Figure 4.S17. Radial distribution functions $g(r)$ of Co(II) ion, Ni(II) ion, and Cr(III) ion in (a) $C_2\text{mimCl}$ mixture, (b) $C_4\text{mimCl}$ mixture, and (c) $C_6\text{mimCl}$ mixture, (d) aqueous solution without ionic liquid.

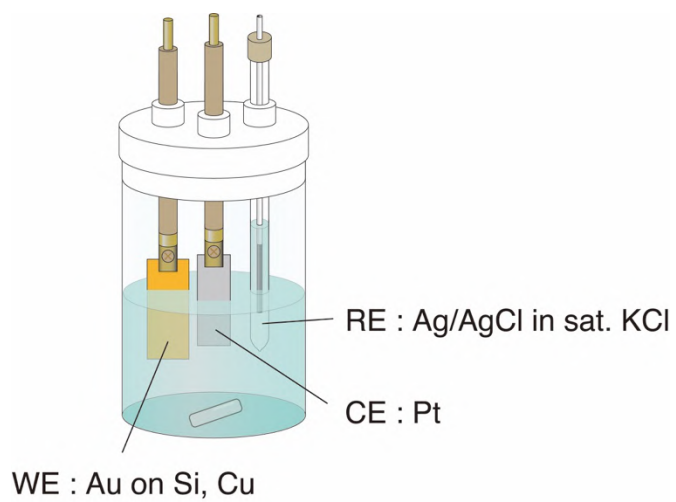


Figure 4.S18. Schematic of our electrochemical cell.

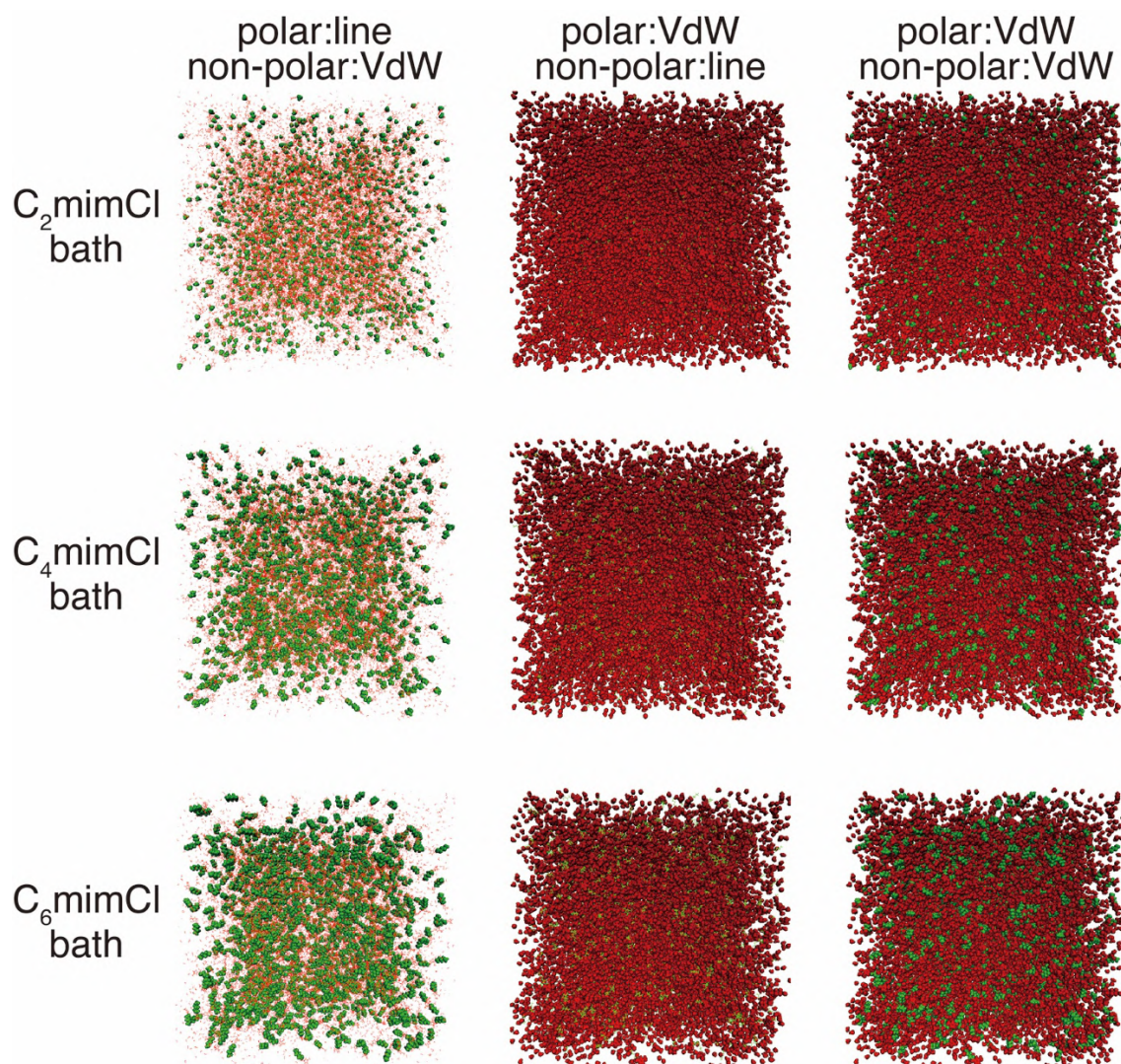


Figure 4.S19. Initial configuration of the three mixtures containing ionic liquids with different alkyl chain lengths, showing polar domains in red and nonpolar domains in green. The left snapshots use the van der Waals (VdW) radii model in green to describe nonpolar molecules and the line model in red to describe polar molecules to emphasize the nonpolar domains. The snapshots in the middle use the VdW radii model to describe polar molecules and the line model to describe nonpolar molecules. The right snapshots use the VdW radii model to describe both polar and nonpolar molecules. Molecules are randomly distributed in a sufficiently large box with a length of 18 nm. These show that in the initial configuration, nonpolar groups do not form aggregates in all mixtures.

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“Electroplating of Wear and Corrosion Resistant CrCoNi Medium-Entropy Alloys beyond Hard Chromium Coatings,”

Yuki Murakami, Shuhei Yoshida, Kosuke Ishii, Naoya Nishi, Akiyuki Ryoki, Nobuhiro Tsuji, Kuniaki Murase, Kazuhiro Fukami,

Advanced Functional Materials **2025**, 35, 2418621.

The final publication is available at Wiley via:

<https://doi.org/10.1002/adfm.202418621>

General Conclusions

This study addressed the challenges in electrodeposition of equiatomic multicomponent alloys, which have been considered highly difficult, by utilizing heterogeneous electrolytes instead of conventional homogeneous solutions. The findings are summarized as follows:

In Chapter 1, a novel electrodeposition method using a water-in-oil emulsion as the electrolyte, where metal ions are confined within small droplets, was developed. This approach successfully achieved the electrodeposition of a CoNiCu medium-entropy alloy (MEA) thin film for the first time. Detailed investigations revealed that the stability of the droplets under electrochemical conditions is critical, and intermittent ultrasonic treatment during electrolysis was found to be essential to maintain emulsion stability.

Chapter 2 extended the findings from Chapter 1, focusing on improving the quality and smoothness of CoNiCu MEA thin films. Stabilization of droplets by surfactants and increased viscosity within the droplets to control metal ion diffusion proved effective. Finite element simulations were employed to study the metal ion concentration within the droplets, providing essential insights into the necessary conditions for successful MEA electrodeposition.

In Chapter 3, the emulsion system was further modified by using a CNT-dispersed oil phase in the water-in-oil emulsion. This enabled the successful electrodeposition of CNT-CoNiCu MEA composite materials, which was previously challenging with conventional aqueous solutions. It was demonstrated that both increased metal ion concentration within the droplets and the incorporation of CNTs enhanced the deposition rate of MEAs.

Chapter 4 introduced a mixed electrolyte system of ionic liquid and

aqueous solution with phase-separated structures smaller than those in emulsions. This system achieved the successful electrodeposition of CrCoNi MEAs composed of nanocrystals, which exhibited superior mechanical properties compared to CrCoNi MEAs fabricated by other methods. Molecular dynamics simulations and X-ray scattering were employed to quantitatively evaluate the phase-separated structure of the electrolyte, revealing that this structure is essential for enabling MEA electrodeposition.

Through these studies, a novel electrodeposition method utilizing mesoscopic phase-separated electrolytes, distinct from conventional homogeneous solutions, was proposed for fabricating thin films of multicomponent equiatomic alloys. This approach has opened new possibilities for the application of high-entropy alloy and medium-entropy alloy thin films, overcoming the long-standing challenges in this field.

List of Publications

Chapter 1

Yuki Murakami, Yuki Maeda, Atsushi Kitada, Kuniaki Murase, Kazuhiro Fukami,

“Electrodeposition of a CoNiCu medium-entropy alloy in a water-in-oil emulsion”

Electrochemistry Communications **2021**, 128, 107057.

Chapter 2

Yuki Murakami, Kuniaki Murase, and Kazuhiro Fukami,

“Smooth Thin Film of a CoNiCu Medium-Entropy Alloy Consisting of Single Nanometer-Sized Grains Formed by Electrodeposition in a Water-in-Oil Emulsion”

The Journal of Physical Chemistry C **2023**, 127, 4696–4703

Chapter 3

Yuki Murakami, Kuniaki Murase, and Kazuhiro Fukami,

“Electrodeposition of a CoNiCu Medium-Entropy Alloy: Promotion of the Electrodeposition Rate and Composite Deposition with Carbon Nanotubes,”

Journal of the Surface Finishing Society of Japan **2023**, 74, 529.

Chapter 4

Yuki Murakami, Shuhei Yoshida, Kosuke Ishii, Naoya Nishi, Akiyuki Ryoki, Nobuhiro Tsuji, Kuniaki Murase, Kazuhiro Fukami,

“Electroplating of Wear and Corrosion Resistant CrCoNi Medium-Entropy Alloys beyond Hard Chromium Coatings”

Advanced Functional Materials **2025**, 35, 2418621.

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March 2025

Yuki Murakami

