Ni-Fe alloys are important materials that have been investigated for multiple applications including magnetic materials, electrochemical multivalent memory, and highly active electrocatalysts of oxygen evolution reaction (OER). Recently, Ni-Fe alloys have attracted much attention because OER is crucial to energy storage/conversion such as rechargeable metal-air batteries and electrochemical water-splitting. For the latter one, the potentials of both electrodes always determine the cell voltage. The OER is usually the rate determining step and contributes more significantly to the amount of potential required beyond the theoretical cell voltage. The cell voltage can be efficiently decreased by using an efficient electrocatalyst as the anode to reduce the overvoltage of OER, but precious metal-containing electrocatalysts should be avoided because of their high cost. Ni-Fe alloys, therefore, show their advantages to be OER electrocatalysts. Ni-Fe alloys are also used for hydrogen evolution reaction (HER) and for the electrodecoration of an important organic molecule, 4-aminophenol. Electrodeposition is widely utilized to prepare metal alloys, including Ni-Fe alloys. Although Ni-Fe alloys can be prepared using various techniques such as sputtering and ball milling, electroplating baths of Ni-Fe alloys are composed of simple salts with solubility. Electrodeposition is widely utilized to prepare metal alloys, including Ni-Fe alloys. Although Ni-Fe alloys can be prepared using various techniques such as sputtering and ball milling, electroplating baths of Ni-Fe alloys are composed of simple salts with solubility.

Ionic liquid 1-butyl-1-methylpyrrolidinium dicyanamide (IL BMP-DCA) was used as the electrolyte to study the voltammetric behavior of Ni(II) and Fe(II) introduced into the IL as their chloride and sulfate salts. Compared with the aqueous system, the separation of redox potential between the Ni(II) and Fe(II) was significantly decreased in this IL. The electrodeposition of Ni-Fe alloys was thus easily achieved using constant-potential electrolysis at copper substrate. No anomalous electrodeposition of Ni-Fe, which is common in aqueous system, was observed in this IL, resulting in the easy control of alloy compositions. The electronic spectra indicated that the coordinations of Ni(II) related to the precursors used in the IL, and the surface morphology of the Ni-Fe alloys was affected by the precursors as well as the electrodeposition potentials. Crystalline Ni and Ni-Fe were obtained from this system but crystalline Fe was only obtained at high temperature. The obtained Ni-Fe alloys were converted to the corresponding metal oxides/hydroxides via electrochemical oxidation in alkaline solution, and the linear scan voltammetric study indicated that these Ni-Fe alloys are potential substrates for Pt as electrocatalysts of oxygen evolution reaction.

Ni-Fe alloys were electrodeposited from an IL and their magnetic properties were studied. Our previous study indicated that electrodeposition of Fe and PtFe was possible in BMP-TFSI and BMP-dicyanamide (BMP-DCA) ILs in which FeCl2 was used to produce Fe(II). FeCl2 is easily dissolved in BMP-DCA because DCA inside a glove box (PL-HE-10-404 from Innovative Technology) and then the BMP-DCA was dried at 100°C under vacuum for one day. The drying process was repeated until no reductive wave of Fe was observed at Pt disk electrode using cyclic voltammetry. NiCl2 (99.99%), NiCl2·6H2O (98%), NiSO4·6H2O (99.9%), FeCl2 (99.99%), FeSO4·7H2O (99.5%), and NaOH (97%) were used as received without purification. The electrochemical experiments were performed either in BMP-DCA inside a glove box (PL-HE-10-404 from Innovative Technology) or without complexing agents. The complexing agent-containing baths are more stable, especially at high pH. However, many organic complexing agents alter the properties of Ni-Fe alloys due to the accumulation of the reductive products of the complexing agents during electrodeposition. An inorganic complexing agent, fluoroboric acid, was thus used. Although some drawbacks exist, Ni-Fe electrodeposition in aqueous solutions is successful. However, the significantly negative reduction potential of Fe might lead to two problems during electrodeposition: hydrogen evolution and the instability of Fe and Fe alloys in acidic baths. Another problem is the need of complexing agents that sometimes induce negative effects to the electrodeposits.

Alternatively, to study the electrodeposition of Ni-Fe alloys in ionic liquids (ILs) is important because ILs are well-known electrolytes excellent for the electrodeposition of metals, alloys, and semiconductors. In addition, hydrogen evolution is usually not an issue and complexing agents are usually unessential for electrodeposition in ILs. The negative effects coming from complexing agents can be avoided by using ILs. However, it seems that no relevant study has been reported. Compared with the traditional chloroaluminate and other metal halides-based ILs, the air- and water-stable ILs composed of no metal halides (the second generation ILs) are more easily handled because air and moisture can be easily removed by vacuum and show no reactivity with the ILs. The electrodeposition of Fe from second generation ILs was rarely reported. IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethyl)sulfonyl)imide (BMP-TFSI) has been used for Fe electrodeposition. Fe(TFSI)2 must be used because of its proven solubility.

Recently, Fe and FeAl alloys were electrodeposited from an IL and their magnetic properties were studied. Our previous study indicated that electrodeposition of Fe and PtFe was possible in BMP-TFSI and BMP-dicyanamide (BMP-DCA) ILs in which FeCl2 was used to produce Fe(II). FeCl2 is easily dissolved in BMP-DCA because DCA exhibits significant ligand property. Here, BMP-DCA was used as the electrolyte for Ni-Fe electrodeposition because many transition-metal salts easily dissolve in it. Chloride and sulfate salts of Ni and Fe were thus used to compare their differences. The electroplating baths are highly stable, and no additive is needed. The surface morphology, crystallinity, atomic compositions, and electrocatalytic property toward OER of the obtained Ni-Fe deposits were studied.

**Experimental**

The IL BMP-DCA was prepared using published procedures, with some modifications. BmpCl and NaDCA in equal moles were dissolved in dried acetonitrile and then mixed together to react in a stirred solution. After one day, the precipitates (NaCl) in the mixture were removed by filtration under nitrogen. The filtrate contained BMP-DCA and acetonitrile. The latter was removed by vacuum, and then the BMP-DCA was dried at 100°C under vacuum for one day. The drying process was repeated until no reductive wave of water was observed at Pt disk electrode using cyclic voltammetry. NiCl2 (99.99%), NiCl2·6H2O (98%), NiSO4·6H2O (99.9%), FeCl2 (99.99%), FeSO4·7H2O (99.5%), and NaOH (97%) were used as received without purification.

The electrochemical experiments were performed either in BMP-DCA inside a glove box (PL-HE-10-404 from Innovative Technology)
or in alkaline aqueous solutions outside a glove box using a CHI 660C electrochemical analyzer (from CH Instruments Inc.). A conventional three-electrode electrochemical cell was used, in which the working electrode was a Pt disk electrode (1.6 mmø) or a piece of Cu wire (1 mmø); the former was used for voltammetric study, and the latter for electrodeposition. The reference electrode was Ag/AgCl immersed in BMP-TFSI containing 0.1 M BMPCl (denoted as Ag/AgClIL. $E_{\text{red}}$ of ferrocene/ferrocinium (Fc/Fc⁺) is 0.508 V vs. Ag/AgClIL; the potential of this reference electrode was frequently checked against Fe/Fc⁺) when the experiments were performed in BMP-DCA inside a glove box. Otherwise, a conventional Ag/AgCl immersed in NaCl-saturated aqueous solution was used. A Pt spiral was used as the counter electrode. In BMP-DCA, a glass tube containing BMP-TFSI with a porous tip was used to separate the Pt spiral from the bulk BMP-DCA to prevent decomposition of IL at the counter electrode. BMP-TFSI instead of BMP-DCA was contained in the glass tube because BMP-DCA shows a passivation effect on Pt.42 For the study of OER using linear sweep voltammetry, high-purity O2 gas was sparged through the 0.1 M NaOH for at least 20 min prior to the electrochemical measurements, and a continuous flow of O2 was kept over the electrolyte during the experiments. Magnetic stirring was used to expel O2 bubbles formed on the electrode surface. For the detection of oxygen produced from water electrolysis, an airtight electrochemical cell was used, and initially filled with dry argon instead of oxygen.

An ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometer (JASCO V-570) was used to obtain the electronic spectra of the Ni(II) and Fe(II) species in BMP-DCA. Electrodeposition of Ni, Fe, and Ni-Fe alloys was achieved using constant-potential electrolysis on Cu wire or Cu foil electrodes in which the conductive areas were restricted by wrapping the electrodes with insulating tape. A field-emission scanning electron microscope (FE-SEM. Supra 55 from Zeiss) coupled with an energy dispersive X-ray spectrometer (EDX) was used for the characterization of the electrodeposits. The crystalline structures of the electrodeposits were studied with a powder X-ray diffractometer (XRD. XRD-7000 from Shimadzu). As for the XRD study, the electrodeposits were formed on Cu foil electrodes.

### Results and Discussion

In this study, Fe(II) and Ni(II) species were introduced into BMP-DCA IL via the addition of FeCl2·FeSO4·7H2O, NiCl2, NiCl2·6H2O, and NiSO4·6H2O in order to understand the effects of the counter anions and water of the hydrates on the spectroscopic and electrochemical behavior of Fe(II) and Ni(II). Figure 1a shows the UV-Vis spectra, and the inset shows the NIR spectra of Fe(II) formed from two precursors. Both Fe(II) species did not absorb the visible radiations but their weak absorption was observed in the NIR region (see inset 800～1100 nm; two absorption peaks near 1200 and 1400 nm, respectively, were also observed for neat IL but IL showed no absorption at 800～1100 nm). According to the literature,43 the observed behavior is a characteristic of octahedral Fe(II) species. However, more experiments are needed to determine their coordinations. Although there is a little difference between the spectra of the two Fe(II) species, it is hard to say whether their coordinations are different.

Figure 1b shows the UV-Vis spectra of Ni(II) in BMP-DCA, which indicates that the same Ni(II) complex ion was formed regardless of the addition of anhydrous NiCl2 or NiCl2·6H2O, indicating that the water molecules have no effect on the Ni(II) coordination if NiCl2 is the precursor. Ni(II) formed from NiSO4·6H2O showed a different spectroscopic behavior, implying that its coordination was different from that of Ni(II) produced by adding NiCl2. The Ni(II) species from NiCl2 shows the as similar feature as the octahedral Ni(II) does in IL BMP-TFSI or in water,44,45 and is different from the tetrahedral Ni(II) in basic chloroaluminate IL.46 However, more experiments are needed to elucidate the coordination of these Ni(II) species in IL BMP-DCA. An interesting thermochromic behavior of the NiSO4·6H2O solution was observed. Its color changed from bright green at 30°C to dark yellow at 80°C. Figure 1c indicates that the color change resulted from the continuous redshift of light absorption with the raising of the temperature. No thermochromic phenomenon was observed for the NiCl2·6H2O solution. Some nickel complexes have been reported to exhibit a thermochromic phenomenon, which resulted from temperature-dependent coordination.47,48 The spectroscopic study, therefore, implies that the coordination of the Ni(II) species from NiCl2 and NiCl2·6H2O did not change with temperature in BMP-DCA but the coordination of Ni(II) from NiSO4·6H2O changed with temperature. The thermochromic behavior is interesting but electrochemistry is focused here. No more thermochromic properties will be discussed.

Based on the above discussion, it is evident that the coordination of the Ni(II) species depends on the precursors used to prepare...
were observed. The two redox couples exhibited similar behavior in both solutions (Figs. 2a and 2b), except the c1/a1 couple in Fig. 2a was more reversible than that in Fig. 2b. This implies that the Fe(II) ions in the two solutions probably exhibited different coordinations although their spectra are almost indistinguishable (Fig. 1a). Otherwise, both species should show identical electrochemical behavior. Figure 2b shows a narrower cathodic limit, which is due to the reduction of water from FeSO₄ · 7H₂O. Figure 2c shows the temperature effects on the CVs of FeCl₂ solution. A typical temperature effect in IL was observed. Namely, the peak current and the reversibility of the redox couples increase with increasing the temperature. This behavior results from the improvement of diffusion and conductivity due to the decrease of viscosity of the IL at higher temperature. Additionally, the electron transfer rate always increases with raising the temperature. Figure 2c shows that wave a1, associated with the stripping of Fe deposited onto the electrode during wave c1, is highly sensitive to temperature. Anions of DCA⁻ and/or Cl⁻ (the latter was released during c1) were needed in the stripping process to coordinate with Fe²⁺ to form Fe(II) complex ions. The diffusion efficiency of the anionic ligands is significantly enhanced at higher temperature, which results in the increase of wave a1 current. The deposited Fe, however, was not completely stripped at wave a1, and the residue was oxidized at wave a₂, making a₂ distorted. At a lower temperature, the distortion was more apparent and the size of wave a₂ was much larger than that of wave c₂. When the temperature was increased, the size of waves c₂ and a₂ gradually became identical, wave a₂ became undistorted, and wave a₁ grew significantly. This behavior shows that the deposited Fe was oxidized at wave a₂ in a greater quantity at a lower temperature. Most of the deposited Fe, however, could be oxidized at wave a₁ while the temperature was increased. The CVs of Fe(II) were also recorded at five selected scan rates to further understand this electrochemical system. The results indicate that the mass transport involved in the c₁/a₁ and c₂/a₂ couples is diffusion-dominated because the peak current linearly depends on the square root of scan rate (Fig. S1, Supplementary Material). Sometimes, a shoulder following wave a₁ was observed, which probably results from the formation of a surface alloy or from a strong interaction between the deposited Fe and the electrode surface.

The temperature effects on the CVs of 20 mM NiCl₂ in BMP-DCA are demonstrated in Fig. 3a. A single redox couple c₁/a₁ associated with Ni(II) + 2e⁻ ↔ Ni²⁺ and a similar temperature effect, as seen in Fig. 2c, were observed. An apparent current loop (intersection of the current-potential curve) was observed at wave c₁, indicating that the electrodeposition of Ni was accompanied with a nucleation mechanism (a high overpotential was needed). Figure 3b shows the CVs of Ni(II) from three precursors with the same concentration. The counter anions of the precursors showed a significant effect on the reductive wave of Ni(II) (wave c₁), indicating that the Ni(II) coordination might be influenced by the counter anions. This observation is consistent to that as shown in Fig. 1b. The c₁/a₁ couple of NiCl₂ · 6H₂O in BMP-DCA exhibited higher peak currents than those of NiCl₂, which might result from the effects of the water molecules in NiCl₂ · 6H₂O on the viscosity and conductivity of ILs. It has been reported that the viscosity of an IL is greatly reduced although only introducing a trace amount of water, which leads to the increase of conductivity and reaction current. However, the measurements using IR compensation function indicated that the resistance of 20 mM NiCl₂ · 6H₂O solution (194 Ω) at open-circuit potential (OCP) was really lower than that (300 Ω) of 20 mM NiCl₂ solution at 30°C; at 80°C, the difference was not apparent (64 and 83 Ω). CVs of two Ni(II) species were recorded under five selected scan rates, and the data indicated that the diffusion-dominated mass transport was followed by the Ni(II) reduction (Fig. S2, Supplementary Material). Sometimes, a shoulder following wave a₁, which might be caused by the same reason for the shoulder wave of wave a₁ (Fig. 2), was observed. The electrodeposition of Fe and Ni was individually achieved using constant-potential electrolysis on a Cu substrate at 80°C. Figure 4 shows the SEM images of Fe obtained at three selected deposition potentials from BMP-DCA containing 50 mM FeCl₂ or FeSO₄ · 7H₂O.
Three cyclic voltammograms recorded on a Pt disk electrode in BMP-DCA containing 20 mM of (a) NiCl₂ at various temperatures and (b) indicated Ni precursors at 80°C. The arrows indicate the initial direction of potential scan. Scan rate: 50 mV·s⁻¹.

The charge density of the deposits was controlled at 2.27 C·cm⁻². It is evident that the surface morphology of the Fe deposits depended on the applied potential and the precursor of Fe(II). At lower reduction potentials (Figs. 2a, 2b, 2d, and 2e), the Fe deposits obtained from the FeSO₄·7H₂O solution were smoother than those obtained from the FeCl₂ solution. The surface morphology might be influenced by the Fe(II) species in the IL.

Figure 5 shows the SEM images of Ni electrodeposited at four selected reductive potentials from BMP-DCA containing 50 mM NiCl₂ or NiSO₄·6H₂O at 80°C. The charge density of the deposits was controlled at 2.27 C·cm⁻². The surface morphology of the Ni deposits showed a significant dependence on the applied potential and the Ni(II) precursors. The Ni deposits were very smooth at lower reduction potentials (Figs. 5e and 5f) when NiSO₄·6H₂O was used. Although the surface became rougher at higher reduction potentials (Figs. 5g and 5h), the surface roughness seemed to be lower than those obtained at the same deposition potential from NiCl₂ solutions (Figs. 5e and 5d). Similar to the Fe deposition, the surface morphology may have been affected by the species of Ni(II).

The cyclic voltammetric behavior of Ni(II)/Fe(II) mixtures prepared from various precursors was studied, and the corresponding CVs are shown in Fig. 6. Figure 6a shows that a new reductive wave c₁′ located between the reductive waves of Ni(II) (c₃) and Fe(II) (c₁) was observed in the Ni(II)/Fe(II) mixture. According to the data below, it is concluded that Ni-Fe codeposits can be obtained at reductive wave c₁′, indicating that wave c₁′ is due to the formation of Ni-Fe alloys. It also can be found in Fig. 6a that a new oxidative wave a₁′ at the potential between the two oxidative waves of Ni (a₃) and Fe (a₁) was observed, and the wave a₁ (oxidation of Fe deposits) disappeared in the Ni(II)/Fe(II) mixture. This behavior is typical of an alloy formation. For the Ni(II)/Fe(II) mixture prepared from NiSO₄·6H₂O and FeSO₄·7H₂O, similar CVs (Fig. 6b) as those shown in Fig. 6a were observed. The mixtures with four selected concentration ratios of [NiCl₂]/[FeCl₂] were studied using cyclic voltammetry, and the CVs can be found in (Fig. S3, Supplementary Material). The electrodeposition of Ni-Fe alloys was achieved by constant-potential electrolysis from these mixtures. The SEM images and the EDX data of these Ni-Fe electrodeposits can be found in (Figs. S4 and S5, Supplementary Material). Although anomalous electrodeposition of Ni-Fe (the less noble metal (Fe in this case) deposits preferentially to the more noble one) was usually observed in aqueous solutions, this phenomenon was not seen in the present study because the atomic content of Fe in the Ni-Fe alloys was always lower than or close to the Fe(II) content in the electroplating baths. Therefore, BMP-DCA provides a very different environment from the aqueous solutions for Ni-Fe electrodeposition. Controlling the composition of Ni-Fe alloys in this IL is thus much easier than in aqueous solutions because anomalous deposition does not happen in BMP-DCA.

As for OER, which will be discussed later, the Ni-Fe alloys with lower Fe content showed better activities and stabilities. BMP-DCA...
Figure 5. SEM images of Ni electrodeposited from BMP-DCA containing 50 mM of (a-d) NiCl₂ and (e-h) NiSO₄·6H₂O at 80°C. The electrodeposition potential is indicated and the accumulated charge density is 2.27 C·cm⁻². A scale bar of 2 μm is shown in (a) and all images have identical magnification.

containing 50 mM Ni(II) and 10 mM Fe(II), therefore, was used for the electrodeposition of Ni-Fe alloys. The corresponding CVs of these solutions are shown in Figs. 6c and 6d; the potential was scanned cathodically and then reversed at various switching potentials. At such conditions, the position and shape of the redox couple c₁′/a₁′ (codeposition/stripping of Ni/Fe) were very similar to those of c₃/a₃ (deposition/stripping of Ni) shown in Fig. 3. However, codeposition of Ni and Fe indeed occurred at wave c₁′, indicating that Ni/Fe codeposition

Figure 6. Cyclic voltammograms recorded on Pt disk electrode in BMP-DCA containing the indicated species at 80°C. The arrows indicate the initial direction of potential scan. Scan rate: 50 mV·s⁻¹.
can be easily achieved by single-potential electrolysis in BMP-DCA although the reduction potentials of Ni and Fe are widely separated in their individual solutions. The SEM images of the Ni-Fe alloys electrodeposited from the solutions, as indicated in Figs. 6c and 6d, are demonstrated in Fig. 7. The charge density of electrodeposition was increased to 7.08 C·cm⁻² using this bath because a thicker film showed a higher activity of OER but an over-thick film was unstable. At lower deposition potentials (Figs. 7a, 7b, 7f, and 7g), the Ni-Fe deposits formed from the NiSO₄·6H₂O/FeSO₄·7H₂O mixture showed smoother surfaces, but there were many aggregated granular deposits distributed on the surfaces, as shown in the inset of Fig. 7g. Figure 7g shows the magnified aggregated granules and the smooth underlayer. When the deposition potential was increased to ~1.5 V, the Ni-Fe deposits obtained from the NiCl₂/FeCl₂ mixture were more compact (Fig. 7c), but those from NiSO₄·6H₂O/FeSO₄·7H₂O contained porous structures (Fig. 7h). After increasing the electrodeposition potential to ~1.7 V (Figs. 7d and 7i), an inverse behavior was observed (more compact deposits were obtained from NiSO₄·6H₂O/FeSO₄·7H₂O). At the most negative potential (~1.9 V, the Ni-Fe deposits showed similar morphology regardless of which Ni(II)/Fe(II) mixture was used (Figs. 7e and 7j). In summary, the surface morphology of the Ni-Fe electrodeposits was controlled by the applied potential as well as the species of Ni(II) and Fe(II) in IL.

EDX was used to semi-quantitatively determine the atomic compositions of the Ni-Fe deposits. The relevant data are shown in Fig. 8, which shows the dependence of Fe atomic content in the Ni-Fe alloys on the applied potential. It is interesting that the Fe content was almost independent of the electrodeposition potential and maintained at ~20% when the Ni-Fe alloys were prepared in the NiCl₂ (50 mM)/FeCl₂ (10 mM) mixture, indicating that the two species might have strong interaction in the solution. However, the Fe content increased with an increase of the deposition potential and reached a maximum (~22%) at ~1.7 V when the NiSO₄·6H₂O (50 mM)/FeSO₄·7H₂O (10 mM) bath was used. As mentioned before, IL is unlike aqueous baths because no anomalous electrodeposition of the obtained Ni-Fe alloys was observed. Because the Fe content in the Ni-Fe alloys from the NiSO₄·6H₂O/FeSO₄·7H₂O bath distributed over a much wider range (from ~5% to ~22%), this bath was used in the following experiments since the OER activity of the Ni-Fe alloys depends on their compositions. In addition, the sulfate salts of Ni²⁺ and Fe³⁺ are much cheaper than their chloride counterparts.

The crystalline structures of the electrodeposited Ni, Fe, and Ni-Fe alloys were studied using powder X-ray diffractometer (Fig. S6, Supplementary Material). Apparent diffraction signals of the electrodeposits were only observed at the 2θ angle lower than 50 degrees. The X-ray diffraction signal of the Ni deposits was very broad and shifted a little bit toward the smaller angle against that of a Ni foil. Increasing the deposition temperature from 80 °C to 110 °C enhanced the diffraction signal of the Ni deposits, indicating that a higher temperature is needed for the formation of crystalline Ni. The broad peak indicates that the crystal size of the Ni deposits was very small. This behavior is consistent with the SEM observation in which the Ni deposits were composed of spherical particles rather than sharp crystals. The electrodeposits of Fe obtained at lower temperature (80 °C) should be amorphous because no diffraction signal was found. A very broad diffraction signal of Fe, however, appeared when the electrodeposition was conducted at 110 °C, indicating that a higher temperature was needed for crystal growth. The broad peak indicates that the Fe deposits exhibited small size of crystal. These observations are consistent with the SEM images in which no sharp crystalline structure can be observed. As for the electrodeposits of Ni-Fe obtained from 80 °C and 110 °C, two phases, fcc (or γ) phase and bcc (or α) phase of Ni-Fe, were observed.22

As mentioned in the introduction, Ni-Fe (or more precisely, Ni-Fe hydroxides) can significantly reduce the overpotential of OER. The cell voltage necessary for water splitting can thus be decreased. The Ni-Fe alloys prepared by electrodeposition in this study, therefore,

![Figure 7](image-url)  
**Figure 7.** SEM images of Ni-Fe alloys electrodeposited from BMP-DCA containing (a-e) 50 mM NiCl₂ and 10 mM FeCl₂ or (f-j) 50 mM NiSO₄·6H₂O and 10 mM FeSO₄·7H₂O. The electrodeposition potential is indicated and the accumulated charge density is 7.08 C·cm⁻². The inset of (g) shows the magnified image. A scale bar of 2 μm is shown in (a) and all images have identical magnification.

![Figure 8](image-url)  
**Figure 8.** Dependence of atomic content of Fe in Ni-Fe alloys on electrodeposition potential at 80 °C. Electroplating bath: BMP-DCA containing the indicated species. Accumulated charge density: 7.08 C·cm⁻².
were assessed to determine whether or not they could be the potential OER electrocatalysts. Four selected \( \text{Ni}_x \text{Fe}_{100-x} \) alloy electrodes with a deposition charge density of 7.08 C·cm\(^{-2}\) were used as the working electrodes, and linear scan voltammetry was conducted in 0.1 M NaOH. Continuous cyclic voltammetry was performed until a stable CV was observed (~5 cycles were needed at 50 mV·s\(^{-1}\)) before linear scan voltammetry was conducted. The Ni-Fe deposits, therefore, were supposed to be converted to Ni-Fe hydroxides during the continuous scans. The corresponding linear scan voltammograms (LSVs) are shown in Fig. 9a. The arrow shows the initial scan direction. Considering the onset potentials and the magnitudes of the reaction current, Fig. 9a indicates that the OER activity of the Ni-Fe electrodes depended on their compositions. The Ni-\( \text{Fe}_{22} \) electrode showed the best performance because it exhibited the least positive onset potential and highest reaction current. Figure 9b shows the LSVs of OER recorded on the selected electrodes. The electrodeposited Ni-\( \text{Fe}_{22} \) electrode (Ni-\( \text{Fe}_{22}/\text{Cu} \)) showed superior activity over other electrodes because of its more negative onset potential, higher oxidative current density, and steeper current/potential slope. The oxidation wave of \( \text{NiO} + \text{OH}^- \rightarrow \text{NiOOH} + e^- \) on Ni-\( \text{Fe}_{22}/\text{Cu} \) shifted positively and became a shoulder wave, compared with that of Ni/Cu electrode. The voltammetric behavior of the Ni-\( \text{Fe}_{22}/\text{Cu} \) electrode was very similar to that of the Ni\( \text{Fe}_{23}/(\text{OH})_2 \) electrode reported in a recent study, which indicates that even trace amount of Fe could greatly improve the activity of the Ni-based OER electrocatalysts. The Fe impurity in the electrolyte can also provide a great enhancement of activity even though the original Ni-based electrocatalysts contained no Fe.\(^{13}\) The authors provided a hypothesis that Fe exerts a partial charge-transfer activation effect on Ni, leading to the enhancement of activity of Ni. The present study, then, has demonstrated that active Ni-Fe electrocatalysts can be prepared by electrodeposition from ILs.

To confirm that \( \text{O}_2 \) was produced from the electrochemical oxidation of water, gas chromatography was used to detect the overhead air in the sealed electrochemical cell in which the bulk electrolysis was conducted using Ni-\( \text{Fe}_{22}/\text{Cu} \) and Pt coil as anode and cathode, respectively, in 0.1 M NaOH. \( \text{O}_2 \) gas was indeed detected and its quantity increased with the electrolysis time, indicating that \( \text{O}_2 \) was produced from the water electrolysis. The stability of the Ni-\( \text{Fe}_{22}/\text{Cu} \) electrode was evaluated by observing the dependence of the electrode potential on electrolysis time (the \( E-t \) curve) under 10 mA·cm\(^{-2}\) in 0.1 M NaOH, and the curve is shown in the inset of Fig. 9b. The electrode potential of the Ni-\( \text{Fe}_{22}/\text{Cu} \) electrode is approximately constant, indicating that the electrode is stable during the electrolysis. Turnover frequency (TOF) value was determined for the Ni-\( \text{Fe}_{22}/\text{Cu} \) electrode using the same method reported in the previous paper.\(^{13}\) TOF in which paper was defined as the moles of \( \text{O}_2 \) evolved per mole of Ni in the catalyst per second. TOF values were determined to be 0.17 at 0.600 V (overpotential \( \eta = 0.339 \) V) and 0.35 at 0.661 V (\( \eta = 0.400 \) V), respectively. Tuning the electrodeposition parameters finely will be needed to produce more active Ni-Fe alloys.

Conclusions

\( \text{Ni}_x \text{Fe}_{100-x} \) alloys are successfully obtained by constant-potential electrodeposition in BMP-DCA IL in which many common inorganic salts of Ni and Fe, such as their chloride and sulfate compounds, are suitable as the precursors for electrodeposition, and the species of Ni and Fe in the IL are determined by the precursors, which shows certain effects on the surface morphology of the obtained Ni-Fe alloys. It needs to be emphasized that hydrated salts can be used for the electrodeposition with no interfering effect. This is important because hydrated salts are usually cheaper than their anhydrous counterparts. Unlike to the electrodeposition of Ni-Fe alloys in aqueous baths, no anomalous electrodeposition of Ni-Fe was observed in this IL, which makes the control of alloy compositions to be easier. Another merit of IL used for Ni-Fe electrodeposition is that no additive is needed, and no hydrogen evolution is observed, which is usually not avoidable in aqueous baths. The obtained Ni-Fe alloys can be converted to the corresponding oxides/hydroxides that show the potential to be substitute for the expensive Pt-based electrocatalysts of OER. In brief, IL is a wise choice as the electrolyte for the electrodeposition of high-quality Ni-Fe alloys. However, low-cost, recyclable, and environmentally friendly ILs are needed to be developed to achieve mass production of electrodeposition materials.

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References

1. G. Y. Chin and J. H. Wernick, in Ferromagnetic Materials, E. P. Wohlfarth, Editor, p. 123, North-Holland Publishing Co., Amsterdam, (1980).
2. I. W. Wolf, J. Appl. Phys., 53, 1152 (1982).
3. P. N. Bartlett, M. A. Ghanem, J. S. El Hallag, P. De Groot, and A. Zhukov, J. Mater. Chem., 13, 2596 (2003).
4. H. Kockar, M. Alper, H. Kurt, and T. Meydan, J. Magn. Magn. Mater., 304, e736 (2006).
5. G. Abellan, J. G. Martinez, T. F. Otero, A. Ribera, and E. Coronado, Electrochem. Commun., 16, 15 (2014).
