Bipolar performance of the electroplated iron–nickel deposits for water electrolysis

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Abstract

The activities of oxygen and hydrogen evolution on Fe–Ni deposits with controllable compositions were systematically compared in the alkaline media. The redox behavior of Fe–Ni deposits prior to oxygen evolution could be generally related to their electrochemical activity for the oxygen evolution reaction meanwhile the activity of hydrogen evolution was found to be generally proportional to the mean roughness factor of deposits. Fe24Ni76, Fe76Ni24 and Fe90Ni10 deposits simultaneously exhibiting good activities of oxygen and hydrogen evolution were employed as electrode materials for water electrolysis in a bipolar hydrogen–oxygen electrolyzer in the stability test, examined at 50 and 200 mA cm−2 in 5 M KOH for 2 weeks. The morphological, compositional and crystalline information of these three materials before and after the bipolar studies were measured by scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD) analysis, respectively. These studies demonstrated the potential applicability of these three deposits in the bipolar electrolyzer for water electrolysis.

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Keywords: Iron-nickel deposit; Water electrolysis; Bipolar electrolyzer; Electroplating

1. Introduction

The magnetic and textural properties of iron-nickel alloys have been widely investigated for last few decades because they are important engineering materials in the microelectronic industry and magnetic-recording media [1–4]. In addition, the electroplating mechanism of Fe–Ni deposits is also widely studied since the deposition of nickel is obviously inhibited by the presence of iron ions and iron atoms are enriched in the binary deposits (i.e. anomalous deposition) [5–10]. On the other hand, nickel-based alloys have been recognized as good electrocatalysts for the hydrogen evolution reaction (HER) [11–14]. Moreover, nickel-based oxides are also employed as the electrocatalysts for the oxygen evolution reaction (OER) [15–17]. Therefore, nickel-based alloys with anodic and cathodic polarization in basic media are expected to be good electrocatalysts for the OER and HER, respectively. On the basis of the above points of view, Fe–Ni alloys with certain compositions may simultaneously exhibit electrocatalytic activities for oxygen and hydrogen evolution, which are very suitable for the bipolar electrolysers of water electrolysis.

Bipolar electrolyzers usually provide an economic advantage in construction materials with smaller plant space while the maximum current density of these electrolysers should be carefully considered [18]. From the design arts of conventional electrolyzers, the electrolytic cells are usually connected in series in a common housing. A bipolar configuration is a cell design where the anode and the cathode in two adjacent cells are mounted on the opposite sides of an electrode. The potential difference between the anode and the cathode of two adjacent bipolar electrodes in a cell is induced via the electrostatic field applied on the two terminal electrodes [18]. Since the electrical resistance between the elements of the bipolar electrode is an important issue during the high current-density operation, a uniform material simultaneously employable as the anode and cathode of an electrolyzer without any other electrical connections should be the best choice for this design configuration.

In general, activated electrodes are preferred to develop because bulk metal is considered to be inapplicable for practical electrolyzers [18,19]. Thus, electrodes with a catalytic coating are going to be developed in this work. The purpose of this work is intended to investigate the effects of composition on the activities of hydrogen and oxygen evolution for...
Fe–Ni deposits in the alkaline media. In addition, the bipolar performance of the deposits with good catalytic activities for both hydrogen and oxygen evolution are examined in a bipolar electrolyzer under relatively high current densities. The compositional, crystalline and morphological information of these potential candidates for the electrode materials of bipolar hydrogen–oxygen generators were, respectively, measured by energy-dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) before and after the bipolar studies.

2. Experimental

The Fe–Ni deposits were electroplated onto commercial pure (99.5%) 1 cm × 2 cm and 5 cm × 10 cm Cu plates for the electrochemical investigation of oxygen and hydrogen evolution, and for the bipolar electrolyzer, respectively. These Cu plates were first cleaned with trichloroethylene, rinsed with pure water, and then, anodized at 40 mA cm⁻² in a 0.1 M NaOH solution for 10 min. After anodizing, these plates were cathodically polarized at 40 mA cm⁻² in another 0.1 M NaOH solution for 1 min, vibrated in an ultrasonic bath for 5 min, acid-cleaned with 0.1 M HCl for 2 min, and finally rinsed with pure water. After cleaning, the 1 cm × 2 cm Cu substrate was placed at the center of a cell between vertical parallel nickel plates of total geometric area 32 cm². For the 5 cm × 10 cm Cu substrate, it was placed vertically at the center of an electroplating cell surrounded by nickel meshes with a total geometric area of 900 cm². The compositions of iron–nickel deposition baths for various Fe–Ni deposits are shown in Table 1. The concentration of Ni ions in the plating bath is kept constant (0.2 M) with pH adjusted with 1 M HCl. Note that the electroplating was ceased when the passed charge was equal to 150 C cm⁻². The concentration of Fe–Ni deposits, also shown in Table 1, was controlled through means of the experimental strategies similar to our previous work [20].

The mean roughness factor (Rₚ) of all deposits was the average value of roughness factor from three positions measured by a profile meter. The average composition of Fe–Ni deposits was measured by means of an energy-dispersive X-ray (EDX) spectroscope with standards at five points using a scanning electron microscope (SEM, JEOL JSM35). The surface morphologies and compositions of the deposits with good electrocatalytic activities for both oxygen and hydrogen evolution were examined by the same equipment before and after the bipolar studies. The crystalline information of these deposits before and after the bipolar studies was also obtained from the X-ray diffraction analysis (XRD, Rigaku X-ray diffractometer using a Cu target).

The electrochemical analyzer system, CHI 633A (CH Instrument, USA) was employed to perform the potentiodynamic experiments for the electrochemical characterization of Fe–Ni deposits. The electrochemical characterization was carried out in a three-compartment cell. An Ag/AgCl electrode (Argenthal, 3 M KCl, 207 mV versus SHE at 25 °C) was used as the reference, and a piece of platinum gauze with an exposed area equal to 4 cm² was employed as the counter electrode. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of the working electrode, was used to minimize errors due to iR drop in the electrolytes.

The apparent activities (i.e. current densities (i) of H₂ and O₂ evolution of different Fe–Ni deposits were compared at the same overpotential (i.e. η = −300 and 400 mV for the HER and OER, respectively) from the Tafel curves. Tafel curves were measured using a pseudo-steady-state polarization method. For the HER, the electrode potential was first set at −1020 mV for 10 min and then scanned at 0.5 mV s⁻¹ to −1150 mV. For the OER, the electrode potentials were first set at 400 mV for 10 min and then scanned at 0.5 mV s⁻¹ to 650 mV. All Tafel curves have been compensated with iR correction (using the positive feedback method) and the log(i)-E curves were completely overlapped in the whole potential region after 3–4 applications of the polarization.

All solutions used in this work were prepared with 18 MΩ·cm water produced by a reagent water system (MILLI-Q SP, Japan) and all reagents not otherwise specified in this work were Merck, GR. The electrolyte, containing 1 M KOH, used to investigate the electrochemical behavior of various Fe–Ni deposits was degassed with purified nitrogen gas before voltammetric measurements and nitrogen was passed over the solution during the measurements. The electrolyte, containing 5 M KOH, used to investigate the performance of the Fe–Ni deposits in the bipolar electrolyzer was further purified by the weak electrolysis for 24 h. In this purification work, a dimensionally stable anode (DSA) and a piece of stainless steel gauze with exposed surface areas of 6 cm² are employed as the anode and cathode, respectively. The applied current density during the weak electrolysis was equal to 8 mA cm⁻² to remove the cations that may be under-potentially deposited on the

### Table 1

<table>
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<tr>
<th>Run Factor</th>
<th>Fe ions (at. %)</th>
<th>pH</th>
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<th>[Fe] (M)</th>
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<tr>
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<td>11</td>
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<td>2</td>
<td>0.1</td>
<td>100</td>
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The concentration of NiSO₄·6H₂O is constant for all plating baths (0.2 M)
surface of cathodes and reduce their hydrogen evolution ability. The solution temperature for the 1 M KOH solution was maintained at 25 °C by means of a water thermostat (HAAKE DC3 and K20) while there is no temperature control for the 5 M KOH solution during the bipolar study.

3. Results and discussion

3.1. Voltammetric behavior and oxygen–hydrogen evolution activities

Typical cyclic voltammograms of Fe$_x$Ni$_{100-x}$ deposits with the x values equal to 0, 33, 64, and 100 are presented as curves 1–4 in Fig. 1 since oxygen evolution is believed to catalyze by the redox transitions of interfacial oxidations between higher and lower oxidation states [15–17]. Thus, the oxygen evolution activity of Fe–Ni deposits should be a function of the electrochemical properties of the redox pair prior to the OER, which can be characterized by using cyclic voltammetry [15–17,19,21]. On curve 1, the redox peaks with the anodic and cathodic peak potentials, respectively, equal to 362 and 265 mV for pure nickel are corresponding to the NiOOH/Ni(OH)$_2$ transition [11,12,15,22]. However, the voltammetric behavior of this pure nickel deposit (i.e. curve 1) is fairly different from that of bulk Ni [23,24]. This difference is attributable to the fact that the electrochemical properties of Ni are strongly dependent upon the preparation and conditions [11,12,15,22]. From a comparison of curves 1 and 2, although the main redox peaks attributed to the NiOOH/Ni(OH)$_2$ transition are clearly found on both curves, a positive shift in peak potentials of curve 2 for the binary deposits with the Fe content of 33 at.% is clearly found. This result indicates that the electrochemical properties of nickel hydroxide have been modified by the co-deposition of Fe into the Ni deposit. Note that the voltammetric charge surrounded by the CV curves is increased with increasing the Fe content when the Fe content within the deposits is <33 at.%. The electroactive sites for the oxygen evolution reaction are thus expected to increase with the mixing of Ni and Fe because voltammetric charge is indicative of the electrochemically active surface area [11,12,15–17,19,21,22]. This statement is further supported by the less positive onset potential of oxygen evolution for the binary deposits (i.e. 490 and 600 mV, respectively, for Fe$_{33}$Ni$_{67}$ and Ni; see Fig. 1). The onset potential of oxygen evolution was defined as the decomposition potential of water under the anodic polarization because the oxygen evolution reaction (OER) is an irreversible reaction with a high activation overpotential [11,12,16,17,19,21,22,25]. Thus, when electrode potentials are located between the equilibrium and the onset potentials of oxygen evolution, currents corresponding to this reaction are irregular and negligible. However, the rate of oxygen evolution becomes regular and significant when the electrode potentials are positive to the onset potential of the OER. Potvin and Brossard [26] proposed that the oxygen evolution activity of Fe–Ni deposits is better than a pure Ni deposit, further supporting the above statement. On the other hand, when the Fe content is ≥33 at.%, voltammetric charge is decreased relatively rapidly and the positive shift in redox peaks for the redox pair prior to the OER is more clearly found (see curve 3 in Fig. 1). The positive shift in redox potentials results in the fact that oxygen evolution commences immediately when the electrode potentials just reach the redox potential of this redox couple, probably indicating a better catalytic activity for the OER. However, the apparent activities of Fe–Ni deposits for the OER should be mainly determined by the much more rapid decrease in electrochemically active surface area. From the above results and discussion, the activity of oxygen evolution on Fe–Ni deposits should be depressed with increasing the Fe content in this composition range. Also, note that there is no obvious Faradaic current on the CV curve of pure Fe, indicating the absence of redox couples of Fe oxides in the potential range of investigation. The above results reveal that the electrochemical characteristics of the redox couple prior to the OER is strongly dependent upon the composition of Fe–Ni deposits, which probably results in different activities for oxygen evolution. Accordingly, the dependence of the anodic peak potential ($E_{pA}$), the cathodic peak potential ($E_{pC}$) and the onset potentials of oxygen evolution on the composition of Fe–Ni deposits is studied and these results are, respectively, shown as curves 1–3 in Fig. 2. From curves 1 and 2, both anodic and cathodic peak potentials are gradually increased with the Fe content in the whole composition range while no redox peak is found for the pure iron deposit. In addition, the onset potential of oxygen evolution is almost independent of the Fe content for binary deposits while it sharply increases for the pure Fe deposit. All the...
above results indicate the significant contribution of the intimate mixing between Ni and Fe atoms within the deposits [19], rendering the variation in activities of oxygen evolution on the binary deposits.

Fig. 3 shows the dependence of oxygen (curve 1) and hydrogen evolution activities (curve 2) obtained from the pseudo-steady-state polarization curves as well as the mean roughness factor ($R_a$, curve 3) on the composition of Fe–Ni deposits. Note that the current density of oxygen evolution is obviously increased with the introduction of Fe atoms into the nickel deposits while a gradual decrease in current densities when the Fe contents are ≥24 at.%, attributable to the decrease in electrochemically active surface area. On the other hand, the dependence of the current density of hydrogen evolution on the composition of Fe–Ni deposits is irregular (see curve 2 in Fig. 3). Thus, it is not easy to predict the hydrogen evolving activity of Fe–Ni deposits through their voltammetric behavior within the potential window of water decomposition. On the other hand, from a comparison of curves 2 and 3, the hydrogen evolving activity is generally proportional to $R_a$, suggesting that the hydrogen evolution activity of Fe–Ni deposits is predominated by their true surface area. From an examination of curves 1 and 2 in Fig. 3, Fe$_{24}$Ni$_{76}$, Fe$_{76}$Ni$_{24}$, and Fe$_{90}$Ni$_{10}$ deposits are suitably employed as electrodes for the bipolar water electrolyzer since these materials simultaneously exhibit highly activities for the OER and HER. Accordingly, these deposits are subjected to the investigation of the bipolar performance.

3.2. Bipolar characterization for the oxygen and hydrogen generation

According to the results and discussion in Section 3.1, the bipolar performance of Fe$_{24}$Ni$_{76}$, Fe$_{76}$Ni$_{24}$, and Fe$_{90}$Ni$_{10}$ deposits were studied in a bipolar water electrolyzer. The cross-sectional view of the bipolar electrolyzer for oxygen and hydrogen generation employed in this work is shown in Fig. 4. There are two cells in this assembly and the distance between adjacent electrodes is only 28 mm. Each cell is divided with a highly conductive polymer membrane (provided by Chuan Jenn Technology Co. Ltd.) to avoid the mixing of hydrogen and oxygen molecules. The aqueous alkaline electrolyte can be continuously supplied into the cell through pumping. During electrolysis, the spaces between the electrodes are fed with 5 M KOH and currents are passed through the cells as shown in Fig. 4 in accordance with the well-known principles to produce hydrogen and oxygen gas. The bipolar electrolyzer constructed according to this configuration can be operated at a high current density (up to 4000 A m$^{-2}$).

Typical cell voltages of the bipolar electrolyzer with Fe$_{24}$Ni$_{76}$, Fe$_{76}$Ni$_{24}$, and Fe$_{90}$Ni$_{10}$ deposits operated under 50mA cm$^{-2}$ are, respectively, represented as curves 1–3 in Fig. 5 meanwhile those operated under 200mA cm$^{-2}$ are shown as curves 4–6, respectively. Note that the cell
Fig. 5. Cell voltages of the bipolar electrolyzer containing (1, 4) Fe_{24}Ni_{76}, (2, 5) Fe_{76}Ni_{24}, and (3, 6) Fe_{90}Ni_{10} deposits for water electrolysis under (1–3) 50 and (4–6) 200 mA cm\(^{-2}\) in 5 M KOH.

Voltages were kept approximately constant in the whole investigated duration, revealing the fact that these Fe–Ni deposits are generally accepted for the application in the bipolar electrolyzers of oxygen and hydrogen generation. The sequence of deposits with respect to increasing the cell voltages is: Fe\(_{24}\)Ni\(_{76}\) < Fe\(_{90}\)Ni\(_{10}\) < Fe\(_{76}\)Ni\(_{24}\). Also note that the cell voltages of curves 4–6 are obviously higher than those on curves 1–3. The significant difference in cell voltages between curves 1–3 and 4–6 should be simultaneously contributed by the \(iR\) drops in the whole assembly since the cell voltage can be expressed as Eq. (1) [18]:

\[
E_{\text{cell}} = E_{\text{e,cell}} + [\eta_A] + [\eta_C] + i(R_{\text{circuit}} + R_{\text{electrode}} + R_{\text{membrane}} + R_{\text{electrolyte}})
\] (1)

where \(E_{\text{e,cell}}\), \(\eta_A\), \(\eta_C\), \(R_{\text{circuit}}\), \(R_{\text{electrode}}\), \(R_{\text{membrane}}\), and \(R_{\text{electrolyte}}\) are, respectively, indicative of the equilibrium cell voltage, anodic overpotential, cathodic overpotential, resistance of circuits, electrodes, membrane and electrolyte. Since both anodic and cathodic overpotentials as well as \(iR\) drops are larger under the operation at a higher applied current density, the larger cell voltages in curves 4–6 are obtained.

Fig. 6a and b, respectively, show the Tafel plots for the HER and OER in 1 M KOH at 25\(^\circ\)C on the Fe\(_{24}\)Ni\(_{76}\) deposit before and after the bipolar investigation. Note that the side of the bipolar electrode used for hydrogen evolution is employed as the test electrode in Fig. 6a while the other side used for oxygen evolution is used as the test electrode in Fig. 6b. In Fig. 6a, the apparent activity of hydrogen evolution on Fe\(_{24}\)Ni\(_{76}\) is obviously promoted by the water electrolysis under 200 mA cm\(^{-2}\) for 2 weeks and a lower Tafel slope of the HER is obtained for this deposit after the bipolar study. A similar phenomenon is also found for this deposit when the applied current density in the bipolar study is equal to 50 mA cm\(^{-2}\). These results indicate that the electrocatalytic activity of Fe\(_{24}\)Ni\(_{76}\) for the HER can be enhanced by the cathodic polarization, likely due to the re-deposition of Fe (and Ni) ions dissolved from the anode (see results and discussion for SEM and EDX). In Fig. 6b, all Tafel curves for the OER are in parallel, implying the same electrochemical kinetics on this deposit without and with the anodic polarization. However, the activity of oxygen evolution on this deposit is slightly depressed after the bipolar investigation although the cell voltages during the bipolar studies are kept approximately constant. For Fe\(_{76}\)Ni\(_{24}\) and Fe\(_{90}\)Ni\(_{10}\), the promotion in apparent activities of hydrogen evolution after the extensive hydrogen evolution under both 50 and 200 mA cm\(^{-2}\) is not found while a minor depression in hydrogen and oxygen evolution activities is found.

From all the above results and discussion, Fe\(_{24}\)Ni\(_{76}\), Fe\(_{76}\)Ni\(_{24}\), and Fe\(_{90}\)Ni\(_{10}\) deposits are concluded to be potential candidates for the electrode materials of bipolar electrolyzers for water electrolysis.

3.3. Crystalline, morphological and compositional information of Fe–Ni deposits before and after the bipolar study

The good bipolar characteristics of Fe\(_{24}\)Ni\(_{76}\), Fe\(_{76}\)Ni\(_{24}\), and Fe\(_{90}\)Ni\(_{10}\) deposits for water electrolysis should be
attributed to the intrinsic texture of these deposits since the gas evolution activities and stability of Fe–Ni alloys are believed to link to their textural properties. In addition, the variation in textural properties of these Fe–Ni deposits after the extensive oxygen and hydrogen evolution may also provide important information in developing optimal electrode materials for the bipolar water electrolyzers. Hence, the Fe$_{24}$Ni$_{76}$, Fe$_{76}$Ni$_{24}$, and Fe$_{90}$Ni$_{10}$ deposits before and after the bipolar investigation are subjected to X-ray diffraction (XRD) analysis. Typical results for the freshly plated deposits, the deposits after extensive oxygen evolution at 200 mA cm$^{-2}$, and the deposits after extensive hydrogen evolution at 200 mA cm$^{-2}$ are shown in Fig. 7a–c, respectively. In curve 1 of Fig. 7a, for Fe$_{24}$Ni$_{76}$ there are three main peaks corresponding to Ni(111), Ni(200) and Ni(220), while no distinguishable peaks corresponding to iron or iron–nickel can be found. In addition, Ni(111) is the preferred orientation of this deposit. On the other hand, only Ni(111) diffraction peak is found on Fe$_{76}$Ni$_{24}$ and a similar result is also obtained on Fe$_{90}$Ni$_{10}$. The absence of Fe–Ni or Fe diffraction peaks indicates the fact that these metallic phases must be in the amorphous structure because iron is the main component in the Fe$_{90}$Ni$_{10}$ and Fe$_{76}$Ni$_{24}$ deposits. Note that a comparison of Fig. 7a–c reveals two facts. First, the intensity of all diffraction peaks on these XRD spectra is very low (smaller than 1200), indicating that the amount of crystalline Ni within these deposits should be low. Second, the XRD spectra of these three deposits are not significantly influenced by both anodic and cathodic polarization at very high current densities, implying their good stability for the bipolar usage.

Fig. 7. XRD patterns for: (1) Fe$_{24}$Ni$_{76}$, (2) Fe$_{76}$Ni$_{24}$, and (3) Fe$_{90}$Ni$_{10}$ deposits (a) before oxygen, (b) after oxygen and (c) hydrogen evolution at 200 mA cm$^{-2}$ for 2 weeks.
Fig. 8. SEM morphologies of: (a–c) Fe$_{24}$Ni$_{76}$, (d–f) Fe$_{76}$Ni$_{24}$, and (g–i) Fe$_{90}$Ni$_{10}$ deposits, where photographs (a, d, g), (b, e, h) and (c, f, i), respectively, indicate the freshly plated deposits, the deposits with hydrogen evolution at 200 mA cm$^{-2}$ and the deposits with oxygen evolution at 200 mA cm$^{-2}$ for 2 weeks.
in water electrolysis. Therefore, Fe$_{24}$Ni$_{76}$, Fe$_{76}$Ni$_{24}$, and Fe$_{90}$Ni$_{10}$ deposits are considered as practically potential electrode materials for the bipolar water electrolyzers.

Scanning electron microscopic (SEM) photographs of Fe$_{24}$Ni$_{76}$, Fe$_{76}$Ni$_{24}$, and Fe$_{90}$Ni$_{10}$ deposits for the freshly plated deposits, the deposits with hydrogen evolution at 200 mA cm$^{-2}$ and the deposits with oxygen evolution at 200 mA cm$^{-2}$ for 2 weeks are shown in Fig. 8a–i. From an examination of Fig. 8a, d and g, the morphologies of freshly plated Fe–Ni deposits are strongly dependent upon the composition that should result from the different electroplating conditions (e.g., different current densities and Fe$^{2+}$ concentrations in Table 1). Moreover, these three deposits show very rough surface (also, see $R_s$ data in Fig. 3). Therefore, the high activity of hydrogen evolution on these deposits is not only due to their catalytic activity but also attributable to their relatively high surface area.

From a comparison of Fig. 8a and b, the morphology of Fe$_{24}$Ni$_{76}$ is changed with the application of hydrogen evolution at 200 mA cm$^{-2}$ for 2 weeks. A similar phenomenon is also found from a comparison of Fig. 8d and e since the surface of Fe$_{76}$Ni$_{24}$ becomes rougher with a cubic morphology after this extensive hydrogen evolution. On the other hand, the morphology of all Fe–Ni deposits should be unchanged with hydrogen evolution because their structure should be not significantly affected by this cathodic reaction unless the deposition of cations dissolved in the electrolyte. This statement is supported by the fact that the surface of Fe$_{90}$Ni$_{10}$ is only covered with some white dendrites when the above cathodic polarization was carried out (see Fig. 8g and h). In addition, from a comparison of Fig. 8g and i, the morphology of both deposits is approximate the same, revealing the insignificant dissolution of Fe$_{90}$Ni$_{10}$ after the extensive oxygen evolution. Therefore, the change in morphology for Fe$_{24}$Ni$_{76}$ and Fe$_{76}$Ni$_{24}$ deposits after hydrogen evolution is reasonably attributed to the re-deposition of dissolved Fe$^{2+}$ and Ni$^{2+}$ (see below).

From a comparison of Fig. 8a and c, most spherical grains with obvious grain boundaries on the Fe$_{24}$Ni$_{76}$ surface disappeared when oxygen evolution at 200 mA cm$^{-2}$ for 2 weeks has been applied. A similar phenomenon is also visible from a comparison of Fig. 8d and f; i.e., most micro-particles on Fe$_{76}$Ni$_{24}$ disappeared when this extensive oxygen evolution was applied to Fe$_{76}$Ni$_{24}$. These results suggest that the disappearance of spherical grains on Fe$_{24}$Ni$_{76}$ and micro-particles on Fe$_{76}$Ni$_{24}$ are attributable to the anodic dissolution of surface metallic atoms after the extensive oxygen evolution, resulting in smoother deposit surfaces. These dissolved Fe$^{2+}$ and Ni$^{2+}$ should be re-deposited onto the cathode during water electrolysis, resulting in the change in morphology for Fe$_{24}$Ni$_{76}$ and Fe$_{76}$Ni$_{24}$ deposits with extensive hydrogen evolution. Thus, it is reasonable to propose that the surface of Fe$_{24}$Ni$_{76}$ covered with a seaweed-like layer (see Fig. 8b) is attributed to the re-deposition of the metal ions dissolved from the anode since the recycled anolyte and catholyte are mixed before being pumped into the cells. On the other hand, the Fe–Ni deposits should not be dissolved seriously since no obvious difference in XRD spectra was found for all deposits when they were subjected to bipolar water electrolysis at 200 mA cm$^{-2}$ for 2 weeks. Hence, their activities and kinetics for water electrolysis are not significantly influenced by the above dissolution and re-deposition phenomena (see Figs. 5 and 6). The insignificant influence of water electrolysis at 200 mA cm$^{-2}$ for 2 weeks on the bipolar performance of these deposits reveals the fact that these deposits can be practically employed as electrode materials in the bipolar water electrolyzers. In addition, the smoother surfaces of Fe$_{24}$Ni$_{76}$ and Fe$_{76}$Ni$_{24}$ with extensive oxygen evolution imply the selective dissolution of surface metal atoms. From an examination of Fig. 8, a minor change in surface morphologies for Fe$_{90}$Ni$_{10}$ and Fe$_{76}$Ni$_{24}$ deposits after the extensive water electrolysis indicates that both deposits are more stable than Fe$_{24}$Ni$_{76}$ under the anodic polarization at 200 mA cm$^{-2}$ in 5 M KOH medium.

In order to confirm the above proposal, the composition of these deposits after the bipolar test was measured and the results are shown in Table 2. Note that the Fe content on all deposits is significantly decreased after the extensive OER. In addition, an opposite result is obtained for the deposits employed as the cathode. The above results are likely due to a combination of the following reasons. First, since diffraction peaks corresponding to Ni are clearly found on these three deposits (see Fig. 7), the Fe–Ni (and Fe) phases are expected to selectively dissolve in the electrolyte under the anodic polarization while the pure Ni phase is not. Accordingly, the Ni content is enriched in the deposits after the anodic polarization. Second, Fe should be preferentially re-plated onto the cathodes during the bipolar test in comparison with the re-deposition of Ni [5–10]. This proposal is supported by the fact that the Fe content of cathodes is increased after the extensive HER in the bipolar test. The performance of these deposits in this bipolar test is not significantly influenced, indicating their application potential in the bipolar water electrolyzer although all deposits in the bipolar study show the (minor) dissolution of surface metal or alloys.

### 4. Conclusions

The redox potentials of the electroactive couple prior to the OER, the onset potentials of oxygen evolution and the electrochemically active surface area were found to strongly depend on the Fe content within the Fe–Ni deposits. The
oxygen evolution activity of Fe-Ni deposits could be generally predicted by their redox behavior prior to the OER, attributable to the intimate mixing between Fe and Ni atoms. Fe_{24}Ni_{76}, Fe_{76}Ni_{24}, and Fe_{90}Ni_{10} deposits were found to simultaneously exhibit good activities for the OER and HER. These materials exhibiting good bipolar performance for water electrolysis at high current densities could be practically employed as electrode materials for the bipolar water electrolyzers. The bipolar stability of Fe_{24}Ni_{76}, Fe_{76}Ni_{24}, and Fe_{90}Ni_{10} deposits is fairly good although minor dissolution of the anodes was found after the bipolar test.

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