Nonanomalous Electrodeposition of Zinc-Iron Alloys in an Acidic Zinc Chloride-1-ethyl-3-methylimidazolium Chloride Ionic Liquid

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The electrodeposition of iron and Zn-Fe alloys on polycrystalline nickel was investigated in the 40.0-60.0 mol % zinc chloride-1-ethyl-3-methylimidazolium chloride (EMIC) melt. Underpotential deposition of zinc on iron was observed prior to the electrodeposition of bulk zinc. Dimensionless chronocoulometric current/time transients for the underpotential deposition of zinc on iron were in good accord with the theoretical transients for the two-dimensional nucleation and/or growth of the nuclei. Zn-Fe alloys could be prepared in the potential range of the underpotential deposition of zinc on iron or the potential range where bulk deposition of zinc occurred. Energy-dispersive spectrometry data indicated that the composition of the Zn-Fe alloys was dependent upon the deposition potential and the iron(II) concentration in the plating solution. The morphologies of the Zn-Fe codeposits were examined by scanning electron microscopy.

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Zn-Fe alloy coating is an excellent material for industrial applications because of its excellent corrosion resistance, mechanical performance, paintability, and weldability. There have been many reports that discuss the electrodeposition of Zn-Fe alloy from different aqueous solutions. Theses reports show that the electrodeposition of Zn-Fe alloy in aqueous is classified as anomalous codeposition because the presence of iron inhibits the electrodeposition of the more noble metal (iron) and the less noble zinc is preferentially deposited. As a result, the Zn/Fe ratio in the deposit is higher than in the electrolyte, and alloys with high iron content are difficult to prepare. Due to such anomalous behavior, the codeposition of Zn-Fe in these solutions does not involve underpotential deposition (UPD) of Zn on Fe, although UPD of Zn at an Fe substrate in iron(II)-free solutions is known. Recently, water stable low temperature dialkylimidazolium chlorozincate ionic liquids resulting from the combination of zinc chloride and 1-ethyl-3-methylimidazolium chloride (EMIC) have been prepared. The Lewis acidity of the ZnCl2-EMIC ionic liquids can be adjusted by varying the molar ratio of ZnCl2 to EMIC in the ionic liquids. In general, ionic liquids that have a ZnCl2/EMIC molar ratio higher than 0.5:1 are acidic because they contain Lewis acidic chlorozincate species such as ZnCl4−, ZnCl52−, and ZnCl64−. On the other hand, ionic liquids that have a ZnCl2/EMIC molar ratio lower than 0.5:1 are considered as basic. The electrochemical window of the ZnCl2-EMIC ionic liquid is dependent upon the Lewis acidity of the melt. For example, increasing the Lewis acidity of the ionic liquid by increasing ZnCl2 mole fraction shifts the cathodic limit, which is due to the deposition of Zn, positively. This means that the potential where Zn can be electrodeposited can be controlled by adjusting the acidity of the melt. The ZnCl2-EMIC ionic liquids have been studied for the electrodeposition of zinc and zinc-containing alloys. These studies revealed that complications associated with hydrogen evolution that often occur in aqueous bath are eliminated in the chlorozincate ionic liquids because the ionic liquids are aprotic solvents. The anomalous codeposition behavior of Zn-Fe in aqueous solution is largely attributed to the formation of Zn(OH)2+ which adsorbs preferentially on the electrode surface and inhibits the effective reduction of iron species. One approach to circumvent this anomaly is to employ the nonaqueous baths that generate no hydroxide. In view of this, the ZnCl2-EMIC ionic liquid should provide a good candidate for nonanomalous codeposition of Zn-Fe alloy because Zn(OH)+ would not form in this media. The aim of this work was to study the behavior of Zn-Fe alloy codeposition by means of cyclic voltammetry in the acidic ZnCl2-EMIC ionic liquid. The electrochemical behavior of zinc and iron in this ionic liquid appeared to be very different from those observed in aqueous solution. In the ZnCl2-EMIC ionic liquid, no anomalous deposition was observed for the deposition of Zn-Fe alloys and the alloys could be obtained via UPD of Zn at Fe.

Experimental

Apparatus.—All electrochemical experiments were conducted inside a vacuum atmosphere glove box filled with dry nitrogen. The moisture and oxygen level in the box was kept lower than 1 ppm. An EG&G model 273A potentiostat/galvanostat controlled with EG&G model 270 software was employed to conduct the electrochemical experiments. A three-electrode electrochemical cell was used for the electrochemical experiments. The electrochemistry of iron(II) was investigated at polycrystalline nickel (geometric area = 0.08 cm2), tungsten (geometric area = 0.08 cm2), and glassy carbon (GC; geometric area = 0.07 cm2) working electrodes. The nickel electrode was received from BAS, and the other two electrodes were fabricated by sealing a piece of tungsten rod (Stream, 99.99%), or a GC rod (Tokai, GC20), into Pyrex tubes followed by cutting off the tip of the tube to expose the electrode surface. All the electrodes were polished successively with increasingly finer grades of emery paper followed by silicon carbide grit, and finally to a mirror finish with aqueous slurry of 0.05 μm alumina, rinsed with distilled water, and dried under vacuum. The counter electrode was a zinc spiral in a fritted glass tube that contained pure ZnCl2-EMIC melt of the same composition as the bulk solution. The reference electrode was a Zn wire placed in a separate fritted glass tube containing pure 50.0-50.0 mol % ZnCl2-EMIC melt. Bulk electrodeposits were prepared on nickel foils (0.5 × 0.5 cm, Aldrich 99.99%). Approximately the same charge density was used for all the deposition experiments. Because the ZnCl2-EMIC ionic liquid does not react violently with water, the residual ionic liquid on the electrodeposits-coated nickel foil electrode was removed easily by rinsing with warm (−50°C) deionized (DI) water following each deposition experiment. A Hitachi S-4200 field effect scanning electron microscope (SEM) with energy-dispersive spectrometer (EDS) working at 15 kV was used to examine the surface topography and the elemental compositions of the electrodeposits.

Chemicals.—The EMIC was prepared and purified according to the method described in the literature. The ZnCl2-EMIC melts

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were prepared in the glove box by mixing proper amounts of ZnCl$_2$ from Aldrich and used as received.

...solutions. Typical stationary staircase cyclic voltammograms in this figure exhibits a reduction wave (c$_1$) and an associated oxidation wave (a$_1$). The magnitude of wave a$_1$ increased as the scan rate was increased. Each of the voltammograms is shown in Fig. 1. These voltammograms were scanned cathodically from 0.40 to -0.20 V and held at this potential for 0, 10, 20, 40 s before scanning in the reverse direction. Each of the voltammograms in this figure exhibits a reduction wave (c$_1$) and an associated oxidation wave (a$_1$). The magnitude of wave a$_1$ increased as the deposition time at -0.05 V increased, indicating that the product resulting from wave c$_1$ accumulated at the electrode surface. Controlled potential electrolysis experiments using nickel flag electrodes were conducted with iron(II) solutions at -0.05 V in attempt to obtain the reduction product of wave c$_1$. At the end of each electrolysis experiment, the electrode surface was coated with a layer of black deposits. EDS analysis of the deposits revealed that iron metal was the only product of wave c$_1$ and no zinc was detected in the deposits. Thus, waves c$_1$ can be attributed to the deposition of iron and wave a$_1$ is due to the anodic stripping of the deposited iron. Integration of the deposition and stripping waves appearing in Fig. 1 indicates that virtually 100% of the deposited iron was recovered during oxidation. The fact that zinc was not deposited before iron suggests that anomalous deposition is not occurring in this ionic liquid system even though the zinc(II) concentration is substantially higher than that of iron(II).

It was noted that the CVs in Fig. 1 did not exhibit the current loop that is typical for an electrodeposition processes requiring nucleation overpotential. Thus, the electrodeposition of iron at nickel electrode did not seem to be complicated by nucleation. However, cyclic voltammetric data collected in Table I show that the peak potential, $E_{p}^{c}$, shifted negatively as the scan rate increased, and the peak potential/half-peak potential separation, $|E_{p}^{c} - E_{p}^a|$, which also increased with increasing scan rate, was larger than the theoretical value, 0.77RT/2F = 0.12 mV, that was expected for a reversible deposition of metals on solid electrodes at this temperature.$^{17}$ These results suggest that the deposition of iron at nickel is a quasi-reversible process.

Iron-zinc alloy deposition at nickel electrode.—Figure 2 shows the CVs of the Fe(II) solution recorded at the same nickel electrode under the same conditions as those in Fig. 1, except that the potential scan was extended to a more negative potential before the onset of the bulk Zn deposition and held at this potential for different time periods before the potential scan was reversed. In this figure, a new reduction wave c$_2$ appeared at about -0.1 V, and a new oxidation wave a$_2$ became apparent as the potential holding period at wave c$_2$ increased. Examination of the EDS data of the electrodosposits obtained at wave c$_2$ reveals that they contained both iron and zinc, indicating that zinc was deposited at wave c$_2$. Because wave c$_2$ occurred at a potential more positive than the onset of the bulk zinc deposition (see inset in Fig. 1 and Fig. 9) this wave may have arisen from the UPD of zinc. UPD is normally expected when the work function, $\phi$, of the deposited metal is fairly smaller than that of the substrate metal. Even the work functions of zinc ($\phi_{Zn} = 4.3$ eV) and iron ($\phi_{Fe} = 4.5$ eV)$^{11}$ are fairly close, and the UPD of zinc at iron in aqueous solution has been reported in the literature.$^{5}$ To further determine if the UPD of zinc indeed occurred at iron wave c$_2$, CVs were recorded at an iron-coated nickel electrode in a iron(II)-free 40.0-60.0 mol % ZnCl$_2$-EMIC ionic liquid. The voltammmograms are shown in Fig. 3. Because UPD of zinc may also have occurred at the nickel electrode, a CV recorded for the same ionic liquid at a bare nickel electrode is also shown in Fig. 3 for comparison. The voltammmograms in Fig. 3 clearly indicate that no reduction wave was observed at the bare nickel electrode whereas wave c$_2$ was evident at the iron-coated electrode at the same potential as in...
Fig. 2. The inset in Fig. 3 shows that a plot of the peak current vs. the scan rate is linear, indicating that, in consistent with a UPD process, this reaction is surface-constrained. Integration of the current under the wave $a_2$ in Fig. 3 reveals that approximately 4 monolayers of zinc were deposited under the conditions of Fig. 3. This high value may partially be a result of the roughness of the electrode surface. Taken together, the above results strongly suggest the UPD of Zn on Fe. However, because the work functions of Zn and Fe are very close, the potential difference between the UPD and bulk deposition of Zn is also very small.

Linear scan stripping voltammograms acquired for electrodeposits that were produced on an iron electrode at the zinc UPD potential with different deposition periods in the 40.0-60.0 mol % ZnCl$_2$-EMIC ionic liquid are shown in Fig. 4. Also shown in Fig. 4 is a stripping voltammogram of the pure iron substrate (deposition time = 0 s). Each of these voltammograms exhibits two separated oxidation waves ($a_1$ and $a_2$) result from the deposits. The fact that these two oxidation waves occurred at potentials different from those of pure iron and pure zinc suggests that the deposited zinc formed an alloy with iron. Wave $a_1$ corresponds to the stripping of the zinc-rich alloy because it occurs at the potential closer to the stripping of bulk zinc (see below). Wave $a_2$, which overlaps partially with the stripping wave of pure iron substrate, is contributed to the oxidation of iron-rich alloy. Figure 4 also shows that both waves $a_2$ and $a_1$ increased with increasing deposition time. Analyzing the amount of charge under the stripping waves shows that the accumulated charge grew with deposition time and leveled off eventually (inset in Fig. 4). In addition, the accumulated charge is much greater than that for tens and hundreds of zinc monolayers. Because the UPD was a two-dimensional (2-D) process, 3-D growth of the deposit on the substrate surface could not occur under the UPD conditions. Thus, the growing of the deposition charge with deposition time, as is illustrated in Fig. 4, suggests that zinc adatoms diffused into bulk iron forming the Zn-Fe alloy, rather than staying on the surface. An EDS line scan of the cross section of a typical deposit sample that was obtained at −0.1 V at an iron substrate in the pure ZnCl$_2$-EMIC ionic liquid is shown in Fig. 5. This figure shows that the Zn content in the sample extended into the Fe substrate and changed with the distance from the electrode surface, confirming the diffusion of Zn into Fe. The diffusion of Zn into Fe observed in this study is interesting because such phenomenon is often seen in high temperature molten salts but is rarely seen at room temperature. A recent example of alloy formation and growth by solid diffusion at ambient temperature was discussed in the study of underpotential deposition of Cd on Au.19

Previous published studies of UPD in aqueous solution have shown that UPD could be complicated by 2-D nucleation and growth process. Although a number of papers have been published describing UPD in ionic liquids, the nucleation process accompanying the UPD was not studied in those reports. Thus, it is of interest to see if the UPD of zinc at iron in this melt involves a nucleation and growth process. Chronoamperometry experiments were performed to study the nucleation process. In those experiments, the potential of an iron working electrode was stepped from an initial value, where no reduction of zinc took place, to potentials around wave $c_2$ to initiate nucleation and growth. Typical current/time transients recorded from these experiments are presented in Fig. 6. All of these transients show clearly the main features associated with a 2-D nucleation process; after the decay of a sharp
electrode double layer charging current, the faradaic current increased due to the nucleation and growth of zinc nuclei. This rising current eventually decays after it reaches a current maximum, $i_m$ at time $t_m$. The current maximum shifted to shorter times when the applied potential was made more negative. There are two limiting cases of the general model for 2-D nucleation and growth. In the first, denoted instantaneous nucleation, the number of nuclei is constant over the whole time of the growth process. In the second case, known as progressive nucleation, new nuclei are formed at all times during the growth process. A method for differentiating between these two models is to express the experimental current/time transients in normalized dimensionless forms to generate plots of $(i/i_m)$ vs. $(t/t_m)$. The experimental plots are compared to the theoretical dimensionless current transients derived for 2-D nucleation/growth:

$$ (i/i_m) = (t/t_m) \exp\left[-(r^2 - t_m^2)/2t_m^2\right] $$

in the case of instantaneous nucleation, and

$$ (i/i_m) = (t/t_m)^2 \exp\left[-2(t^3 - t_m^3)/3t_m^3\right] $$

in the case of progressive nucleation. The experimental and theoretical plots are shown in Fig. 7. This figure shows that the UPD of zinc on iron substrates fits better to the 2-D instantaneous nucleation/growth model. However, it should be noted that in this study, the nucleation was studied at a polycrystalline surface, and the behavior may not have represented the behavior at the well-defined surface of a single crystal electrode. The UPD nucleation at the single crystal surface will be studied further in the future.

Figure 8 shows the CVs collected at a nickel electrode in the 40.0-60.0 mol % ZnCl$_2$-EMIC ionic liquid containing various amounts of iron(II). As expected, the deposition current of iron (wave $c_1$) increased with increasing iron(II) concentration. Furthermore, wave $c_2$ also increased with increasing iron(II) concentration because, when Zn was deposited on Fe through UPD at this potential, more Fe deposits were continuously produced at the same time to provide new surface for the UPD of zinc to occur. Also seen in
Fig. 8 is that whereas wave a1 grew significantly with increasing iron(II) concentration, wave a2 did not. Because wave a1 corresponds to the stripping of the iron-rich Zn-Fe alloy, the growing of wave a2 indicates that the iron content in the Zn-Fe alloy increased with iron(II) concentration.

Figure 9 shows a typical CV of the iron(II) solution recorded at the same nickel electrode under the same conditions as those in Fig. 1, except that the cathodic potential scan was reversed at a more negative potential where the bulk deposition of zinc occurred (wave c1). For comparison, the background CV recorded for a pure 40.0-60.0 mol % ZnCl2-EMIC ionic liquid without iron(II) is also included in this figure. Examination of Fig. 9 reveals that the onset of the deposition of bulk zinc (wave c1) in the iron(II) solution shifted to a potential more positive than that is observed in the pure ZnCl2-EMIC melt. In addition, anodic stripping wave of the bulk zinc deposit that is observed in the voltammogram of the pure ZnCl2-EMIC melt is absent in the voltammogram of the iron(II) solution, but stripping waves a1, a2 and a2' are apparent in the voltammogram of the iron(II) solution. These phenomena indicate that alloy formation between the electrodeposited zinc and iron occurred. Because deposition of bulk zinc occurred at wave c1 and the zinc(II) concentration was considerably higher than that of iron(II) in the solution, electrodeposits obtained at wave c1 contained more zinc-rich Zn-Fe alloy than the deposits obtained at the zinc UPD potential (wave c2). This is indicated by the relatively higher wave a2 (in comparison to wave a2') shown in Fig. 9.

Staircase CVs for Fe(II) solution were also recorded at polycrystalline tungsten and GC electrodes. The results show that at tungsten electrode, the reduction of Fe(II) shifted negatively to approximately the potential where UPD of zinc at iron occurred. Further shifts of the reduction of Fe(II) was observed at the GC electrode; Fe(II) was not reduced until the bulk reduction of Zn(II) occurred. These results suggest that the reduction of iron at tungsten and GC electrodes is kinetically less favorable than at the nickel electrode. No further study was carried out at these two electrodes.

Preparation of Zn-Fe alloy electrodeposits.—Zn-Fe codeposits were prepared with constant potential electrolysis on nickel substrates from the 40.0-60.0 mol % ZnCl2-EMIC ionic liquid containing iron(II). Following each deposition experiment, the deposits-coated electrode was rinsed with warm DI water to remove residual ionic liquid and dried. The compositions of the deposits were analyzed with EDS, and the surface morphologies were examined with
SEM, EDS detected no trace of chlorine in the deposits, indicating that there was no residual ionic liquid remaining in the deposits. Figure 10 shows plots of iron content in the electrodeposits that were obtained at different deposition potentials from ionic liquid solutions containing different amounts of iron(II). At each iron(II) concentration, the iron content in the deposits decreased slowly with decreasing applied potential in the zinc UPD potential range, and decreased more rapidly when the applied potential approached the bulk zinc deposition potential. This behavior suggests that the bulk zinc deposition proceeded at a faster rate than the zinc UPD. Figure 10 also shows that at each applied potential, the iron content in the deposits increased with increasing iron(II) concentration in the plating bath. Because the concentration of zinc(II) was in large excess over the iron(II) concentration in the plating bath, the dependency of the deposits composition on the iron(II) concentration suggests that the zinc codeposition process was kinetically limited in comparison with the deposition of iron. Similar behavior has been reported for the electrodeposition of Al-Ni and Al-Co alloys in acidic AlCl₃-EMIC ionic liquids.

Typical morphologies of Zn-Fe electrodeposits are shown in Fig. 11. Deposits prepared at the onset potential of the zinc UPD (containing 76 atom % in iron) consist fine particles forming dense and compact nodules (Fig. 11a). When the iron content in the deposits decreased to 47 atom % the deposits turned into pyramidal shape particles (Fig. 11b). Further decreasing the iron content in the deposits made the hexagonal thin plates even more evident (Fig. 11c). These observations are similar to those reported in the literature.

Conclusions

Cyclic voltammetric data shows that the electrochemical reduction of iron(II) in the acidic 40.0-60.0 mol % ZnCl₂-EMIC ionic liquid on polycrystalline nickel substrate occurred at a potential more positive than the reduction of zinc(II). The electrodeposition of iron on nickel was a quasi-reversible charge transfer process but was not complicated by overpotential nucleation. At potential more negative than the deposition of iron, UPD of zinc on iron was evident. Analysis of the chronoumperometric data shows that the UPD of zinc on iron involved the instantaneous 2-D nucleation/growth process. The diffusion of the deposited zinc into iron was indicated by the fact that the charge accumulated during the UPD of zinc on iron substrate was much more than that required for monolayer deposition. EDS analysis indicates that Zn-Fe alloys with various compositions can be prepared in this ionic liquid by controlling the deposition potential and iron(II) concentration. SEM micrographs
show that the morphologies of the Zn-Fe codeposits are similar to those reported in literature. Because ZnCl₂-EMIC ionic liquid does not generate hydroxide ions, the Zn-Fe alloys in the ionic liquid was not produced by anomalous deposition and Zn-Fe alloys of high iron content can be prepared more easily than in aqueous plating baths.

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