Electrodeposition of Cadmium from Lewis Basic Hydrophobic Room-temperature Ionic Liquid

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ABSTRACT
Electrodeposition of cadmium (Cd) was investigated in a hydrophobic room-temperature ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) using CdCl₂ as the source of Cd species in the presence of excess chloride ion. Raman spectroscopy and potentiometric measurement suggested formation of a cadmium tetrachlorocomplex, [CdCl₄]²⁻, in BMPCl/BMPTFSA. Cyclic voltammetry showed the possibility of electrochemical reduction from [CdCl₄]²⁻ to Cd(0) with interesting unusual electrochemical behavior, probably derived from the potential-dependent electric double layer structure typical to the ionic liquid. Electrodeposition of Cd was performed by potentiostatic electrolysis and the deposits were characterized by X-ray diffraction, energy dispersive X-ray analysis and scanning electron microscopy.

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1. Introduction
Room-temperature ionic liquids (ILs) have been considered to be the alternative electrolytes for electrodeposition of metals and metal alloys due to their such advantageous characteristics as wider electrochemical potential window, less flammability, less volatility, and wider usable temperature range, as compared with conventional aqueous and organic electrolytes. Historically, chloroaluminate/zincate ILs have been explored for the electrodeposition of various metals and alloys. However, simultaneous deposition of aluminum/zinc is a common phenomenon during electrodeposition of metals using chloroaluminate/zincate ILs at the negative potential region. Furthermore, the high reactivity of these chloroaluminate/zincate ILs against moisture prevents their practical application. Therefore, hydrophobic ILs have drawn much attention as the electrolytes for electrodeposition of metals and their alloys due to their high stability against moisture and water. Among hydrophobic non-chloroaluminate/zincate ILs, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) has not only little reactivity towards water and moisture but also high cathodic stability, low melting point, and acceptable conductivity. Therefore, BMPTFSA has been considered as a potential electrolyte for electrodeposition of various metals and alloys.

Cadmium electroplating has been utilized for manifold applications, especially in the automobile, marine, and aerospace field due to its high corrosion resistance and superior lubricity. Numerous studies are available in the literature on the electrochemical behavior of cadmium in aqueous solutions. The effects of electrode material, bath composition, and additives on cadmium reduction mechanism have been analyzed extensively. However, post-baking is sometimes required to prevent the hydrogen embrittlement caused by the negative reduction potential of cadmium species in aqueous solutions. Thus, aprotic ILs are expected to be one of the promising alternatives to the conventional aqueous media because hydrogen evolution does not occur in aprotic ILs. Besides, there are a few reports in the literature on the electrochemical behavior of cadmium in ILs. Dymek et al. investigated the possibility of a cadmium bromine rechargeable battery using basic EMICl-AlCl₃ (EMI⁺ = 1-ethyl-3-methylimidazolium). Noel and Osteryoung explored CdCl₂/[CdCl₄]²⁻ as a buffer for neutral EMICl-AlCl₃. Chen and Sun investigated the electrodeposition of cadmium species in basic EMICl-CIF₃. Huang and Sun reported the electrodeposition of cadmium and zinc in Lewis acidic EMICl-ZnCl₂. Pan and Freyland investigated the under potential deposition of Cd on a gold electrode in Lewis acidic BMICl-AlCl₃ (BMI⁺ = 1-butyl-3-methylimidazolium). In the previous studies, mostly, Cd electrodeposition has been investigated in chloroaluminate/zincate ILs. Recently, we demonstrated the electrochemical behavior of Cd in BMPTFSA using Cd(TFSA)₂ as the source of Cd species. However, Cd(TFSA)₂ is not always suitable for practical applications because Cd(TFSA)₂ is unavailable commercially. Thus, it is expected that a more common cadmium salt, CdCl₂, can be used as the Cd source by adding BMPCl into BMPTFSA, as reported in basic chloroaluminate/zincate ILs while there’s no report on the electrochemical behavior of the chlorocomplex of Cd in BMPTFSA. In the present study, electrodeposition of Cd was investigated in BMPTSA in the presence of excess chloride ion. The coordination environment of the dissolved Cd species was also studied using Raman spectroscopy and potentiometric measurement.

2. Experimental
1-Methylpyrrolidine (Tokyo Chemical Industry, >98%) was reacted with butyl bromide (Tokyo Chemical Industry, >98%) in dehydrated acetonitrile (Wako Pure Chemical Industries, 99.5%) in order to synthesize BMPBr. The reaction was carried out at room temperature under N₂ atmosphere. BMPBr was purified by recrystallization and finally stored after vacuum drying at 100°C for 24 hours. Proton nuclear magnetic resonance spectroscopy showed the signals assignable only to BMP⁺ except very weak signal of water. Then, BMPBr was used for the metathesis reaction with
LiTfSA (Solvay) in deionized water in order to prepare BMPTFSA. Dichloromethane (Junsei Chemical, 99.5%) was used to extract BMPTFSA and then dried under vacuum at 120°C for 24 hours. The water content in the synthesized BMPTFSA was below 10 ppm, which was determined by Karl Fischer titration (Metrohm, 831 KF Coulometer). BMPCl, used as the source of Cl⁻, was prepared by the reaction of 1-methylpyrrolidine and butyl chloride (Wako Pure Chemical Industries, >98%) in dehydrated acetonitrile at 75°C for 24 hours.26,27 BMPCl was purified and stored in the same way, as described for BMPBr. Anhydrous CdCl₂ (Wako Pure Chemical Industries, 95%), as the source of Cd species, was used as received. A colorless electrolyte was obtained by dissolving CdCl₂ into BMPCl/BMPTFSA. Cd(TFSA)₂ was prepared as described earlier.34 BMIFSA (Kanto Chemical) and BMICl (Kanto Chemical) were used as received. The electrolyte containing CdCl₂ in BMICl/BMIFSA was prepared in the same way as BMPTFSA. An argon-filled glovebox (Miwa MFG, DBO-1K-SH) was used for storing and handling all the hygroscopic reagents. The solubility of CdCl₂ was determined by measuring the concentration of Cd in the supernatant BMPTFSA containing excess amount of CdCl₂ in the absence and presence of 0.15 M BMPCl using inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent Technologies, 5100).

A Teflon-made air-tight three-electrode cell was used for conducting the electrochemical and electrodeposition experiments. For the electrochemical measurements, a glassy carbon (GC, Tokai Carbon, GC-20SS), platinum (Pt), and cadmium (Cd) disk electrode were used as the working electrodes after mirror polishing. The geometric surface areas of the GC and Pt working electrode were 7.07 × 10⁻² cm² and that of the Cd working electrode was 3.14 × 10⁻² cm². The counter electrode was a platinum wire. Whereas, a GC substrate (1.54 cm²) after mirror polishing and Cd (Nillaco) sheet were used as a working and counter electrode, respectively, for the electrodeposition experiments. A silver wire immersed in BMPTFSA containing 0.1 M AgCl₂SO₄ (Aldrich, >99.0%) isolated by porous Vycor glass from the main electrolyte was used as a reference electrode in all the electrochemical and electrodeposition experiments. The potential of ferrocenium/ferroence (Fc⁺/Fc) was −0.43 V versus this Ag|AgCl reference electrode.28 All electrochemical experiments were carried out using potentialstat/galvanostat (Hokuto Denko, HABF5001, HSV-110, or HZ-7000). After electrodeposition, the electrodes were washed with acetone and dried in open air. Characterization of the deposits was performed using an X-ray diffractometer (XRD, Rigaku, MiniFlex600). The Raman spectra of BMPTFSA containing excess Cl⁻ with and without CdCl₂ were obtained by a Raman spectrometer (Renishaw, InVia Raman Microscope) using the excitation light with the wavelength of 785 nm.

3. Results and Discussion

3.1 Dissolved species of Cd(II) in BMPCI/BMPTFSA

The solubility of CdCl₂ in BMPTFSA at 25°C was found to be less than the lower detection limit of ICP-OES, indicating CdCl₂ could be regarded as insoluble. On the other hand, CdCl₂ was soluble in 0.15 M (4.4 mol%) BMPCI/BMPTFSA to give a colorless IL. The solubility of CdCl₂ in 0.15 M BMPCI/BMPTFSA at 25°C was estimated to be 0.051 M, which was corresponding to about one third of BMPCI in the ionic liquid.

Electrochemical behavior of metal ion species in ILs shows significant dependence on their solvation state. The coordination environment of Cd(II) in several ILs has been reported in literature.18,21,24,25 In some basic ILs having free Cl⁻, Cd(II) cations are reported to form a tetrachlorocomplex, [CdCl₄]²⁻. Since CdCl₂ dissolved in BMPTFSA in the presence of excess Cl⁻, [CdCl₄]²⁻ was expected to form also in the TFSA⁻-based IL. Figure 1 shows the Raman spectra of 0.6 M BMPCI/BMPTFSA with and without 0.2 M CdCl₂. An intense Raman band found at 279 cm⁻¹ both with and without addition of CdCl₂ was assigned to the Cd₂ rocking ρ(CF₃) vibration of free TFSA⁻.30 On the other hand, 0.6 M BMPCI/BMPTFSA containing 0.2 M CdCl₂ gave a Raman band at 263 cm⁻¹ assignable to ν₁ for tetrahedral [CdCl₄]²⁻, which was reported to be found at 262 cm⁻¹ in basic EMICl-AlCl₃ and at 265 cm⁻¹ in a molten potassium tetrachloroaluminate.29,31 Therefore, the dissolved species of Cd(II) in BMPTFSA in the presence of excess Cl⁻ was confirmed to be [CdCl₄]²⁻.

The coordination number of Cd(II) in BMPCI/BMPTFSA was further investigated electrochemically by measuring the open circuit potentials (OCPs) of a Cd electrode immersed in 0.15 M BMPCI/BMPTFSA containing CdCl₂ at various concentrations. The concentrations of CdCl₂ were varied between 0.01 to 0.05 M. In each case, a stable OCP was observed after immersing the Cd electrode into the IL, indicating a redox equilibrium between a cadmium chlorocomplex and the Cd electrode was attained as follows,

\[
[CdCl₂x+\text{Cl}^-]^{x+} + 2e^- \rightarrow \text{Cd} + (2 + x)\text{Cl}^- \quad (1)
\]

where \(x\) is the number of Cl⁻ taken up by each CdCl₂. The corresponding Nernst’s equation of the above redox reaction (Eq. (1)) can be written as:32

\[
E = E^0 + \frac{2.303RT}{2F} \log \left[\frac{[CdCl₂x+\text{Cl}^-]^{x+}}{[\text{Cl}^-]^{x+}}\right] \quad (2)
\]

where, \(E\) is the electrode potential, \(E^0\) is the formal potential of Cd(II)/Cd, \(R\) is the gas constant, \(T\) is the absolute temperature, and \(F\) is the Faraday constant. The Nernst’s plot according to the Eq. (2) gave a straight line with a slope of 29 mV decade⁻¹, which was close to that of the theoretical value for a two electron transfer process at 25°C (30 mV decade⁻¹),33 only when \(x\) was 2, as shown in Fig. 2, indicating formation of a Cd tetrachloroaluminate, [CdCl₄]²⁻, according to Eq. (3) in 0.15 M BMPCI/BMPTFSA.

\[
\text{CdCl}_2 + 2\text{Cl}^- \rightarrow [\text{CdCl}_4]^{2-} \quad (3)
\]

The formal potential of [CdCl₄]²⁻/Cd was calculated to be −2.01 V, which was close to that reported in basic EMICl-AlCl₃ (around −1.9 V vs. Ag|AgCl in BMPTFSA).30

3.2 Electrochemical behavior of Cd(II) in BMPCI/BMPTFSA

Figure 3 shows the cyclic voltammograms of a GC electrode in 0.15 M BMPCI/BMPTFSA containing 0.05 M CdCl₂ with various
scan rates at 25°C. Interesting unusual electrochemical behavior was observed with a small cathodic current peak around $-2.35 \text{ V}$ during the cathodic scan followed by a cathodic and anodic current peak during the anodic scan. The small cathodic current peak around $-2.35 \text{ V}$ during the cathodic scan was prominent at relatively slower scan rates probably because the number of Cd nuclei formed on the electrode surface increased with a decrease in the scan rate. Electrodeposition of Cd was attempted by potentiostatic cathodic reduction at $-2.35 \text{ V}$ and the obtained deposit was confirmed to be metallic Cd by the EDX spectrum and XRD pattern, as shown in Fig. 4. Therefore, the observed peak at $-2.35 \text{ V}$ was assigned to reduction of $[\text{CdCl}_4^{2-}]^{2-}$ to metallic Cd. The reduction potential of $[\text{CdCl}_4^{2-}]^{2-}$ was more negative than that of Cd(II), which was considered to be $[\text{Cd(TFSA)}_3]^{+}$, in BMPTFSA without free Cl$^-$. The formal potential for $[\text{Cd(TFSA)}_3]^{+}$/Cd in BMPTFSA without free Cl$^-$ was also determined to be $-0.71 \text{ V}$ from the OCP of a Cd electrode in BMPTFSA containing Cd(TFSA)$_2$ at different concentrations, as shown in Fig. 5. The slope of the regression line in Fig. 5 was $28 \text{ mV decade}^{-1}$, which was in good agreement with the two-electron transfer reaction at 25°C, as represented by the following Nernst's equation:

$$E = E^{\theta} + \frac{2.303RT}{2F} \log C_{\text{Cd(II)}}$$

where, $C_{\text{Cd(II)}}$ is the concentration of $[\text{Cd(TFSA)}_3]^{+}$. Thus, the difference in the formal potentials of the $[\text{Cd(TFSA)}_3]^{+}$/Cd redox couple in BMPTFSA with and without excess Cl$^-$ could be ascribed.
The unusual electrochemical behavior found in Fig. 3 is considered attributed to a consequence of such a negative reduction potential of \([\text{CdCl}_4]^{2-}\). The cathodic current peak during the anodic scan was observed in all the scans rates while the smaller cathodic current peak was observed during the preceding cathodic scan, suggesting nucleation and crystal growth process were hindered during the cathodic scan due to the potential-dependent electric double layer structure. At the negative potential region, accumulation and orientation of the cations of ILs on the electrode surface were reported by several researchers.\(^{35}\) Recently, Magnusen et al. investigated the potential dependent adlayer structure of the IL/electrode interface using BMPTFSA.\(^{36}\) The structure of the inner layer of BMP\(^{+}\) cations was found to depend on the applied potential and became more compact at the more negative potential region. At the negative potential, where \([\text{CdCl}_4]^{2-}\) is reduced, strong attraction and high crowding of BMP\(^{+}\) cations at the electrode surface can hinder nucleation and crystal growth of cadmium during the cathodic scan. On the other hand, the degree of interaction between BMP\(^{+}\) cations and the electrode surface is supposed to decrease during the anodic scan, resulted in promotion of reduction of \([\text{CdCl}_4]^{2-}\) on the Cd nuclei and enlargement of the cathodic current peak during the anodic scan. A recent report by Sun et al. also shows such anomalous voltammetric behavior in BMPDCA (DCA\(^{-}\) = dicyanamide) containing InCl\(_3\) caused by the adsorption/desorption of BMP\(^{+}\).\(^{37}\) On the other hand, the broad anodic current peak during the anodic scan was ascribed to stripping of the deposited Cd. The cadmium stripping process was probably affected by the Cl\(^{-}\) concentration near the electrode surface. The Cl\(^{-}\) concentration adjacent to the working electrode was considered to decrease readily due to the consumption of four Cl\(^{-}\) by each Cd\(^{2+}\) during the stripping process in order to form the stable chlorocomplex. Thus, further stripping of Cd could be hindered until diffusion of sufficient Cl\(^{-}\) to the electrode surface from the bulk. Such a broadness of Cd dissolution peak in basic ILs has been also discussed in the literature.\(^{21}\)

The effect of temperature on the reduction process of \([\text{CdCl}_4]^{2-}\) was also investigated. Figure 6 shows the cyclic voltammograms of a GC electrode in 0.15 M BMPCl/BMPTFSA containing 0.05 M CdCl\(_2\) at different temperatures. The overpotential for the reduction of \([\text{CdCl}_4]^{2-}\) was found to decrease with elevating temperature probably due to ease of nucleation. At the higher temperature, a faster charge transfer process may also be a reason for lowering of the overpotential. The cathodic peak current density during the cathodic scan was also found to increase with elevating the temperature probably due to the facilitated nucleation and crystal growth process in addition to an increase in the mobility of the electroactive species in the IL. The effect of temperature on the electric double layer structure of IL may also affect the reduction overpotential and current density. At the higher temperatures, reduction of \([\text{CdCl}_4]^{2-}\) could be facilitated due to the thermal perturbation of the cations and anions accumulated on the electrode surface. However, the cathodic current peak during the anodic scan was found at all the temperatures, as can be seen in Fig. 6. The cathodic current during the cathodic scan in the cyclic voltammogram in the Fig. 6 was almost negligible while a cathodic current during the cathodic scan was observed at the potentials more negative than \(-2.3 \text{ V}\) in the cyclic voltammogram at 50 mV s\(^{-1}\) in Fig. 3. The cathodic current was observed probably because the electrode surface was changed by repetition of cyclic voltammetry on the electrode at different scan rates although the every scan was conducted after anodic dissolution of Cd deposited during the preceding scan.

Figure 7 shows the cyclic voltammograms of a Pt and Cd electrode in 0.15 M BMPCI/BMPTFSA containing 0.05 M CdCl\(_2\). The cyclic voltammograms of the Pt and Cd electrode were similar to that of the GC electrode (Fig. 3) along with the cathodic and anodic current peaks during the anodic scan. During the cathodic scan, the Pt electrode showed an increase in current at the potentials more negative than \(-2.3 \text{ V}\) without any obvious current peak, whereas the Cd electrode showed a well-shaped cathodic current peak around \(-2.15 \text{ V}\). Electrodeposition of a metal on the same metal substrate requires no nucleation, resulted in a decrease in the overpotential for electrodeposition process. Although the reduction overpotential on the Cd substrate was smaller than that on GC and Pt, the cathodic current peak during the anodic scan was found. Furthermore, the cyclic voltammogram of a GC electrode in a different IL, BMICl/BMITFSA, also showed the similar electrochemical behavior with cathodic current during the anodic scan, as shown in Fig. 8. However, the cathodic current peak during the cathodic scan in BMICl/BMITFSA was larger than that in BMPCI/BMPTFSA (Fig. 3), suggesting the difference in the interfacial structures (solvation layers) and the mobility of Cd species with the change of organic cation of ILs. A multilayer architecture is known to form by the ions of the IL at the IL/electrode interface. The multilayer architecture has been reported to change with the change.

**Figure 6.** Cyclic voltammograms of a GC electrode in 0.15 M BMPCl/BMPTFSA containing 0.05 M CdCl\(_2\) at different temperatures. Scan rate: 50 mV s\(^{-1}\). The temperature was elevated from 25 to 100°C successively.

**Figure 7.** Cyclic voltammograms of a Pt and Cd electrode in 0.15 M BMPCI/BMPTFSA containing 0.05 M CdCl\(_2\) at the scan rate of 50 mV s\(^{-1}\). Temperature: 25°C.
of the cation of ILs. Pyrrolidinium cation has been reported to be adsorbed more strongly on the electrode surface than imidazolium cation, and thereby influencing the electrochemical reactions in ILs.\textsuperscript{40,41} Thus, the result suggested stronger accumulation of BMP\textsuperscript{+} cations on the electrode surface compared to that of BMI\textsuperscript{+} cations at the negative potential region.

3.3 Electrodeposition of Cd in BMPCl/BMPTFSA

Potentiostatic electrodeposition of cadmium on a GC substrate from 0.15 M BMPCl/BMPTFSA containing 0.05 M CdCl\textsubscript{2} was performed at $-2.35$ and $-2.5$ V. Figure 9 shows the SEM images of the electrodeposited Cd. The morphology of the deposits was found to be dependent on the deposition potential. Sponge- and/or needle-like deposits were found at $-2.35$ V. Whereas, granular deposits were obtained at $-2.5$ V. The crystallite sizes estimated by the 101 reflection of Cd in the XRD patterns of the deposits were calculated using Scherrer equation. The crystallite size of the deposit obtained at $-2.35$ V was found to be larger (61 nm) than that of the deposit obtained at $-2.5$ V (45 nm), indicating hindrance of crystal growth at the more negative potential. The difference in the morphology of the deposits may be explained by hindrance of the nucleation and crystal growth owing to the potential-dependent electric double layer structure, as described above.

4. Conclusions

Raman spectroscopy and potentiometric measurement indicated that CdCl\textsubscript{2} dissolves in BMPCl/BMPTFSA by formation of a cadmium tetrachlorocomplex, [Cd(Cl\textsubscript{4})]\textsuperscript{2-}. Electrochemical reduction of [Cd(Cl\textsubscript{4})]\textsuperscript{2-} was possible on a GC electrode in BMPCl/BMPTFSA at 25°C, leading to deposition of metallic Cd. Cyclic voltammograms in the ILs containing [Cd(Cl\textsubscript{4})]\textsuperscript{2-} species showed unusual electrochemical behavior, regardless of electrode materials and ILs, probably related to the interaction between the cations of ILs and the electrode surface. The reduction overpotential of [Cd(Cl\textsubscript{4})]\textsuperscript{2-} on a GC electrode shifted towards the more positive side with elevating temperature probably due to ease of nucleation and/or faster charge transfer process. On the other hand, the reduction overpotential of [Cd(Cl\textsubscript{4})]\textsuperscript{2-} on a Cd substrate lowered since electrodeposition of a metal on the same metal substrate requires no nucleation. The deposits obtained by potentiostatic cathodic reduction showed morphological variation with the change of applied potential may be due to the difference in accumulation of BMP\textsuperscript{+} cations on the electrode surface at different applied potentials.

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