



Electrodeposition of NdFeB films in DMI–LiNO₃ ionic liquid analogs at room temperature

Xiao-qing LU^{1,2}, Ai-min LIU¹, Feng-guo LIU¹, Xian-wei HU¹, Zhong-ning SHI¹

1. Key Laboratory for Ecological Metallurgy of Multimetallic Mineral (Ministry of Education), Northeastern University, Shenyang 110819, China;
2. School of Metallurgy, Northeastern University, Shenyang 110819, China

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Abstract: The feasibility and reaction mechanism of NdFeB film electrodeposition in 1,3-dimethyl-2-imidazolidinone (DMI)–LiNO₃ ionic liquid analogs at room temperature were investigated. Cyclic voltammetry indicated that the reduction peak at -1.83 V (vs Ag) was related to the reduction of Fe(II) to Fe, while the reduction peak at -2.01 V (vs Ag) was related to the reduction of B(III) to B. The electrochemical reduction reaction of Fe(II) and B(III) were irreversible processes controlled by diffusion, and the diffusion coefficients of Fe(II) and B(III) at 313 K were 3.03×10^{-6} and 6.74×10^{-7} cm²/s, respectively. In addition, XRD analysis suggested that the product obtained by the electrodeposition in DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs for 2 h on the Al substrate contained NdFe₃B₃. SEM and EDS analysis showed that Nd, Fe, and B in the cathode product were uniformly distributed. XPS analysis revealed that the mass fractions of Nd, Fe, and B on the W substrate were 27.44%, 27.90%, and 7.51%, respectively.

Key words: ionic liquid analogs; electrodeposition; NdFeB film; cyclic voltammetry

1 Introduction

With excellent magnetic, optical, and electrical properties, rare earth elements are indispensable strategic resources in modern industry [1]. For example, NdFeB is widely used in many high-tech fields due to its advantages of small size, light mass, and excellent magnetic properties [2]. Molten salt electrolysis can realize the industrial production of rare earth metals, but it has the shortcoming of high energy consumption. If electrolysis is carried out at room temperature, the energy consumption will be reduced. Ionic liquids with low melting points provide a new approach for the green low-carbon production of rare earth metals [3,4]. Under the background of carbon peaks and carbon

neutrality, it is important to investigate the electrodeposition of rare earth metals in ionic liquids.

There are many reports on the electrodeposition of rare earth metals in ionic liquids [5–10]. For instance, JIN et al [5] electrodeposited La in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM]BF₄)–LaCl₃–LiCl ionic liquid, and found that the reduction of La(III) was a one-step irreversible reaction. HASMU et al [6] reported that the reduction of Ce(III) in 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆)–ethylene glycol (EG)–CeCl₃ ionic liquid was an irreversible reaction controlled by diffusion, and the product obtained by electrodeposition at 353 K for 0.5 h included metallic Ce. KONDO et al [7] revealed that the reduction of Nd(III) in triethylpentyl-

phosphonium bis(trifluoromethyl-sulfonyl) amide ([P₂₂₂₅][TFSA]) ionic liquid was an irreversible reaction controlled by diffusion, and the product produced by the electrodeposition at -3.1 V (vs ferrocenium/ferrocene (Fc^+/Fc)) for 3 h contained metallic Nd. OTA et al [8] obtained a black and uniform Nd coating by electrodeposition at -3.2 V (vs Fc/Fc^+) and 373 K in [P₂₂₂₅][TFSA] ionic liquid. ANDREW et al [9] prepared metallic Sm by electrodeposition in 1-butyl-1-methylpyrrolidinium dicyanamide ([BMP][DCA]) ionic liquid. KAZAMA et al [10] suggested that the reduction of Dy(III) in [P₂₂₂₅][TFSA] ionic liquid was a two-step irreversible process, and the product prepared by electrodeposition at -3.8 V (vs Pt) and 393 K consisted of metallic Dy and its oxides.

Furthermore, the electrodeposition of rare earth alloy films in ionic liquids has attracted great attention [11–15]. For example, CHEN et al [11] electrodeposited Sm–Co films in 1-ethyl-3-methylimidazolium chloride (EMIC)– SmCl_3 – CoCl_2 ionic liquid, and the crystallinity of Sm–Co was improved when the concentration of SmCl_3 increased. YANG et al [12] produced Ni–La films by electrodeposition in EMIC–EG ionic liquids, and the La content in the Ni–La films increased with increasing current density and temperature. XU et al [13] prepared Nd–Fe films containing 13% Nd via the pulse-current technique in 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) ionic liquid at 383 K. LIU et al [14] prepared a dense and uniform Co–Nd film by electrodeposition in urea and choline chloride deep eutectic solvents at -3.5 V (vs Ag) and 373 K. XU [15] electrodeposited uniform and bright Tb–Fe–Co films in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄])– $\text{Fe}(\text{BF}_4)_2$ – $\text{Co}(\text{BF}_4)_2$ – $\text{Tb}(\text{BF}_4)_3$ ionic liquid with the addition of butylenediol.

Recently, ZHANG et al [16] reported the production of metallic La by electrodeposition in 1,3-dimethyl-2-imidazolidinone (DMI)– LiNO_3 – LaCl_3 ionic liquid analogs at -2.5 V (vs Ag/Ag^+) and 323 K for 2 h. Furthermore, $\text{Nd}(\text{CF}_3\text{SO}_3)_3$ can be dissolved in DMI– LiNO_3 ionic liquid analogs, and the electrodeposit at -4 V (vs Ag) and 323 K contained metallic Nd [17,18]. In this work, the feasibility of NdFeB film electrodeposition in DMI– LiNO_3 – $\text{Nd}(\text{CF}_3\text{SO}_3)_3$ – FeCl_2 – H_3BO_3 ionic

liquid analogs at room temperature was investigated, and the electrochemical reductions of Fe(II) and B(III) were explored by cyclic voltammetry. Meanwhile, the investigation of NdFeB electrodeposition at room temperature can provide a technical reserve for the green low-carbon development of the rare earth metallurgy industry.

2 Experimental

DMI (98%), lithium nitrate (LiNO_3 , 99.9%), boric acid (H_3BO_3 , 99.99%), and ferrous chloride (FeCl_2 , 99.5%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. $\text{Nd}(\text{CF}_3\text{SO}_3)_3$ (98%) was purchased from Alfa Aesar Chemical Co., Ltd., China. The preparation of ionic liquid analogs was conducted in a glovebox filled with argon gas (99.99%), where the contents of water and oxygen were kept below 0.0001%. The DMI– LiNO_3 ionic liquid analogs were prepared by adding 0.5 mol/L LiNO_3 to the DMI solvent on a magnetic heating plate at 313 K. Similarly, DMI– LiNO_3 – FeCl_2 , DMI– LiNO_3 – H_3BO_3 , and DMI– LiNO_3 – $\text{Nd}(\text{CF}_3\text{SO}_3)_3$ – FeCl_2 – H_3BO_3 ionic liquid analogs were prepared by adding 0.005 mol/L FeCl_2 , 0.01 mol/L H_3BO_3 , and 0.05 mol/L $\text{Nd}(\text{CF}_3\text{SO}_3)_3$ to the DMI– LiNO_3 ionic liquid analogs.

Cyclic voltammetry curves were measured in the glovebox using an electrochemical workstation (CHI600E, Shanghai Chenhua Instrument Co., Ltd., China). A tungsten wire (99.95%, diameter of 1 mm) was used as the working electrode, while a platinum sheet (99.99%, 2 cm²) and silver wire (99.99%, diameter of 0.5 mm) were applied as the counter electrode and reference electrode, respectively. Before each measurement, the electrodes were polished with sandpaper and cleaned with deionized water. The electrodeposition experiments were also carried out in a glovebox using an electrochemical workstation. The working electrode was aluminum sheet (99.999%, 1.6 cm²) and tungsten sheet (99.99%, 2 cm²), while the counter electrode and reference electrode were platinum sheet (99.99%, 2 cm²) and silver wire (99.99%, diameter 0.5 mm), respectively. After electrodeposition, the working electrode was cleaned with acetonitrile, immersed in a bottle filled with dimethyl carbonate, and stored in a glovebox. Before characterization, the electrode was cleaned with deionized water and ethanol to remove dimethyl carbonate from the

electrode surface. The products were characterized by X-ray diffractometry (XRD, D8 ADVANCE, Bruck, Germany), scanning electron microscopy (SEM, Gemini 300, ZEISS, Germany), X-ray energy dispersive spectroscopy (EDS, Xplore 30, Oxford, Britain), and X-ray photoelectron spectroscopy (XPS, Scientific K-Alpha, Thermo, America).

3 Results and discussion

3.1 Electrochemical reduction of Fe(II) in DMI–LiNO₃ ionic liquid analogs

The cyclic voltammetry curves of DMI–LiNO₃ and DMI–LiNO₃–FeCl₂ ionic liquid analogs at 313 K are shown in Fig. 1(a). The scan rate was 20 mV/s. As shown in Curve 1 in Fig. 1(a), the reduction peak p at –3.30 V (vs Ag) corresponded to the electrodeposition of Li, while the oxidation peak p' was related to the oxidation of Li [16,18]. After the addition of 0.005 mol/L FeCl₂, two reduction peaks were observed within the electrochemical window of the DMI–LiNO₃ ionic

liquid analogs (as seen in Curve 2 in Fig. 1(a)). According to the literature [19,20], Fe(II) ions in the electrolyte can be partially oxidized to Fe(III) ions during the experiment. Therefore, the reduction peak m at –1.21 V (vs Ag) was related to the reduction of Fe(III) to Fe(II), while the reduction peak n at –1.83 V (vs Ag) was attributed to the reduction of Fe(II) to Fe.

To further investigate the electrochemical reduction of Fe(II), cyclic voltammetry curves of DMI–LiNO₃–FeCl₂ ionic liquid analogs at 313 K were tested at scan rates of 20, 40, 60, 80, and 100 mV/s. As shown in Fig. 1(b), when the scan rate increased from 20 to 100 mV/s, the potentials of the reduction peaks moved toward the negative direction, while the potentials of the oxidation peaks moved toward the positive direction. In addition, the absolute value of the reduction peak current density increased with increasing scan rate. When the scan rate was 20 mV/s, the potential difference between the reduction peak and the oxidation peak was 290 mV, which was much larger

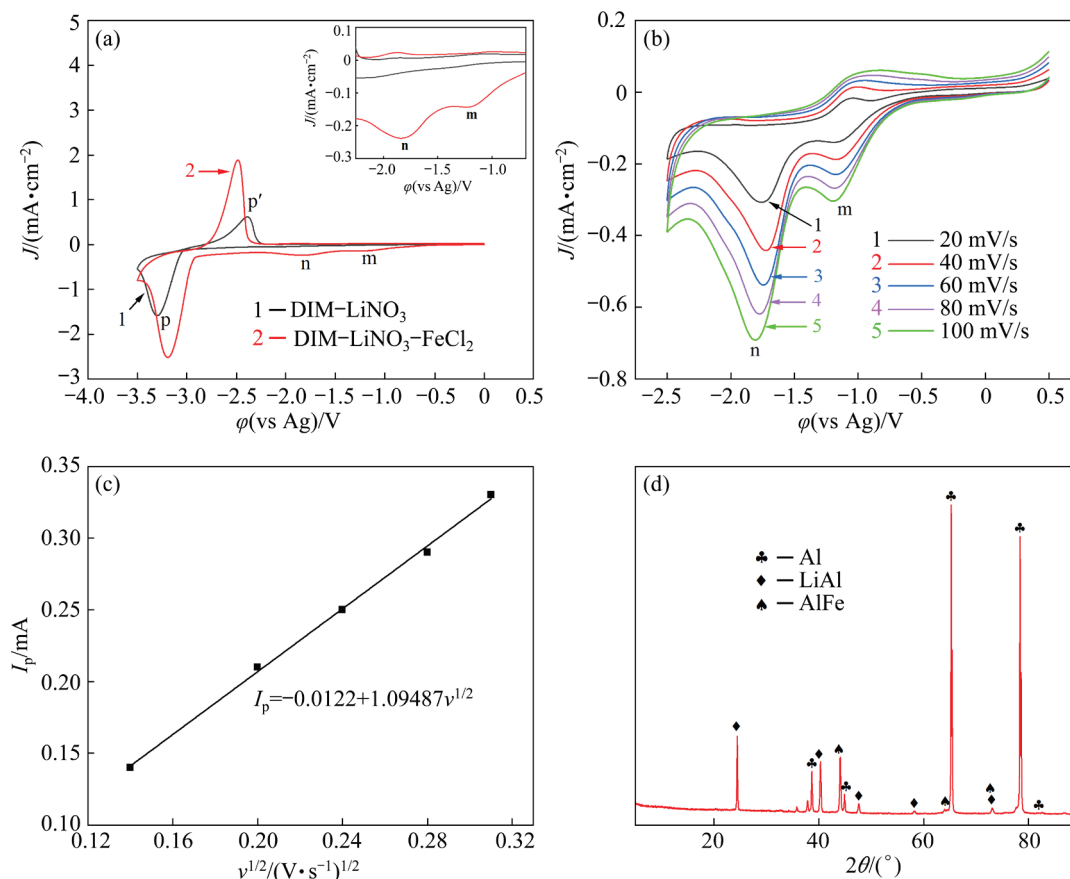


Fig. 1 Cyclic voltammetry curves of DMI–LiNO₃ and DMI–LiNO₃–FeCl₂ ionic liquid analogs at 313 K (a), cyclic voltammetry curves at different scan rates (b), relationship between I_p and $\nu^{1/2}$ for Fe(II) reduction peak (c), and XRD pattern of cathode product obtained by electrodeposition at –2.8 V (vs Ag) and 313 K for 2 h in DMI–LiNO₃–FeCl₂ ionic liquid analogs (d)

than the potential difference for the reversible reaction (31 mV). Based on the above characteristics, the reduction of Fe(II) in DMI–LiNO₃–FeCl₂ ionic liquid analogs was an irreversible process controlled by diffusion.

For irreversible electrode reactions, the charge transfer coefficient can be calculated using Eq. (1) [21].

$$|\varphi_p - \varphi_{p/2}| = 1.857RT/(\alpha nF) \quad (1)$$

where φ_p is the peak potential of Fe(II) reduction (V), $\varphi_{p/2}$ is the half-peak potential of Fe(II) reduction (V), R is the molar gas constant (8.314 J/(mol·K)), T is the experimental temperature (313 K), α is the charge transfer coefficient, n is the number of transferred electrons, and F is the Faraday constant (96485 C/mol). According to the data derived from Fig. 1(b), the average value of the charge transfer coefficient α for Fe(II) reduction in DMI–LiNO₃–FeCl₂ ionic liquid analogs was calculated to be 0.1055.

The diffusion coefficient can be calculated using Eq. (2) [21]:

$$I_p = 0.4958nFAC_0D^{1/2}\nu^{1/2}[anF/(RT)]^{1/2} \quad (2)$$

where I_p is the peak current of Fe(II) reduction (A), A is the surface area of the working electrode (0.471 cm²), C_0 is the concentration of Fe(II) ions (5.0×10⁻⁶ mol/cm³), D is the diffusion coefficient (cm²/s), and ν is the scan rate (V/s). As seen in Fig. 1(c), the peak current has a linear relationship with the square root of the scan rate. According to the slope of the fitted line in Fig. 1(c), the diffusion coefficient of Fe(II) in DMI–LiNO₃–FeCl₂ ionic liquid analogs at 313 K was determined to be 3.03×10⁻⁶ cm²/s. As shown in Table 1, the diffusion coefficient of Fe(II) in DMI–LiNO₃–FeCl₂ is smaller than that in (NH₄)₂SO₄–FeSO₄ aqueous solutions and ChCl–EG–FeCl₂ system [22,23]. In addition, the diffusion coefficient of Fe(II) in the

DMI–LiNO₃–FeCl₂ is larger than that in BMPTFSA–Fe(TFSA)₂ and TMPAC–EG–FeCl₂ because of different temperatures and electrolytes [24,25].

Electrodeposition experiments were conducted in DMI–LiNO₃–FeCl₂ ionic liquid analogs at a constant potential of –2.8 V (vs Ag) for 2 h. As shown in Fig. 1(d), XRD analysis indicated that the main phases of the electrodeposit were Al, LiAl, and AlFe. The existence of AlFe alloy verified the electrochemical reduction of Fe(II) to metallic Fe on the Al substrate in DMI–LiNO₃–FeCl₂ ionic liquid analogs.

To study the microstructure and element composition of the electrodeposit, the cathode product was analyzed by SEM and EDS. As demonstrated in Fig. 2(a), the electrodeposit exhibited a loose porous morphology, and the EDS spectrum indicated that the electrodeposit was mainly composed of Al, Fe, and O elements, which was in agreement with the result from XRD analysis. Among them, Al was observed due to the Al substrate, and O was detected because the electrodeposition product was oxidized in air. The mass fraction of Fe in the cathode product was 20.61%. Figure 2(b) showed that Fe and Al were evenly distributed on the surface of the Al substrate. Figure 2(c) showed the SEM image and EDS spectrum of the cathode product obtained by electrodeposition at –2.2 V (vs Ag) and 313 K for 4 h on the W substrate. The electrodeposit exhibited some sparsely distributed particles. The EDS spectrum showed that the electrodeposit was mainly composed of W and Fe elements. As shown in Fig. 2(d), Fe was evenly distributed on the surface of the W substrate.

3.2 Electrochemical reduction of B(III) in DMI–LiNO₃ ionic liquid analogs

The cyclic voltammetry curves of DMI–LiNO₃ and DMI–LiNO₃–H₃BO₃ ionic liquid analogs at 313 K are shown in Fig. 3(a). The scan rate was 20 mV/s. After the addition of 0.01 mol/L H₃BO₃ to the DMI–LiNO₃ ionic liquid analogs, a reduction peak appeared at –2.01 V (vs Ag), which was corresponding to the reduction of B(III) to B. In addition, the oxidation peak at –1.99 V (vs Ag) was attributed to the oxidation of B.

To further investigate the electrochemical reduction of B(III), the cyclic voltammetry curves of

Table 1 Comparison of diffusion coefficients of Fe(II) in different solutions

Electrolyte system	<i>T</i> /K	<i>D</i> /(cm ² ·s ⁻¹)	Resource
(NH ₄) ₂ SO ₄ –FeSO ₄	298	1.50×10 ⁻⁵	[22]
ChCl–EG–FeCl ₂	333	5.34×10 ⁻⁶	[23]
BMPTFSA–Fe(TFSA) ₂	298	6.91×10 ⁻⁷	[24]
TMPAC–EG–FeCl ₂	333	1.10×10 ⁻⁷	[25]
DMI–LiNO ₃ –FeCl ₂	313	3.03×10 ⁻⁶	This study

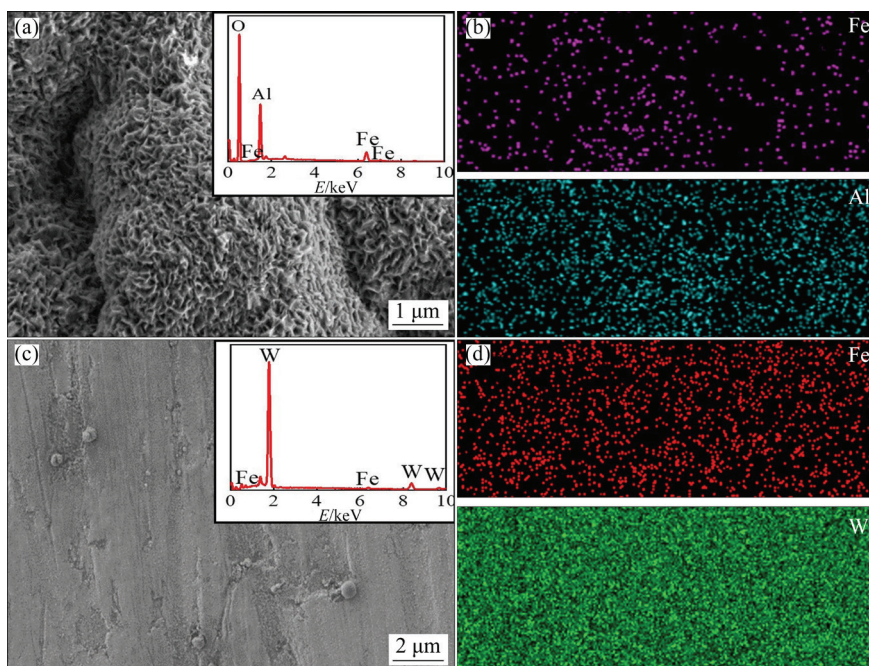


Fig. 2 SEM images and EDS spectra of cathodic product obtained by electrodeposition at 313 K in DMI–LiNO₃–FeCl₂ ionic liquid analogs: (a, b) SEM image, EDS spectrum, and EDS mapping images for elements Fe and Al at –2.8 V (vs Ag) for 2 h on Al substrate, respectively; (c, d) SEM image, EDS spectrum, and EDS mapping images for elements Fe and W at –2.2 V (vs Ag) for 4 h on W substrate, respectively

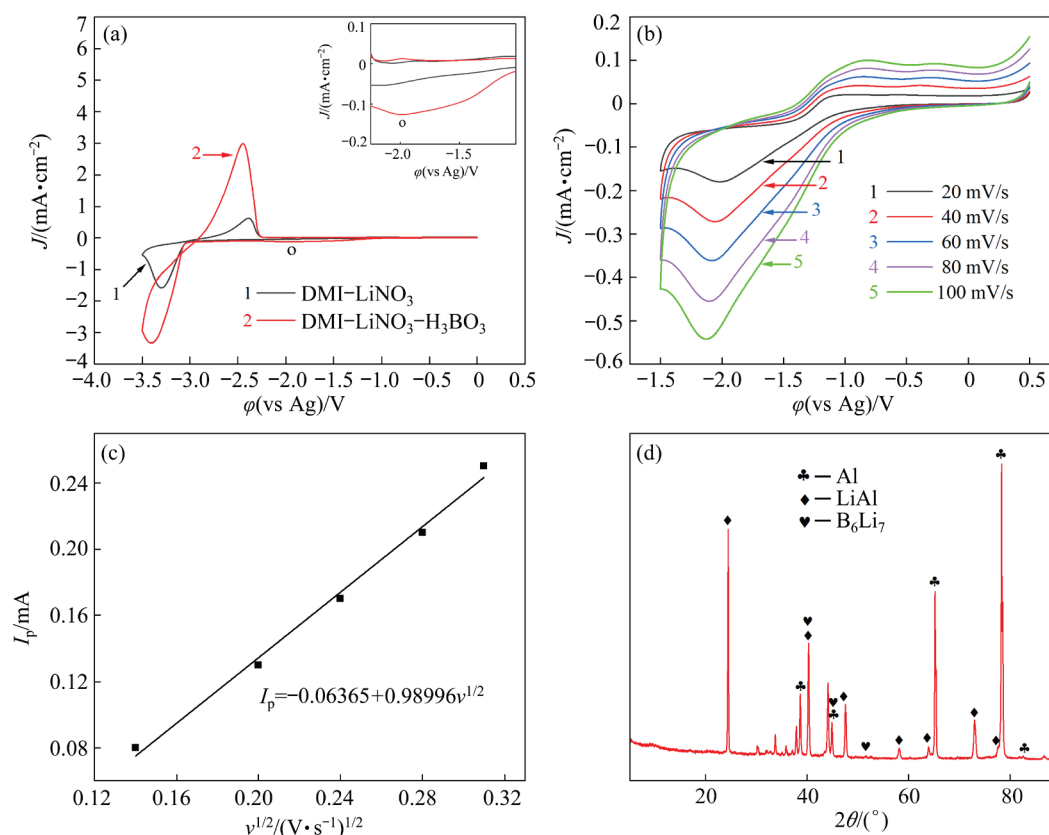


Fig. 3 Cyclic voltammetry curves of DMI–LiNO₃ and DMI–LiNO₃–H₃BO₃ ionic liquid analogs at 313 K (a), cyclic voltammetry curves at different scan rates (b), relationship between I_p and $v^{1/2}$ for B(III) reduction peak (c), and XRD pattern of cathode product obtained by electrodeposition at –3.0 V (vs Ag) and 313 K for 2 h in DMI–LiNO₃–H₃BO₃ ionic liquid analogs (d)

DMI–LiNO₃–H₃BO₃ ionic liquid analogs at 313 K were tested at scan rates of 20, 40, 60, 80, and 100 mV/s. As shown in Fig. 3(b), when the scan rate increased from 20 to 100 mV/s, the absolute value of the reduction peak current density gradually increased, and the potentials of the reduction peaks gradually moved toward the negative direction. When the scan rate was 20 mV/s, the potential difference between the reduction peak and the oxidation peak was 194 mV, which was much larger than the potential difference for the reversible reaction (21 mV). According to the above characteristics, the reduction of B(III) in DMI–LiNO₃–H₃BO₃ ionic liquid analogs was an irreversible process controlled by diffusion.

Based on Eq. (1) and the data derived from Fig. 3(b), the average value of the charge transfer coefficient α for B(III) reduction in DMI–LiNO₃–H₃BO₃ was determined to be 0.0275. As shown in Fig. 3(c), the peak current has a linear relationship with the square root of the scan rate. According to the slope of the fitted line in Fig. 3(c), the diffusion coefficient of B(III) in DMI–LiNO₃–H₃BO₃ ionic liquid analogs at 313 K was calculated to be $6.74 \times 10^{-7} \text{ cm}^2/\text{s}$. As seen in Table 2, the diffusion coefficient of B(III) in DMI–LiNO₃–H₃BO₃ is of the same order of magnitude as the value in

KF–KBF₄ molten salts [26]. Furthermore, the diffusion coefficient of B(III) in DMI–LiNO₃–H₃BO₃ is much larger than that in KF–LiF–KBF₄ molten salts [27,28], which is caused by different temperatures and systems.

Table 2 Comparison of diffusion coefficients of B(III) in different solutions

Electrolyte system	<i>T</i> /K	<i>D</i> /(cm ² ·s ^{−1})	Source
KF–KBF ₄	1153	7.85×10^{-7}	[26]
KF–LiF–KBF ₄	1078	4.50×10^{-10}	[27]
KF–LiF–KBF ₄	1103	1.13×10^{-10}	[28]
DMI–LiNO ₃ –H ₃ BO ₃	313	6.74×10^{-7}	This study

Electrodeposition experiments were performed in DMI–LiNO₃–H₃BO₃ ionic liquid analogs at −3.0 V (vs Ag) and 313 K for 2 h. As shown in Fig. 3(d), XRD analysis showed that the main phases of the electrodeposit were Al, LiAl, and B₆Li₇. The formation of B₆Li₇ confirmed the electrochemical reduction of B(III) to B on the Al substrate in DMI–LiNO₃–H₃BO₃ ionic liquid analogs.

Figure 4(a) shows the SEM image and EDS spectrum of the cathode product obtained by the

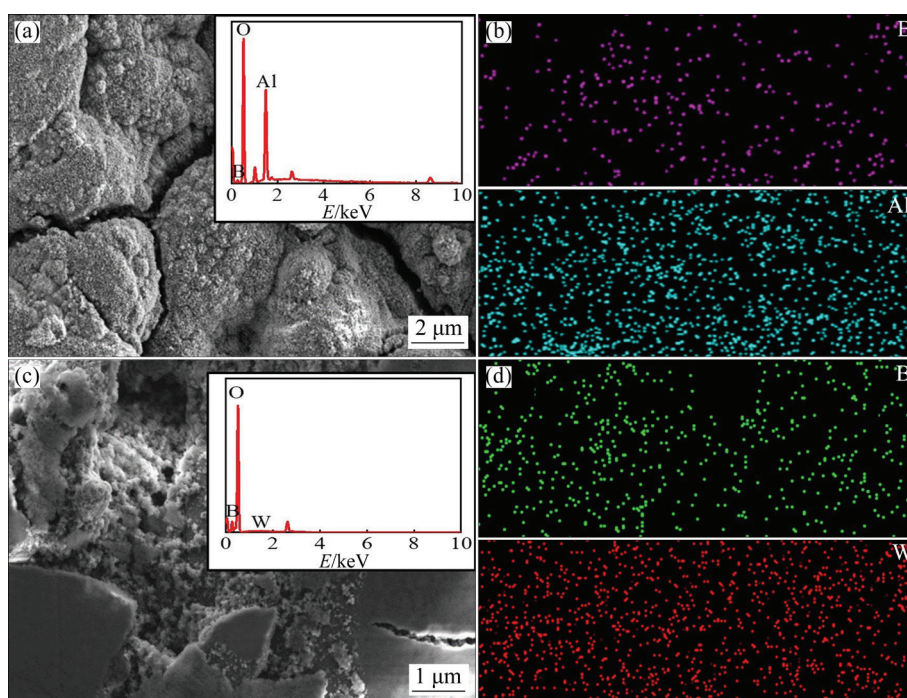


Fig. 4 SEM image and EDS spectra of cathode product obtained by electrodeposition at −3.0 V (vs Ag) and 313 K in DMI–LiNO₃–H₃BO₃ ionic liquid analogs: (a, b) SEM image, EDS spectrum, and mapping images for elements B and Al for 2 h on Al substrate, respectively; (c, d) SEM image, EDS spectrum, and EDS mapping images for elements B and W for 4 h on W substrate, respectively

electrodeposition at -3.0 V (vs Ag) and 313 K for 2 h in DMI–LiNO₃–H₃BO₃ ionic liquid analogs. The electrodeposit appeared as large masses composed of fine particles, and obvious cracks were observed between the masses. The EDS spectrum showed that the electrodeposit was mainly composed of Al, B, and O elements, which was consistent with the result from XRD analysis. Al was detected because the applied cathode of the electrodeposition experiment was an Al substrate. The mass fraction of B in the cathode product was 16.03% . Figure 4(b) indicated that B was evenly distributed on the surface of the Al substrate. Figure 4(c) showed the SEM image and EDS spectrum of the cathode product obtained by electrodeposition at -3.0 V (vs Ag) and 313 K for 4 h on the W substrate. The electrodeposit exhibited granular and chunky shapes. The EDS spectrum displayed that the electrodeposit was mainly composed of W and B elements. As shown in Fig. 4(d), B was uniformly distributed on the surface of the W substrate.

3.3 Electrodeposition of NdFeB films in DMI–LiNO₃ ionic liquid analogs

The cyclic voltammetry curves of DMI–LiNO₃ and DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs at 313 K are displayed in Fig. 5(a). The scan rate was 20 mV/s. After the addition of 0.05 mol/L Nd(CF₃SO₃)₃, 0.005 mol/L FeCl₂, and 0.01 mol/L H₃BO₃ to the DMI–LiNO₃ ionic liquid analogs, obvious current signals appeared in the potential range from -1.0 to -2.2 V (vs Ag). According to our previous study [18], when 0.05 mol/L Nd(CF₃SO₃)₃ was added to the DMI–LiNO₃ ionic liquid analogs at 303 K, the reduction peak at -2.5 V (vs Ag) in the cyclic voltammetry curve was related to the reduction of Nd(III) to metallic Nd. Based on the results from Fig. 1(a) and Fig. 3(a), the peak potentials of Fe(II) and B(III) reduction in DMI–LiNO₃ ionic liquid analogs were -1.83 and -2.01 V (vs Ag), respectively. Thus, the current signals between -1.0 and -2.2 V were concerned with the electrodeposition of Fe, B, and Nd.

To further investigate the electrochemical reduction mechanism, cyclic voltammetry curves of DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs at 313 K were tested at scan rates of 20 , 40 , 60 , 80 , and 100 mV/s. As shown in

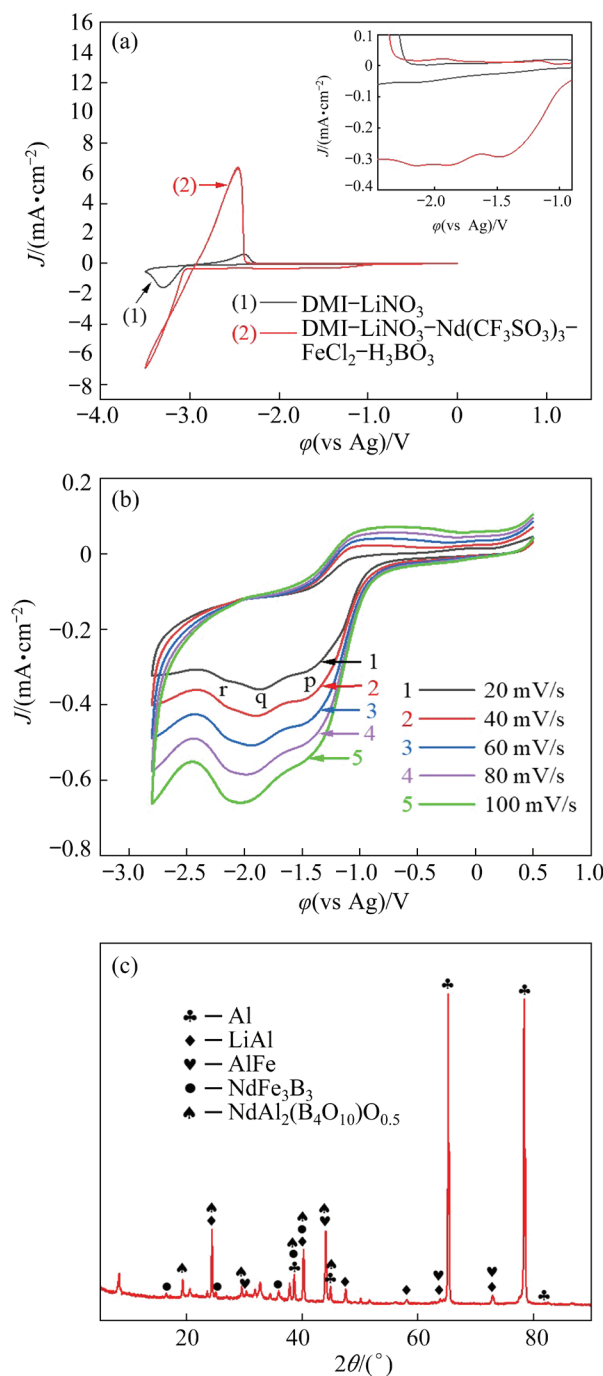


Fig. 5 Cyclic voltammetry curves of DMI–LiNO₃ and DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs at 313 K (a), cyclic voltammetry curves at different scan rates (b), and XRD pattern of cathode product obtained by electrodeposition at -3.5 V (vs Ag) and 313 K for 2 h in DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs (c)

Fig. 5(b), when the scan rate was 20 mV/s, three reduction peaks p, q and r appeared at -1.48 , -1.88 and -2.15 V (vs Ag), which corresponded to the electrodeposition of Fe, B and Nd, respectively.

When the scan rate increased to 100 mV/s, the three reduction peaks were gradually superimposed to form a reduction peak.

Electrodeposition experiments were performed in DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs at –3.5 V (vs Ag) for 2 h. As seen in Fig. 5(c), XRD analysis revealed that the main phases of the electrodeposit were Al, LiAl, AlFe, NdFe₃B₃, and NdAl₂(B₄O₁₀)O_{0.5}. The existence of NdFe₃B₃ proved that it is feasible to electrodeposit NdFeB film in DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs.

Figure 6(a) shows the SEM image and EDS spectrum of the cathode product obtained by electrodeposition at –3.5 V (vs Ag) and 313 K for 2 h in DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs. The electrodeposit exhibited granular and flake shapes. The EDS spectrum indicated that the electrodeposit mainly contained Al, Nd, Fe, B, and O, which is in agreement with the result from XRD analysis. Al was observed because the applied cathode of the electrodeposition

experiment was an Al substrate, while O was due to the oxidation of the alloy in air. The mass fractions of Nd, Fe and B were 22.00%, 1.36% and 7.68%, respectively. Figure 6(b) showed the uniform distribution of Nd, Fe and B on the surface of the Al substrate. In addition, Nd was more densely distributed than Fe and B due to the larger mass fraction of Nd in the cathode product.

Figure 7(a) showed that the electrodeposit exhibited a loose lamellar structure with holes. According to the EDS analysis (inset of Fig. 7(a)), the deposited film was mainly composed of Nd, Fe, B and W. W was detected because a W substrate was used for the electrodeposition experiment. In addition, the results from EDS mapping images (Fig. 7(b)) indicated that Nd, Fe and B in the electrodeposit were uniformly distributed. Therefore, a NdFeB film can be prepared by electrodeposition on the surface of a W substrate at 313 K.

The cathode product was further analyzed by XPS. As shown in Fig. 8(a), the peaks of Nd 3d, Fe 2p, O 1s and B 1s were observed at binding

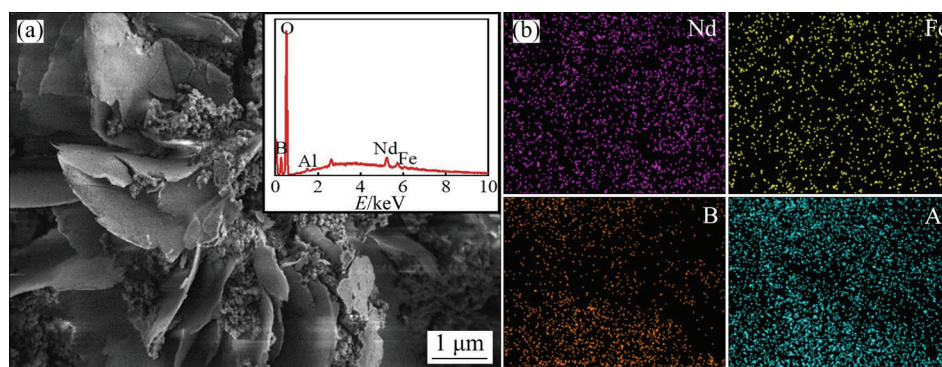


Fig. 6 SEM image, EDS spectrum, and mapping images of cathode product obtained by electrodeposition at –3.5 V (vs Ag) and 313 K for 2 h in DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs: (a) SEM image and EDS spectrum; (b) EDS mapping images for element Nd, Fe, B and Al on Al substrate

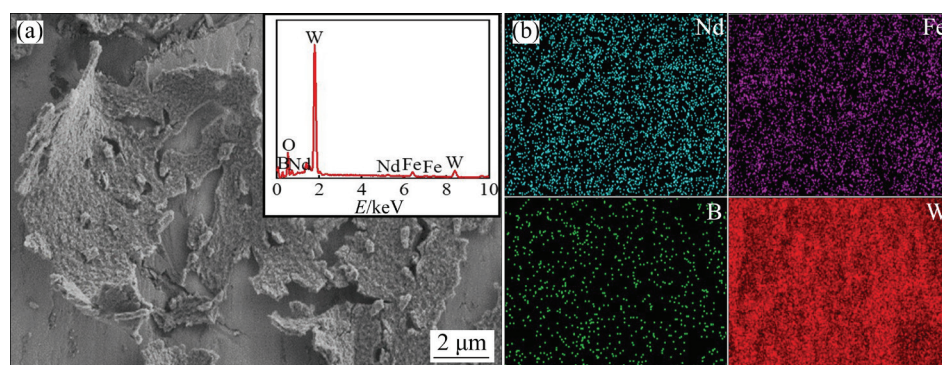


Fig. 7 SEM image, EDS spectrum, and mapping images of cathode product obtained by electrodeposition at –2.5 V (vs Ag) and 313 K for 4 h in DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs: (a) SEM image and EDS spectrum; (b) EDS mapping image for elements Nd, Fe, B and W on W substrate

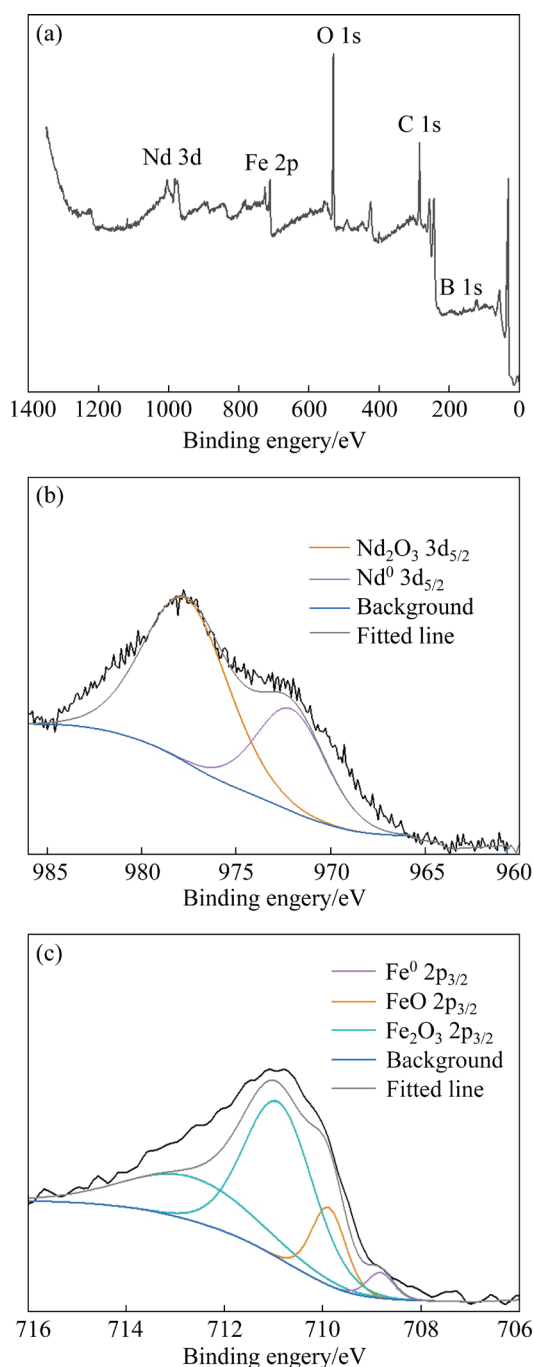


Fig. 8 XPS survey of cathode product obtained by electrodeposition at -2.5 V (vs Ag) and 313 K for 4 h on W substrate in DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs: (a) Full spectrum; (b) Fine spectrum of Nd; (c) Fine spectrum of Fe

energies of 977.0, 710.9, 529.9 and 196.4 eV, respectively [24,29–31]. Furthermore, XPS analysis indicated that the mass fractions of Nd, Fe and B in the electrodeposit on the W substrate were 27.44%, 27.90% and 7.51%, respectively. To determine the chemical states of Nd in the cathode product, the

fine-scanned Nd 3d spectrum is shown in Fig. 8(b). The band at a binding energy of 977.0 eV corresponded to Nd₂O₃, while the band at a binding energy of 972.0 eV corresponded to metallic Nd [29]. In addition, XPS analysis revealed that the mass fraction of metallic Nd in Nd was 33.66% [18,29]. Figure 8(c) displayed the fine-scanned Fe 2p spectrum to determine the chemical states of Fe in the cathode product. The bands at binding energies of 709.9 and 710.9 eV corresponded to FeO and Fe₂O₃, respectively, while the band at a binding energy of 708.8 eV corresponded to metallic Fe [32]. XPS analysis revealed that the mass fraction of metallic Fe in the element Fe was 4.81% [33].

4 Conclusions

(1) The reduction peak at -1.83 V (vs Ag) in the cyclic voltammogram of DMI–LiNO₃–FeCl₂ was ascribed to the reduction of Fe(II) to Fe. The electrochemical reduction of Fe(II) is an irreversible diffusion-controlled process with a diffusion coefficient of 3.03×10^{-6} cm²/s, and the electrodeposit at -2.2 V (vs Ag) on the W substrate contained metallic Fe.

(2) The reduction peak at -2.01 V (vs Ag) in the cyclic voltammogram of DMI–LiNO₃–H₃BO₃ was corresponding to the reduction of B(III) to B. The electrochemical reduction of B(III) is an irreversible diffusion-controlled process with a diffusion coefficient of 6.74×10^{-7} cm²/s, and the electrodeposit at -3.0 V (vs Ag) on the W substrate contained B.

(3) In DMI–LiNO₃–Nd(CF₃SO₃)₃–FeCl₂–H₃BO₃ ionic liquid analogs, the main phases of the electrodeposit on the Al substrate at -3.5 V (vs Ag) contained NdFe₃B₃, and the mass fractions of Nd, Fe and B in the cathode product by electrodeposition at -2.5 V (vs Ag) and 313 K on the W substrate were 27.44%, 27.90% and 7.51%, respectively.

CRedit authorship contribution statement

Xiao-qing LU: Writing – Original draft, Investigation, Data curation, Validation, Writing – Reviewing and editing; **Ai-min LIU:** Conceptualization, Investigation, Resources, Supervision, Writing – Reviewing and editing, Project administration; **Feng-guo**

LIU and Xian-wei HU: Supervision; **Zhong-ning SHI:** Methodology, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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DMI-LiNO₃ 离子液体类似物室温电沉积钕铁硼薄膜

鲁小青^{1,2}, 刘爱民¹, 刘凤国¹, 胡宪伟¹, 石忠宁¹

1. 东北大学 多金属共生矿生态化冶金教育部重点实验室, 沈阳 110819;

2. 东北大学 冶金学院, 沈阳 110819

摘要: 研究 1,3-二甲基-2-咪唑啉酮(DMI)-LiNO₃ 离子液体类似物在室温条件下电沉积钕铁硼薄膜的可行性和反应机理。结果表明, 循环伏安曲线中-1.83 V (vs Ag)处的还原峰对应于 Fe(II)被还原为金属 Fe, -2.01 V (vs Ag)处的还原峰对应于 B(III)被还原为 B。Fe(II)和 B(III)的电化学还原反应是受扩散控制的不可逆过程, 313 K 下 Fe(II)和 B(III)的扩散系数分别为 3.03×10^{-6} 和 $6.74 \times 10^{-7} \text{ cm}^2/\text{s}$ 。此外, XRD 分析表明, 在 DMI-LiNO₃-Nd(CF₃SO₃)₃-FeCl₂-H₃BO₃ 体系中以铝为基底电沉积 2 h 的产物含有 NdFe₃B₃; SEM 和 EDS 分析表明, 阴极产物中 Nd、Fe 和 B 元素呈均匀分布; XPS 分析表明, 钕基底表面中 Nd、Fe 和 B 的质量分数分别为 27.44%、27.90%和 7.51%。

关键词: 离子液体类似物; 电沉积; 钕铁硼薄膜; 循环伏安法

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