

Cite this article as: Hu Yi, Xu Jingsong, Zhong Hang, et al. Preparation of La Thin Film in BMIMPF₆ Ionic Liquid at 298 K by Electrodeposition[J]. Rare Metal Materials and Engineering, 2021, 50(07): 2288-2292.

ARTICLE

Preparation of La Thin Film in BMIMPF₆ Ionic Liquid at 298 K by Electrodeposition

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Abstract: Lanthanum (La) thin film was electrodeposited at room temperature (298 K) using lanthanum nitrate, ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) and cosolvent acetone as the electrolyte. Results show that the reduction from La³⁺ to La⁰ involves the transformation of La³⁺→La²⁺ occurring at around -1.7 V vs. Pt and La²⁺→La⁰ occurring at around -2.1 V vs. Pt. The electrolyte BMIMPF₆ exhibits an electrochemical window from -2.5 V vs. Pt to 1.5 V vs. Pt. The low hygroscopic property of BMIMPF₆ allows La electrodeposition under air atmosphere. The precipitate films were observed by scanning electron microscopy and metallographic microscope, showing a dense texture. Then the films were characterized by energy dispersive spectrometry and X-ray photoelectron spectroscopy, confirming therein a large amount of La. The electrochemical tests of changing voltage scan rate and the concentration of lanthanum nitrate reveal that the reduction of La³⁺ is an irreversible process. The diffusion coefficient of La³⁺ in BMIMPF₆ is calculated as 1.47×10⁻⁹ cm²·s⁻¹. This research provides a simple approach to obtain La thin film, which can be used for the electrodeposition of other lanthanides thin film.

Key words: ionic liquid; lanthanum; BMIMPF₆; electrodeposition

Lanthanum (La) metal and oxides have been widely used as catalysts^[1-3]. La metal is very sensitive to O₂ atmosphere and water, and can be oxidized easily under these conditions. In order to prepare active metals such as La metal, one of the most potential approaches is electrolysis which is controllable, convenient and safe. However, it is difficult to electrodeposit La metal in aqueous electrolytes because the reduction potential of lanthanum ion is much more negative than that of water.

Ionic liquid is a candidate to replace water as the electrolyte solvent, consisting of many kinds of cations and anions, such as [1-butyl-3-methylimidazolium (BMIM)]⁺, [1-ethyl-3-methylimidazolium (EMIM)]⁺, [1-butyl-1-methylpyrrolidinium (BMP)]⁺, [1-octyl, methyl pyrrolidine (OMP)]⁺, [AlCl₄]⁻, [PF₆]⁻, [CF₃SO₃]⁻ and [BF₄]⁻. So far, ionic liquids as electrolyte solvent have received extensive attention due to their moderate conductivity, high thermal stability, low vapor pressure, and low flammability^[4-6]. The wide electrochemical window of ionic liquids is a specific advantage, which maintains their electrochemical stability against the oxidation and reduction

processes^[7]. These properties of ionic liquids make them a good electrolyte solvent for the electrolytic reduction of many metallic ions^[8-15], especially for the very active metals^[16-23]. Tsuda et al^[24] achieved La metal electrodeposits in the ionic liquid of aluminum trichloride-chlorinated 1-ethyl-3-methylimidazole salt with LiCl and SOCl₂. Legeai et al^[25] obtained La electrodeposition at room temperature in the ionic liquid of 1-octyl, methyl pyrrolidine (trifluoromethyl sulfonyl) imide salt. Zhang et al^[26] prepared La metal with nanostructure in the ionic liquid of 1-butyl-3-methylimidazole dicyandiamide (BMI-DCA) with LaCl₃.

Achieving better water/air resistance and solubility of La salt in ionic liquid is still a strategy for improving the performance of La electrodeposition in ionic liquids. Herein, the ionic liquid of 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) was adopted as solvent for electrolyte La(NO₃)₃. Using acetone as an auxiliary solvent^[25,27], the moderate solubility and low viscosity of La(NO₃)₃ in BMIMPF₆ was reached. Electrodeposition of La thin film was achieved at room temperature under air atmosphere.

Received date: July 13, 2020

Foundation item: National Key Research and Development Program (2017YFE0301506); National Natural Science Foundation of China (21573223); Foundation from Institute of Materials CAEP (TP01201603, TP03201703)

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1 Experiment

The materials used in the experiments were prepared as follows. A certain amount of lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, purity of 99.5%, Aladdin) was dried in a vacuum oven at 373 K for 24 h. Similarly, the ionic liquid BMIMPF₆ (purity of 99%, Shanghai Cheng Jie Chemical Co., Ltd) was dried at 373 K for 24 h, and then sealed. Due to the low boiling point of acetone, it was dehydrated using 3A molecular sieve which was washed by deionized water and dried at 473 K for 4 h. Since the lanthanum salt is difficult to directly dissolve in the ionic liquid, the dried acetone as a cosolvent was used for improving the solubility of the lanthanum salt. Further, the acetone was removed by heating.

The electrochemical tests were performed on a three-electrode system connected to an electrochemical workstation (CHI 660 E, Cheng Hua Instrument Inc). A platinum column with a diameter of 1 mm served as the reference electrode. One platinum plate (10 mm×10 mm) served as the working electrode and the other platinum plate served as the counter electrode. Prior to use, these Pt electrodes were polished, soaked in dilute HCl acid solution for 5 min to remove the surface oxides, soaked in NaOH solution for 5 min to remove the grease stains, ultrasonically cleaned in anhydrous ethanol for 5 min to remove organic contaminants, washed with ultrapure water (18.2 MΩ·cm) and finally dried.

The morphology and element analysis were obtained by scanning electron microscopy (SEM, FEI, Sirion-200) combined with energy dispersive spectrometry (EDS, 10 kV, 10⁻⁵ Pa). The morphology was also obtained by an optical microscope (OM). X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250) with monochromatic Al Kα line (1486.6 eV) was applied to determine the elements and the valence states of the products.

2 Results and Discussion

2.1 Electrodeposition of La³⁺ in BMIMPF₆

Fig. 1 shows the room-temperature cyclic voltammograms (CVs) of 0, 20, 40 and 60 mmol/L $\text{La}(\text{NO}_3)_3$ dissolving in ionic liquid BMIMPF₆. It can be seen that the BMIMPF₆ is stable in the voltage range of -2.5~1.5 V vs. Pt. The reduction peak at around 0.5 V vs. Pt probably results from an impurity, whereas the redox peaks at around -1.3 V vs. Pt are attributed to the reaction of residual water^[8,28,29]. In the case of $\text{La}(\text{NO}_3)_3$ dissolving in BMIMPF₆, two reduction peaks appear at -1.7 and -2.1 V vs. Pt, which are suggested as the reduction process of $\text{La}^{3+} \rightarrow \text{La}^{2+}$ and $\text{La}^{2+} \rightarrow \text{La}^0$ ^[30], respectively. Moreover, no corresponding oxidation peak occurs, indicating that the reduction process is irreversible.

Further, the electrodeposition was carried out at -2.4 V vs. Pt for 60 mmol/L $\text{La}(\text{NO}_3)_3$ dissolving in BMIMPF₆. As shown in Fig. 2, the electrodeposition process at 298 K lasts for 2 h. A thin film on the Pt electrode could be observed. After the electrodeposition, the precipitate on electrode was stored in anhydrous ethanol for later use.

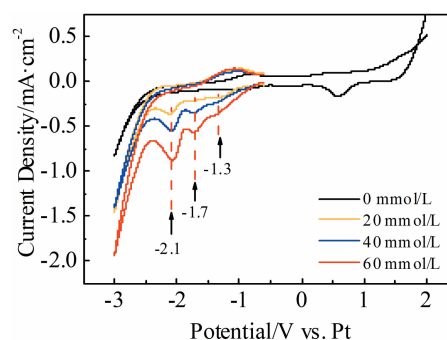


Fig.1 Cyclic voltammogram of $\text{La}(\text{NO}_3)_3$ with different concentrations dissolving in BMIMPF₆ at 298 K (scan rate: 10 mV·s⁻¹)

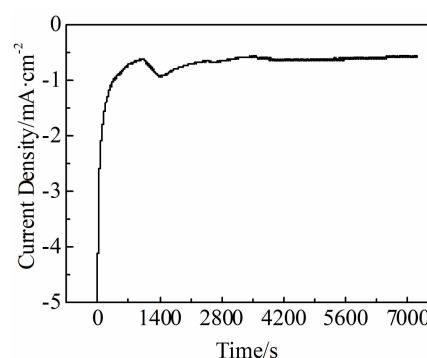


Fig.2 La^{3+} deposition curve under applied potential of -2.4 V vs. Pt at 298 K for 2 h

2.2 Characterization of electrodeposited La thin film

The electrodeposited film under the potential of -2.4 V vs. Pt was analyzed by OM, SEM, and EDS; and the results are shown in Fig. 3a, 3b and 3c, respectively. The OM image clearly shows a thin film on the substrate, and the SEM image displays the film with small particles and flocculants on the top. EDS analysis exhibits that this precipitate film contains a large amount of La and a small amount of C, N, F, and P, which confirms the reduction process of La^{3+} and La deposition on the electrode. During the deposition process, some BMIMPF₆ coprecipitate maybe is adsorbed on the La sediments.

To further determine the valence state of the deposited La, the samples were measured by XPS. As shown in Fig. 4a, La 3d_{5/2} and La 3d_{3/2} signals appear at 835.17 and 851.99 eV, respectively. O 1s signal appears at 530.03 eV in Fig. 4b. Compared to the standard XPS peaks of metal lanthanum^[26,31], these results illustrate that the measured sample is lanthanum oxide. The shoulder signals at higher energies in Fig. 4a imply that there are complexes containing La^{3+} or La element in slightly different valance states^[26]. In brief, the result suggests that the measured thin film is mainly composed of La_2O_3 , which may form through the oxidation of electrodeposited lanthanum thin film under exposure to air when it was transferred to the XPS chamber.

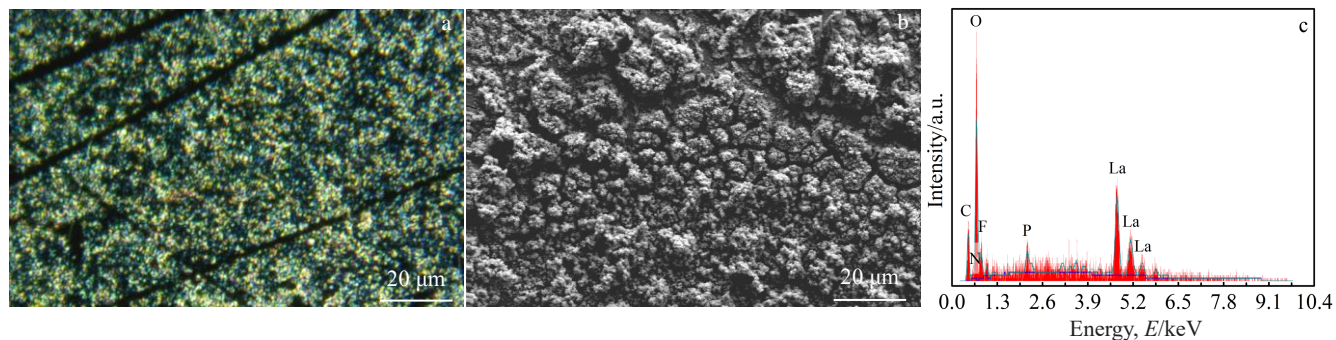


Fig.3 OM (a) and SEM (b) images and EDS spectrum (c) of precipitate film obtained by electrodeposition at -2.4 V vs. Pt for $\text{La}(\text{NO}_3)_3$ dissolving in BMIMPF_6

2.3 Electrochemical behavior of La^{3+} in BMIMPF_6

In detail, cyclic voltammetry experiments were performed to investigate the deposition kinetic and determine the diffusion coefficient of La^{3+} in BMIMPF_6 . Fig. 5a shows the result of voltammetric experiments under different voltage scanning rates (ν) in the case of 6 mmol/L $\text{La}(\text{NO}_3)_3$ dissolving in BMIMPF_6 . As can be seen from Fig. 5a, the cathodic peak potential (E_p) of the reduction of La^{3+} to La^{2+} decreases with the increase of voltage scanning rate. Furthermore, the relationship between E_p and $\ln(\nu)$ can be fitted as a straight line (Fig. 5b), indicating that the reduction process of La^{3+} to La^{2+} is irreversible. The relationship between E_p and half cathodic peak potential ($E_{p/2}$) for this irreversible reduction reaction can be expressed by Eq.(1):

$$|E_p - E_{p/2}| = \frac{1.857RT}{anF} \quad (1)$$

where R , T , a , n and F represent the gas constant, absolute temperature, average mass transfer coefficient, electron transfer number, and Faraday constant, respectively^[16,23,26]. Since n equals 1 for the reduction of La^{3+} to La^{2+} , a is calculated as 0.0784 in average (Table 1).

The linear relationship between the cathodic peak current (I_p) and the square root of ν (Fig. 5c) indicates that the electrodeposition of La in BMIMPF_6 is a diffusion-controlled process. The diffusion coefficient can be determined by Eq.(2):

$$I_p = 0.4958n^{3/2}ACD^{1/2}\nu^{1/2}\left(\frac{aF^3}{RT}\right)^{1/2} \quad (2)$$

where A , C , and D represent electrode area, solution concentration and diffusion coefficient, respectively^[23]. Based on the obtained average mass transfer coefficient a , the diffusion coefficient D is calculated as $1.47 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$. The influence of La^{3+} concentration on the electrodeposition of La in BMIMPF_6 was also investigated. With increasing the initial concentration of $\text{La}(\text{NO}_3)_3$ dissolving in BMIMPF_6 , the cathodic peak current (I_p) obviously increases while the E_p shifts to higher values, as shown in Fig. 5d. This result further confirms the diffusion-controlled electrodeposition process of La in this case.

A summary of electrochemical studies on the diffusion coefficients of some lanthanide ions in different ionic liquids is listed in Table 2. From Table 2, the temperature, La

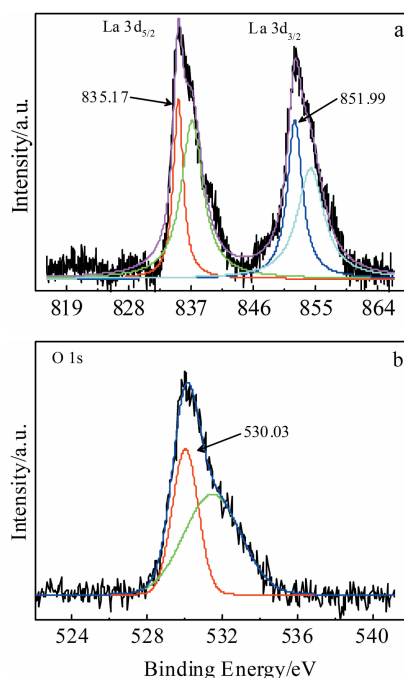


Fig.4 XPS spectra of La 3d (a) and O 1s (b) on electrodeposited La thin film

precursors and the type of ionic liquid obviously affect the diffusion coefficient. High viscosity of ionic liquids is a crucial factor leading to the slow mobility of La^{3+} or La-complex ions in ionic liquids. Because raising the temperature reduces the viscosity, the poor solubility of metal ions in ionic liquids should be taken into consideration.

In order to prepare the highly active La film by electrodeposition under mild conditions, the ionic liquid BMIMPF_6 was used in this work. This hydrophobic ionic liquid shows advantages for the electrodeposition of light rare earth elements: wide electrochemical window, low hygroscopy, low viscosity, good ionic conductivity, and low solubility in water. Although BMIMPF_6 might decompose to release HF gas when it is heated to around 453 K, $[\text{BF}_6]^-$ is more stable than other anions, such as $[\text{BF}_4]^-$ and $[\text{SbF}_6]^-$ ^[5,32,33]. La thin film was obtained by electrodeposition in BMIMPF_6 at 298 K through a

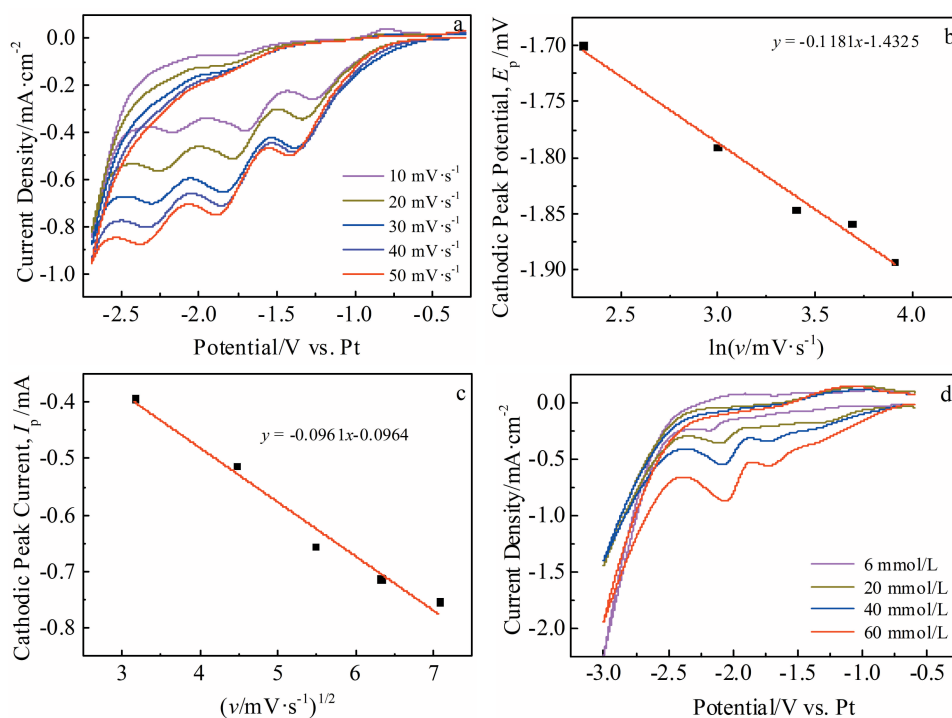


Fig.5 CVs of 6 mmol/L $\text{La}(\text{NO}_3)_3$ dissolving in BMIMPF_6 under different voltage scanning rates (a); relationship between cathodic peak potential of reduction of La^{3+} to La^{2+} and voltage scanning rate (b); relationship between cathodic peak current of the reduction of La^{3+} to La^{2+} and voltage scanning rate (c); CVs of $\text{La}(\text{NO}_3)_3$ with different concentrations dissolving in BMIMPF_6 (d)

Table 1 Related parameters for CVs of $\text{La}(\text{NO}_3)_3$ dissolving in BMIMPF_6 under different voltage scanning rates

$v/\text{mV}\cdot\text{s}^{-1}$	$E_p/\text{V vs. Pt}$	$E_{p2}/\text{V vs. Pt}$	I_p/mA	$ E_p - E_{p2} /\text{V vs. Pt}$	a
10	-1.700	-1.146	-0.3938	0.554	0.0861
20	-1.790	-1.199	-0.5126	0.591	0.0807
30	-1.846	-1.200	-0.6556	0.646	0.0738
40	-1.859	-1.227	-0.7128	0.632	0.0755
50	-1.893	-1.263	-0.7532	0.630	0.0757

Table 2 Diffusion coefficients of lanthanide ions under different conditions

Electrolyte system	Temperature, T/K	Diffusion coefficient, $D/\text{cm}^2\cdot\text{s}^{-1}$	Ref.
$\text{LaCl}_3\text{-LiCl-EMIMBF}_4$	298	1.19×10^{-6}	[23]
$\text{La}(\text{NTf}_2)_3\text{-MPPiNTf}_2$	323	2.88×10^{-7}	[29]
$\text{LaCl}_3\text{-BMIDCA}$	333	1.17×10^{-10}	[26]
$\text{NdTFSA}_3\text{-[P2225][TFSA]}$	373	$\sim 10^{-7}$	[20]
$\text{La}(\text{NO}_3)_3\text{-BMIMPF}_6$	298	1.47×10^{-9}	This work

Note: EMIMBF_4 : 1-ethyl-3-methylimidazolium tetrafluoroborate; MPPiNTf_2 : N-methyl-N-propylpiperidinium bis(trifluoromethylsulfonyl)imide; BMIDCA : 1-butyl-3-methylimidazolium dicyanamide; P2225 : triethyl-pentyl-phosphonium bis(trifluoromethyl-sulfonyl)amide; TFSA : trifluoromethanesulfonate.

more convenient way in this research, whereas most results were reported with the electrodeposition at higher temperatures in a glovebox^[16,26,29]. It must be mentioned that La^{3+} salts show poor solubility in ionic liquids. In this work, cosolvent acetone significantly improves the solubility of $\text{La}(\text{NO}_3)_3$ in BMIMPF_6 . $\text{La}(\text{NO}_3)_3$ can dissolve in acetone, which completes the coordination sphere of La^{3+} . Besides, the acetone can dissolve well in BMIMPF_6 . Many anionic metal ion complexes

dissolve more easily in ionic liquids than metal cations do^[34]. As the acetone is removed from the mixture ($\text{La}(\text{NO}_3)_3\text{-acetone-BMIMPF}_6$), La^{3+} might be extracted into the ionic liquid as an anionic nitrification, namely $[\text{BMIM}]_n\text{-La}(\text{NO}_3)_m$ ^[25,27,35].

3 Conclusions

1) 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF_6) exhibits an electrochemical window between -2.5~

1.5 V vs. Pt with good cathodic stability. After adding the cosolvent acetone, BMIMPF₆ shows moderate solubility for La(NO₃)₃.

2) La thin film was successfully fabricated by electro-deposition in ionic liquid BMIMPF₆ at 298 K using a three-electrode system. The reduction of La³⁺ to La²⁺ and La²⁺ to La⁰ occurs at around -1.7 and -2.1 V vs. Pt, respectively.

3) The reduction process of La³⁺ in BMIMPF₆ is an irreversible and diffusion-controlled electrodeposition process. The diffusion coefficient of La³⁺ is 1.47×10⁻⁹ cm²·s⁻¹.

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298 K下离子液体BMIMPF₆中电沉积制备镧金属薄膜

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摘要: 以无水硝酸镧、1-丁基-3-甲基咪唑六氟磷酸 (BMIMPF₆) 和助溶剂丙酮为电解液, 在室温 (298 K) 下电沉积制得镧金属薄膜。电解液 BMIMPF₆ 的电化学窗口为 -2.5~1.5 V vs. Pt, La³⁺ 还原为 La²⁺ 发生于 -1.7 V vs. Pt, La²⁺ 还原为 La⁰ 发生于 -2.1 V vs. Pt。BMIMPF₆ 的低吸湿性有利于在空气气氛下电沉积镧。使用扫描电子显微镜和光学显微镜观察到所制备的薄膜结构致密, 经能量色散谱和 X 射线光电子能谱对沉积薄膜进行了表征, 确定了薄膜中含有大量镧元素。通过探究电压扫描速率和硝酸镧浓度对 La³⁺ 的电化学行为的影响, 证明 La³⁺ 的还原反应是一个受物质扩散控制的不可逆过程, La³⁺ 在 BMIMPF₆ 中的扩散系数为 1.47×10⁻⁹ cm²·s⁻¹。本研究为获得金属镧薄膜和镧氧化物薄膜提供了一种简便的方法, 并且有望用于电沉积制备其它镧系元素薄膜。

关键词: 离子液体; 镧; BMIMPF₆; 电沉积

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