Electrochemical Study of the Diffusion and Nucleation of Gallium(III) in [Bmim][TfO] Ionic Liquid

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Abstract

The electrochemical behaviors of Ga^{3+} ions in 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][TfO]) ionic liquid are investigated by electrochemical methods and SEM. The cyclic voltammetry study reveals that both the temperature and the material of the electrodes have a significant influence on the electrochemical kinetics. The three methods involved rotating disk electrode have been used to obtain the diffusion coefficient (around $5.57 \times 10^{-8} \text{ cm}^2/\text{s}$) of Ga^{3+} ions in [BMIM][TfO] ionic liquid at 70 °C. Meanwhile, the diffusion coefficients at 40, 50, 60 °C and the activation energy are obtained by two of the three methods. By analyzing the current transients and the SEM images of the Ga particles formed during the transients, it is found that the nucleation of Ga on both the glass carbon electrode and the Mo electrode in [BMIM][TfO] ionic liquid is a 3-D instantaneous process at 70 °C, while a 3-D progressive process on GCE at 25 °C. The compact and smooth Ga layer is

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electrodeposited on Mo film sputtered on ITO glass at -1.5 V (vs Pt) and 20 °C from the [BMIM][TfO] ionic liquid. Increasing the overpotential of the electrodeposition makes the Ga layer more porous. When the temperature is higher than the melting point of gallium metal, it has no significant influence on the morphology of the Ga deposits.

Keywords: Nucleation; Diffusion coefficient; Electrodeposition; Gallium; Ionic liquid

1 Introduction

Gallium is the key element of CIGS thin film, which is recognized as a promising candidate of solar cell materials [1]. On the other hand, as the backbone of the electronics industry, gallium has been widely used in the optoelectronics (e.g., LED's), telecommunication, aerospace, and many commercial and household items such as alloys, computers, and DVD's [2]. Increasing attention is paid to the electrodeposition of Ga and its alloy, especially relevant to CIGS, because electrodeposition is a low cost and simple method. In aqueous baths, the electrodeposition of Ga is disturbed by hydrogen evolution, which makes it difficult to control the content of gallium in its alloy deposits [3, 4]. Recent years, electrodeposition from ionic liquids has sprung up as a new trend, because ionic liquid has some advantageous physico-chemical properties, such as wide potential windows and high solubility of metal salts [5].

So far only a few reports can be found about the Ga electrodeposition from ionic liquids. By using microcylinder electrodes, Verbrugge, M. W. and Carpenter, M. K. [6]

1 obtained the thermodynamic, transport, and kinetic data of Ga electrodeposition process
2 in the gallium trichloride/1-methyl-3-ethylimidazolium chloride room-temperature
3 molten. Sun, I. W. et al. [7] prepared Ga electrodeposits on tungsten wires at 30 °C
4 from a solution of Ga^+ in the 60.0/40.0 mol % $\text{AlCl}_3/\text{MEIC}$ melt. They demonstrated the
5 electrochemical behaviors of $\text{Ga}^{3+}/\text{Ga}^+$ redox reaction on glass carbon and tungsten
6 electrodes, which involves slow charge-transfer kinetics. In addition, they found that the
7 electrodeposition of Ga from Ga^+ on glassy carbon involves instantaneous
8 three-dimensional (3-D) nucleation with diffusion-controlled growth of the nuclei.

9 Gasparotto, L. H. S. et al. [8] studied Ga electrodeposition from GaCl_3 in the air-
10 and water-stable ionic liquid 1-butyl-1-methylpyrrolidinium
11 bis(trifluoromethylsulfonyl)amide by in situ STM. They showed that Ga can be depos-
12 ited from the employed ionic liquid on Au (111) electrode by both electroless deposition
13 and electrodeposition. They analyzed the two cathodic peaks of the cyclic
14 voltammogram on Au (111): the one at lower overpotential might be attributed to the Ga
15 deposition on the Ga layer generated during an electroless process at OCP, and the other
16 one at higher overpotential might be attributed to the further Ga deposition. Freyland, W
17 et al.[9] investigated Ga electrodeposition on Au (111) from two lewis acidic ionic liq-
18 uids, a chloroaluminate melt and a chlorogallate melt in comparison. Beside the Ga-Au
19 surface layer resulting from underpotential deposition (UPD), they also showed that 3-D
20 Ga clusters in the size range from 5-30 nm are formed at the potentials more negative

1 than the UPD. Seddon, K. R. et al. [10] reported that buffered chlorogallate (III) ionic
2 liquids can be used to obtain the Ga electrodeposits with improved morphology, com-
3 pared to that electrodeposited from the unbuffered ionic liquids.

4 Several groups [11-13] have used a deep eutectic solvent, namely reline, consisting
5 of choline chloride and urea, for the electrodeposition of CIGS. Among the groups,
6 Phillip J. Dale and his coworkers systemically investigated the electrodeposition of Ga
7 [12, 14], Cu-Ga [14], and In-Ga [12] from the deep eutectic solvent for the CIGS solar
8 cell. However, all the experiments using reline is conducted in inert conditions, because
9 reline is hygroscopic and will spontaneously adsorb water in the open air [15]. Ionic
10 liquids based on more hydrophobic anions, such as trifluoromethanesulfonate,
11 bis-(trifluoromethanesulfonyl) imide and tris-(trifluoromethanesulfonyl) methide, have
12 low reactivity with water and large electrochemical windows [16]. Our group have pub-
13 lished a short report about the preparation of CIGS thin film by one pot
14 electrodeposition from 1-butyl-3-methylimidazolium trifluoromethanesulfonate
15 ([BMIM][TfO]) [17], and further and more detailed study has being carried out.

16 In the present paper we demonstrate the electrochemical behaviors of Ga^{3+} in
17 [BMIM][TfO] ionic liquid, including cyclic voltammograms, diffusion coefficient, nu-
18 cleation process, and the morphology of Ga electrodeposits. The focus is paid on inves-
19 tigating the diffusion coefficient and nucleation process, for which rotate disk electrode

(RDE) technology and chronoamperometry combined with SEM images have been employed.

2 Experimental

[BMIM][TfO] ionic liquid (99%) was purchased from Lanzhou Greenchem ILs (China). Prior to using the ionic liquid it was dried under vacuum at 80 °C for more than 24 hours. The GaCl₃ mother solutions were prepared in argon filled glove box with water and oxygen contents below 1 ppm, because ultra-dry gallium (III) chloride has a very strong ability of absorbing water in the open air. All the other experiments were carried out in the open air, in which condition the water contents of the solutions were about 237 ppm determined by METTLER TOLEDO volumetric Karl Fischer compact Titrator V20. The measured water content is close to the value (250 ppm) in vacuum-dried reported by Aoife M. O'Mahony, et al [18]. The electrochemical measurements were conducted in a three-electrode cell, with a platinum wire as the reference electrode and a platinum plate as the counter electrode. A glass carbon electrode (GCE, $\Phi = 3$ mm), a Mo electrode ($\Phi = 3$ mm), and a glass carbon RDE (GCRDE) ($\Phi = 5$ mm) were used as the working electrodes for different measurements. The Mo electrode is used as the work electrode because one possible application of Ga electrodeposits is in CuInGaSe thin film for solar cell that uses Mo thin film as the substrate. The electrodeposition experiments were performed in the same cell, while the working electrode was the molybdenum (Mo) film sputtered on the ITO coated glass. The densities

and viscosities of [BMIM][TfO] ionic liquid dissolving 0.5 M GaCl₃ with temperature dependence were measured by a rotational automated viscometer Anton Paar Stabinger SVM3000. The measurements at each temperature were repeated three times and the average values were used. Scanning electron microscope (SEM, Hitachi SU8010) was used to reveal the morphology of the Ga deposits.

3 Results and discussion

3.1 Electrochemical stability of [BMIM][TfO] ionic liquid

The electrochemical windows of [BMIM][TfO] ionic liquid on GCE and Mo electrodes were studied by cyclic voltammetry. The voltammograms at various temperatures are presented in Figure 1. For both electrodes, with the temperature increasing from 20 to 80 °C a slight diminish can be observed in the absolute value of the cathodic limits of the voltammograms., while a relatively bigger diminish occurs in the anodic limits. If the anodic and cathodic limits are defined as the potential at the current density of 1 mA/cm², the two limits and the windows of [BMIM][TfO] ionic liquid on the two electrodes at various temperatures are listed in Table 1. The values on the GCE are in accord with the results reported in the literatures [18, 19]. According to Table 1, the electrochemical window of [BMIM][TfO] ionic liquid on the GCE is wider than that on the Mo electrode. In addition, both the cathodic and the anodic limiting potentials almost do not change when the ionic liquid is open in the air for more than one day. This indicates that [BMIM][TfO] is not too sensitive to the air although [TfO]⁻ is relatively hydrophilic

[18]. Therefore, the following experiments, including electrochemical measurements and electrodeposition, are carried out in the open air.

3.2 Cyclic voltammetry for discharge process

The cyclic voltammograms of Ga^{3+} ions (0.5 M GaCl_3) in [BMIM][TfO] ionic liquid are recorded on GC and Mo electrodes at 25 and 70 °C. The potential scan, with a rate of 50 mV/s, starts from the rest potential toward negative direction. All the cyclic voltammograms on the two electrodes, presented in Figure 2, have the similar profile. In the forward scan, when the scanning potential reaches a relatively negative value (E_o , onset potential) the current begins to increase and then decreases, which results in a cathodic peak. When the potential scans toward positive direction from the switching potential, the cathodic current decreases very slowly, which makes the reverse curve intersect the forward curve. This forms a “hysteresis loop”, also called “nucleation loop” [20], which is the characteristic of nucleation process. This behavior is more obvious at 70 °C than that at 25 °C. Only a quite small anodic peak at 0 ~ -0.25 V is recorded in the reverse curve of the cyclic voltammograms on both electrodes. This demonstrates that the Ga deposits are difficult to be anodically oxidized in [BMIM][TfO] ionic liquid.

As displayed in Figure 2, each nucleation loop has two crossover points at which the potential can be defined as, at least approximate to, the nucleation potential (E_n) and reversible potential (E_c), according to the literatures [21-23]. Table 2 lists the calculated nucleation overpotentials (ΔE_N) of Ga on both electrodes by using the potential values of

the crossover points. At 25 °C all the absolute values of E_c , E_n , and ΔE_N of the GCE are bigger than that of the Mo electrode. At 70 °C Mo and GC have almost the same E_c while the E_n of GCE is 100 mV more negative than that of Mo electrode. On the other hand, all the absolute values of E_c , E_n , and ΔE_N of the two electrodes are bigger at 25 °C than those at 70 °C correspondingly. These results indicate that both the temperature and the material of the electrodes have a significant influence on the electrochemical kinetics.

3.3 Diffusion coefficient of Ga^{3+} in [BMIM][TfO]

The diffusion coefficient of Ga^{3+} in [BMIM][TfO] ionic liquid is a key parameter for the electrodeposition process because of the relatively big viscosity of the ionic liquid compared to the aqueous solutions [5]. Forced convection hydrodynamic methods by using rotating disk electrode are most convenient and widely used to obtain the information about mass transport of reactants [24]. In the present work three operation ways have been employed to obtain the diffusion coefficients of Ga^{3+} in [BMIM][TfO] ionic liquid at various temperatures.

The first operation way (I) is to record the current along with scanning the potential when the rotation rate of the electrode is kept constant. The results are showed in Figure 3 (a), in which the voltammetry curves have the typical characteristic of diffusion controlled process: the diffusion-limited current density increases with the increase of the rotation rates of the RDE. However, the increasing part of the curves does not have the

typical behaviors: the polarization decreases and the potential range of the increasing part shifts toward positive when the rotation rate increases. This indicates that the surface of the GCE do not have a well consistency at the low potential scan rates, which may be related to the liquid state of Ga deposit at this condition.

The second method (II) is to record the current at a constant step potential with the uncontinuous increase of the rotation rate of the RDE. In order to reach the steady state diffusion each rotation rate is kept for several seconds. The current density versus time ($j - t$) curves at various temperatures are displayed in Figure 3 (b). The third method (III) is to record the $j - t$ curve at a constant step potential and constant rotation rate. As a representative, Figure 3 (c) shows the $j - t$ curves at various rotation rates and 70 °C. All the $j - t$ curves in Figure 3 (c) reach the steady state diffusion and have a peak corresponding to the nucleation process which will be discussed in detail in the next section.

As displayed in Figure 3 (d), the Levich plots obtained by using the above three methods at 70 °C have no significant differences. In fact the plots from the first two methods almost overlap with each other. According to Levich equation, equation(1) [24], the calculated diffusion coefficients from the above three methods are $5.85 \times 10^{-8} \text{ cm}^2/\text{s}$, $6.03 \times 10^{-8} \text{ cm}^2/\text{s}$, and $5.32 \times 10^{-8} \text{ cm}^2/\text{s}$, respectively.

$$j_d = 0.62nFD^{2/3}\nu^{-1/6}C_o^*\omega^{1/2} \quad (1)$$

Where j_d is the diffusion-limited current density (A cm^{-2}), n is the number of electrons transferred in this reaction, F is Faraday constants (C mol^{-1}), D is the diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$), ν is the kinematic viscosity of the solution ($\text{cm}^2 \text{ s}^{-1}$), C_O^* is the bulk concentration of the electroactive ions (mol cm^{-3}), and ω is angular rotation speed (rad s^{-1}). The kinematic viscosity is the ration of dynamic viscosity η to density ρ , which are listed in Table 3.

The above result indicates that the last two methods ((II) and (III)) are equally effective to get the diffusion coefficient, compared with the first traditional method. Because method (II) and (III) are more convenient and time saving, they are carried out at various temperatures to get the activation energy of diffusion and to corroborate each other.

The Levich plots, j_d versus $\omega^{1/2}$, at various temperatures obtained by using the two methods are shown in Figure 4. At all temperatures the j_d varies linearly with $\omega^{1/2}$, and the plots have a zero interception, which matches the predictions of the Levich equation. The diffusion coefficients calculated from the slopes of the Levich plots are listed in Table 3, in which the values obtained by using the two methods are close at each experimented temperature. The diffusion coefficient at 60°C has the same order of magnitude with the results in choline chloride/urea ionic liquid reported by Marc Steichen et al [14]. The diffusion activation energies (E_a) from the slopes of the plots of $\ln D - 1/T$

(Figure 5) are 52.42 and 41.80 KJ/mol for the two methods, respectively, according to equation(2) [25].

$$D = A_0 e^{-E_a/RT} \quad (2)$$

Where A_0 is the pre-exponential factor (J mol^{-1}), R is the universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), and T is the thermodynamic temperature (K).

3.4 Chronoamperometry for nucleation

Chronoamperometry is a convenient method to study the electrocrystallization process, as a quite mature theory based on the analysis of potentiostatic current transient has been developed [26-28]. The potentiostatic current transients of GCE in the [BMIM][TfO] ionic liquid containing 0.5 M GaCl_3 at 70 °C and various potentials are shown in Figure 6 (a). All the current transients have the typical characteristics of the three dimensional (3-D) heterogenous nucleation, with the step potentials from the open circuit potential to the range from -1.4 to -1.6 V. Firstly, the current decays sharply to near zero at the very moment after a potential step to the experimented value, which is attributed to the charging of the double layer. Preceding the onset, the current keeps at a quite small value for a period which is called the induction time (t_i) [29, 30]. Then the current rises up to the maximum j_m at t_m and falls subsequently because of the linear diffusion which can be described by Cottrell equation [22, 27].

For the instantaneous nucleation process, the rising portion of the current transient obeys equation(3), considering the induction time [27, 31].

$$j(t) = \frac{nF\pi(2DC_o^*)^{3/2}M^{1/2}N_0(t-t_i)^{1/2}}{\rho^{1/2}} \quad (3)$$

Where M is the mole mass of the metal (g mol^{-1}), N_0 is the number density of the active sites (cm^{-2}), and ρ is the mass density of the metal (g cm^{-3}). Figure 6 (b) shows the $j^2 - t$ plots corresponding to the rising portion of the current transients in Figure 6 (a). All the plots show a good linear response, which means the data obey equation(3). Listed in Table 4, the t_i calculated from the horizontal axis intercepts of the $j^2 - t$ plots decreases with the increase of the overpotential.

According to the report in the literature [27], the relationship between the j_m and the corrected t_m , $t_m - t_i$, can be described by equation(4). The diffusion coefficients calculated according to equation(4) at various potentials are also listed in Table 4. The values obtained at -1.50 and -1.55 V are quite close to those obtained by forced convection hydrodynamic in section 3.3.

$$j_m^2(t_m - t_i) = 0.1629(nFC_o^*)^2 D \quad (4)$$

For the diffusion-controlled growth of hemispheric nuclei, a dimensionless equation has been derived to calculate the nucleation parameters N_0 and A (the nucleation rate constant) quantitatively or to determine the nucleation mode qualitatively by using the current transients [28]. Considering induction time t_i , the relationship between $(j/j_m)^2$ and $(t-t_i)/(t_m-t_i)$ obeys equation(5) [28, 31].

$$\left(\frac{j}{j_m}\right)^2 = \left(\frac{t}{t_m - t_i}\right)^{-1} \frac{\{1 - \exp[-xt / (t_m - t_i)] + \alpha(1 - e^{-xt / (t_m - t_i)})\}^2}{\{1 - \exp[-x + \alpha(1 - e^{-x / \alpha})]\}^2} \quad (5)$$

Where $x = b(t_m - t_i)$, and $\alpha = b/A$. There are two limiting cases of equation(5): (i) $\alpha \rightarrow 0, x \approx 1.2564$ corresponding to equation(6) for instantaneous nucleation mode, and (ii) $\alpha \rightarrow \infty, x \approx 2.3367$ corresponding to equation(7) for progressive nucleation mode [28]. Figure 7 displays the comparison of the experimental $(j/j_m)^2 - (t - t_i)/(t_m - t_i)$ curves corresponding to Figure 6 with the theoretic instantaneous and progressive curves derived from equation(6) and (7). The $(j/j_m)^2 - (t - t_i)/(t_m - t_i)$ curves at all experimental potentials are close to the theoretic instantaneous curves, which indicates the instantaneous nucleation mode can describe the nucleation process of Ga on GCE in [BMIM][TfO] ionic liquid at 70 °C.

$$\left(\frac{j}{j_m}\right)^2 = 1.9542 \left(\frac{t}{t_m - t_i}\right)^{-1} \{1 - \exp[-1.2564 \left(\frac{t}{t_m - t_i}\right)]\}^2 \quad (6)$$

$$\left(\frac{j}{j_m}\right)^2 = 1.2254 \left(\frac{t}{t_m - t_i}\right)^{-1} \{1 - \exp[-2.3367 \left(\frac{t}{t_m - t_i}\right)^2]\}^2 \quad (7)$$

Nonlinear fitting of the $(j/j_m)^2 - (t - t_i)/(t_m - t_i)$ curves according to equation(5) is carried out to extract quantitative information on the nucleation kinetic parameters of Ga on the GCE. The fitting results are shown in Figure 8. The obtained parameters (x and α) of equation(5) and the kinetic parameters (A and N_0) are listed in Table 5. The value of x and α at all potentials are close to the limiting case for instantaneous nucleation mode, as the x is about 1.3 and α is about 0.08. N_0 increases with the increase of the overpotential and A also has the same trend.

In order to confirm the above conclusions, SEM are employed to observe the initial stages of Ga electrodeposition on the GCE from the [BMIM][TfO] ionic liquid contain-

ing 0.5 M GaCl₃ at 70 °C and -1.6 V. Figure 9 displays the SEM images of the Ga nuclei on the GCE by electrodepositing for 2s, 6s, 15s, and 30s. The densities of nuclei at 2s and 6s (Figure 9 (a) and (b)) have no significant differences, while the nuclei at 6s have a bigger size than those at 2s. These are the characteristics of instantaneous nucleation mode: all the nuclei are formed simultaneously and grow subsequently with an identical rate [32]. However, with the increase of deposition time from 6s to 30s (Figure 9 (b), (c), and (d)), the density of nuclei decreases and the nucleus size increases. This can be explained by considering that with increasing deposition time, the nuclei grow big and touch the neighbor ones so that the neighboring ones merge into one. These results may be related to the fact that Ga has a low melting point and is in molten state at 70 °C.

A more detailed analysis is carried out on the cases of deposition for 2s and 6s (Figure 9 (a) and (b)). The nonlinear fitting of the current transients and the nuclei with number mark in the SEM images are shown in the two families of figures in Figure 10. The densities of nuclei obtained by counting are 3.050×10^9 and $3.075 \times 10^9 \text{ cm}^{-2}$ for the cases at 2s and 6s, respectively, which are two order of magnitude bigger than that obtained by nonlinear fitting. Similar discrepancy is found in the study of the nucleation of copper on TiN in pyrophosphate solution, reported by Aleksandar Radisic et al[33]. The formation of multiple nuclei with a single diffusion zone is speculated as the reason [33].

In order to clear the influence of temperature on the nucleation process of Ga on GCE, the qualitative analysis has been made on the current transients of GCE in the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 25 °C. Figure 11 shows the current transients, the corresponding $j^{2/3} - t$ plots, and the comparison of the experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves with the theoretic instantaneous and progressive curves. The experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves at all potentials are close to the theoretic progressive one, which indicates the nucleation process of Ga on GCE in the [BMIM][TfO] ionic liquid at 25 °C can be described by the progressive nucleation mode. In addition, the induction time t_i for this case are obtained from the $j^{2/3} - t$ plots corresponding to the rising portion of the current transients, because the progressive nucleation process obeys equation(8) in the rising portion of the current transients [27, 31].

$$j(t) = \frac{2nFAN_0\pi(2DC_o^*)^{3/2} M^{1/2} (t-t_i)^{3/2}}{3\rho^{1/2}} \quad (8)$$

Figure 12 displays the SEM images of the initial stages of Ga electrodeposits on the GCE from the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 25 °C and -2.0 V. It can be observed that the nuclei obtained by depositing for 50s have a bigger density and larger average size than that by depositing for 20s. This is the typical characteristic of progressive nucleation mode: the nuclei are formed continually and grow to different sizes at different rates.

Figure 13 shows the current transients of Mo electrode in the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 70 °C and step potentials, corresponding $j^2 - t$ plots, and the comparison of the experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves with the theoretic instantaneous and progressive curves. Same as the case on GCE at 70 °C, the experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves at all potentials are close to the theoretic instantaneous curve, which indicates the nucleation of Ga on Mo electrode in [BMIM][TfO] ionic liquid at 70 °C can also be described by instantaneous nucleation mode.

3.5 Potentiostatic electrodeposition

The Ga layers were obtained by potentiostatic electrodeposition on the Mo films sputtered on ITO glass, which are used as the substrate for CuInGaSe thin film [34]. The influences of the deposition potential and the temperature on the morphology of the Ga layers are investigated. The SEM images of the Ga layers electrodeposited from the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at various conditions are displayed in Figure 14 and Figure 15. As shown in Figure 14, the Ga layers consist of spherical grains, similar to the results reported by Marc Steichen et al [14]. The Ga layer (Figure 14 (a) and (A)) obtained at -1.5 V is compact and smooth, and the layer (Figure 14 (b) and (B)) obtained at -1.8 V shows some pores, which is so obvious on the layer (Figure 14 (c) and (C)) obtained at -2.4 V that it already becomes porous structure. The pores on the layers obtained at -2.4 V may be caused by the gas produced by the decomposition of the [BMIM][TfO].

Figure 15 presents the SEM images of the Ga layers potentiostatically electrodeposited on the Mo film from the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at -1.5 V and 20, 40, and 60 °C. The spherical grains in the Ga layer obtained at 20 °C have a smaller average size than those in the Ga layers obtained at 40 °C. However, no significant differences can be observed in the grain size of the layers obtained at 40 and 60 °C, which may be attributed to low melting point of Ga metal. This indicates that temperature above the melting point of Ga metal has no significant influences on the morphology of the Ga deposits.

4 Conclusions

Cyclic voltammetry study shows that the electrochemical windows of [BMIM][TfO] ionic liquid on three electrodes have the following order: GCE > Pt electrode > Mo electrode. According to the analysis of Cyclic voltammetry, temperature has a big influence on the electrochemical kinetics of the reduction of Ga³⁺ ions in [BMIM][TfO] ionic liquid. At 25 °C the absolute values of E_c, E_n, and η_N of the three electrodes have the same order: Mo < Pt < GC.

Three methods involved RDE have obtained the equally effective diffusion coefficient (around 5.57×10^{-8} cm²/s) of Ga³⁺ ions in [BMIM][TfO] ionic liquid at 70 °C. The diffusion coefficients at each temperature (40, 50, 60, 70 °C) and the activation energy of diffusion obtained by the latter two methods are close to each other.

The combination of the analysis of the current transients and SEM images shows that the nucleation of Ga on GCE from [BMIM][TfO] ionic liquid is a 3-D instantaneous process at 70 °C while a 3-D progressive process at 25 °C. The nucleation of Ga on Mo electrode is also a 3-D instantaneous process at 70 °C.

Compact and smooth Ga layer is electrodeposited on the Mo film sputtered on ITO glass at -1.5 V and 20 °C from the [BMIM][TfO] ionic liquid. The Ga layers become more porous with the increase of the deposition potential from -1.8 to -2.4 V. The spherical grains in the Ga layers increase with the temperature increased from 20 to 40 °C. Temperature above the melting point of Ga metal has no significant influences on the morphology of the Ga deposits.

Acknowledge

This work was supported by National Natural Science Foundation of China (No.51474080) and the National Science Foundation of Heilongjiang Province in China (No. ZD201107) and State Key Laboratory of Urban Water Resource and Environment (Harbin Institute of Technology) (No. 2015DX09).

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18

19

List of tables

Table 1 Cathodic and anodic limiting potentials vs Pt wire of [BMIM][TfO] ionic liquid on GCE at various temperatures.

Electrode	$T/^{\circ}\text{C}$	$E_{(\text{cathodic})}/\text{V}$	$E_{(\text{anodic})}/\text{V}$	$E_{(\text{total})}/\text{V}$
GC	25	-2.36	2.10	4.46
	40	-2.31	2.03	4.34
	60	-2.25	1.98	4.23
	80	-2.20	1.90	4.10
Mo	25	-1.93	0.73	2.66
	40	-1.90	0.53	2.43
	60	-1.88	0.52	2.40
	80	-1.84	0.517	2.36

Table 2 The nucleation overpotential (ΔE_N) of Ga on three different electrodes in [BMIM][TfO] ionic liquid containing 0.5 M GaCl_3 at 25 and 70 $^{\circ}\text{C}$. The data is obtained from the nucleation loops of the cyclic voltammograms in Figure 2.

	25 $^{\circ}\text{C}$			70 $^{\circ}\text{C}$		
	E_c/V	E_n/V	$\Delta E_N/\text{V}$	E_c/V	E_n/V	$\Delta E_N/\text{V}$
GC	-1.58	-2.09	0.51	-1.13	-1.44	0.31
Mo	-1.48	-1.73	0.25	-1.13	-1.34	0.21

Table 3 The diffusion coefficients calculated from the slopes of the Levich plots in Figure 4. II and III are corresponding to Figure 4 (a) and (b), respectively.

$T/^{\circ}\text{C}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	$D/10^{-8}\text{ cm}^2\text{ s}^{-1}$	
			II	III
40	1.3155	45.65	1.04	1.26
50	1.3072	31.95	1.93	2.42
60	1.2989	22.50	3.48	3.44
70	1.2907	17.25	6.03	5.32

Table 4 The induction time (t_i) from Figure 6 (b) and the diffusion coefficients of Ga^{3+} in [BMIM][TfO] ionic liquid obtained from the j_m and $t_m - t_i$.

E vs Pt/V	t_i/s	$D/10^{-8}\text{ cm}^2\text{ s}^{-1}$
-1.40	14.42	2.65
-1.43	6.15	2.29
-1.45	3.10	4.37
-1.50	1.85	3.95
-1.55	0.79	5.29
-1.60	0.45	5.74

Table 5 The nucleation kinetic parameters of Ga on the GCE in [BMIM][TfO] ionic liquid at 70 $^{\circ}\text{C}$ obtained by nonlinear fitting the $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves in Figure 8.

E/V	x	α	A	$N_0/10^6\text{ cm}^{-2}$
-1.40	1.2513	0.0804	3.321	4.521
-1.43	1.3678	0.0672	7.752	8.821
-1.45	1.3984	0.0314	19.706	10.477
-1.50	1.4594	0.0835	14.164	20.026
-1.55	1.5879	0.0955	17.284	27.950
-1.60	1.5355	0.0935	28.073	44.445

1 List of figures

Figure 1 The voltammograms of the pure [BMIM][TfO] ionic liquid on GCE (a) and Mo electrode (b) at various temperatures , The scanning rate is 50 mV/s.

Figure 2 Cyclic voltammograms of GC and Mo electrodes in [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 25 and 70 °C. The scanning rate is 50 mV/s.

Figure 3 (a) Voltammetry curves of the GC-RDE at various rotation rates, the scan rate of 1 mV/s, and 70 °C. (b) $j - t$ curves when keeping the overpotential constant and discontinuously increasing the rotation rate of the GC-RDE at various temperatures. (c) $j - t$ curves at various rotation rates of the GC-RDE, -1.8 V, and 70 °C. (d) Comparison of the Levich plots obtained with the above three methods at 70 °C, in which (I) is correspond to (a), (II) to (b), and (III) to (c). The solution is [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃.

Figure 4 Levich plots at various temperatures obtained with two methods. (a) and (b) are corresponding to the methods demonstrated by Figure 3 (b) and (c), respectively.

Figure 5 $\ln D - 1/T$ plots of Ga^{3+} in [BMIM][TfO] ionic liquid obtained with the two methods. (a) and (b) are corresponding to Figure 4 (a) and (b), respectively.

Figure 6 (a) Current transients of GCE in the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 70 °C and various step potentials; (b) $j^2 - t$ plots corresponding to the ascent stages of the current transients in (a).

Figure 7 Comparison between the experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves corresponding to Figure 6 and the theoretic instantaneous and progressive curves.

Figure 8 Comparison between the experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves corresponding to Figure 6 and the theoretic curves obtained by non-linearly fitted according to equation(5). The step potentials are (a) -1.40 V, (b) -1.43 V, (c) -1.45 V, (d) -1.50 V, (e) -1.55 V, and (f) -1.60 V.

Figure 9 SEM images of the initial stages of Ga electrodeposition on the GCE from the [BMIM][TfO] ionic liquid containing 0.5 M GaCl_3 at 70 °C and -1.6 V vs Pt. The deposition time is (a) 2s, (b) 6s, (c) 15s, and (d) 30s.

Figure 10 (a) Local SEM image with the particles marked by numbers, (b) the $j-t$ curve, (c) the j^2-t plot, and (d) the comparison between the experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curve and the theoretic one corresponding to Figure 9 (a). (e) Local SEM image with the particles marked by numbers, (f) the $j-t$ curve, (g) the j^2-t plot, and (h) the comparison between the experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curve and the theoretic one corresponding to Figure 9 (b).

Figure 11 (a) Current transients of GCE in the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 25 °C and various step potentials. The inset is the $j^{2/3} - t$ plots corresponding to the ascent stages of the $j - t$ curves. (b) Comparison between the corresponding experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves and the theoretic instantaneous and progressive curves.

Figure 12 SEM images of the initial stages of Ga electrodeposition on the GCE from the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 25 °C and -2.0 V vs Pt. The deposition time is (a) 20s and (b) 50s.

Figure 13 (a) Current transients of Mo electrode in the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 70 °C and various step potentials. The inset is the $j^2 - t$ plots corresponding to the ascent stages of the $j - t$ curves. (b) Comparison between the corresponding experimental $(j/j_m)^2 - (t-t_i)/(t_m-t_i)$ curves and the theoretic instantaneous and progressive curves.

Figure 14 SEM images of the Ga layers potentiostatically electrodeposited on the Mo films from the [BMIM][TfO] ionic liquid containing 0.5 M GaCl₃ at 20 °C. The deposition potentials are (a) -1.5 V, (b) -1.8 V, and (c) -2.4 V. (A), (B), and (C) are the partial enlarged details corresponding to (a), (b), and (c), respectively. The deposition time is 30 min.

Figure 15 SEM images of the Ga layers potentiostatically electrodeposited on the Mo films from the [BMIM][TfO] ionic liquid containing 0.5 M GaCl_3 at -1.5 V. The temperatures are (a) 25 °C, (b), 40 °C, (c) 60 °C. (A), (B), and (C) are the partial enlarged details corresponding to (a), (b), and (c), respectively. The deposition time is 30 min.