

## A Preliminary Study of Electrocristallization of Bismuth on Glassy Carbon

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**Abstract:** The electrocrystallization of bismuth on glassy carbon electrodes (GCEs) from nitrate solutions was studied by cyclic voltammetry and chronoamperometry. Cyclic voltammograms exhibit a crossover between the cathodic and anodic branches, characteristic of the formation of bismuth nuclei on GCEs, and show that the bismuth electrocrystallization on GCEs is a diffusion-controlled reaction. The current transients were analyzed with the Scharifker and the Heerman equations. With the increase of  $\text{Bi}^{3+}$  concentration, the non-dimensional plots leaned to the theoretical curve for 3D instantaneous nucleation and growth. The overpotential dependence of nucleation and growth mechanism was also found. With the increase of overpotential, the non-dimensional curve approaches closer the limit for 3D instantaneous nucleation and growth. A quantitative analysis further shows that the nucleation rate constant ( $A$ ) and the number density of active sites ( $N_0$ ) exponentially grow with the increase of overpotential, and the diffusion coefficient ( $D$ ) decays in an exponential mode, which was not reported before. A comparison between the kinetic parameter values obtained from the Scharifker equation and those from the Heerman equation was made, showing the very close  $N_0$  and  $D$  values and the distinct  $A$  values (especially at  $-300$  and  $-350$  mV). However, under the experimental conditions of this work, both of the equations can be used for describing the electrocrystallization of bismuth on GCEs.

**Key words:** Electrocristallization, Bismuth, Glassy carbon electrode, Nucleation, Growth, Scharifker equation, Heerman equation

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### 1 Introduction

Due to its unique physical and chemical properties, bismuth has been attracting many electrochemistry researchers. Most of the studies involving electrochemistry and bismuth can be divided into five classes: (a) a promising electrochromic material<sup>[1]</sup>, (b) electrocatalytic activity of bismuth monolayer/sub-monolayer (underpotential deposition of bismuth) on some noble metal surfaces, as well as the effect of

bismuth adatoms<sup>[2,3]</sup>, (c) an attractive alternative to the traditionally used mercury film electrode in electroanalysis<sup>[4]</sup>, (d) correlations between the morphologies and sizes of metallic bismuth with large magnetoresistance<sup>[5]</sup> or thermoelectric efficiency<sup>[6]</sup>, and (e) overpotential deposition of bismuth onto several electrode materials<sup>[7,8]</sup>. It should be noted that, compared with the researches of the electrocrystallization of other metals such as copper, cobalt, and silver, the study of the mechanism of bismuth electrocrystal-

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lization is very insufficient, and the growth mechanism of bismuth during bulk deposition is little understood<sup>[8,9]</sup>, especially the early stages of electrocrystallization.

Electrochemical techniques such as cyclic voltammetry (CV) and chronoamperometry (CA) played a dual role: serving as the methods for metal deposition, and being used as diagnostic tools for the determination of reaction mechanisms<sup>[7]</sup>. To extract kinetic parameters from the experimental CA data, the Scharifker general equation<sup>[10]</sup> and the Heeman equation<sup>[11]</sup> were widely used. Milchev and Heeman<sup>[12]</sup> made a comment that, the Scharifker general equation underestimated the current at short times but described rigorously the long time, "Cottrell" behavior, whereas the Heeman equation predicted correct values for the current at short times but overestimated the current in the long time region. This paper will explore the mechanism of bismuth electrocrystallization on glassy carbon electrodes (GCEs) from nitrate solutions, and make a comparison between the Scharifker and the Heeman equations.

## 2 Experimental Section

### 2.1 Apparatus

Electrochemical measurements were performed with a CHI 440 electrochemical analyzer (CH Instruments), in connection with a personal computer. A GCE (3mm in diameter, CH Instruments, Austin, TX) served as the working electrode, with the Ag/AgCl (3 mol · L<sup>-1</sup> KCl) electrode and platinum wire as the reference and counter electrodes, respectively. All potentials were given versus the Ag/AgCl (3 mol · L<sup>-1</sup> KCl) electrode.

### 2.2 Chemicals and Reagents

All chemicals were of analytical grade. Bi(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O was obtained from China Medicine (Group) Shanghai Chemical Reagent Corporation. Nitric acid (65%) was purchased from Beijing Beihua Fine Chemicals Co. Ltd. All solutions were prepared with deionized water produced by a Millipore system (Simplicity 185, Millipore).

## 2.3 Procedures

Prior to the electrochemical experiments, GCEs were hand-polished to a mirror-like finish with a slurry of alumina on Microcloth (Buehler), then cleaned in an ultrasonic bath of deionized water for 10 min and finally dried in a stream of nitrogen gas. Cyclic voltammetric measurements were performed at different scan rates. Chronoamperometric experiments were carried out by using a cathodic pulse from 0 mV to different deposition potentials from -50 mV to -500 mV. In order to clear out the residual metal, before the next measurement, a cleaning step was applied by holding the working electrode at +500 mV for 2 min.

## 3 Results and Discussion

### 3.1 Cyclic Voltammetry Study

Fig. 1 shows the representative cyclic voltammogram for 20 mmol · L<sup>-1</sup> Bi<sup>3+</sup> / 1 mol · L<sup>-1</sup> HNO<sub>3</sub> obtained on GCEs at a scan rate of 500 mV / s. Potential scan started from +500 mV, reversed at -500 mV and terminated at +500 mV. A couple of well-defined cathodic and anodic peaks and a crossover between the cathodic and anodic branches were observed clearly. The presence of the crossover is diagnostic for the formation of bismuth nuclei on GCEs.

In order to determine the type of control limiting the deposition process, besides the cyclic voltammograms for different Bi<sup>3+</sup> concentrations obtained at 50

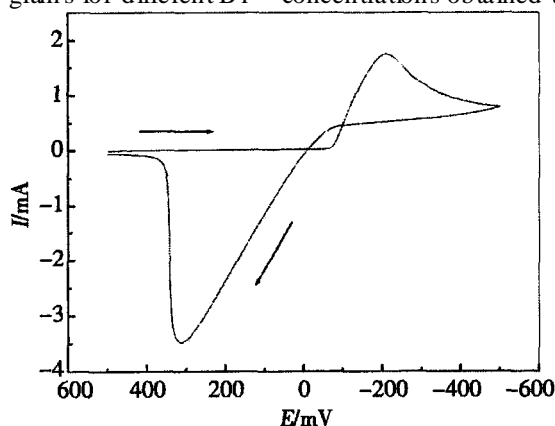


Fig. 1 Cyclic voltammogram for bismuth electrocrystallization onto glassy carbon electrodes from 20 mmol · L<sup>-1</sup> Bi<sup>3+</sup> / 1 mol · L<sup>-1</sup> HNO<sub>3</sub> at a scan rate of 500 mV / s

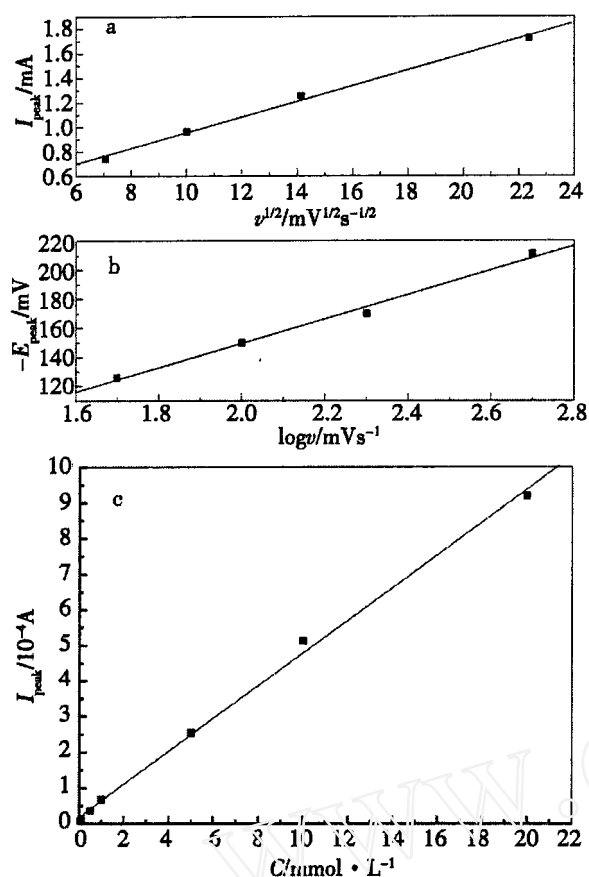


Fig 2 Plots of cathodic peak currents ( $I_{\text{peak}}$ ) vs the square roots of the scan rates ( $v^{1/2}$ ) (a,  $20 \text{ mmol} \cdot \text{L}^{-1} \text{Bi}^{3+}$ ), of cathodic peak potentials ( $E_{\text{peak}}$ ) vs the logarithms of the scan rates ( $\log v$ ) (b,  $20 \text{ mmol} \cdot \text{L}^{-1} \text{Bi}^{3+}$ ), and of  $I_{\text{peak}}$  vs  $\text{Bi}^{3+}$  concentrations (c,  $50 \text{ mV/s}$ )

$\text{mV/s}$ , a group of cyclic voltammograms for  $20 \text{ mmol} \cdot \text{L}^{-1} \text{Bi}^{3+} / 1 \text{ mmol} \cdot \text{L}^{-1} \text{HNO}_3$  were recorded at different scan rates:  $50, 100, 200$ , and  $500 \text{ mV/s}$ . Fig 2 presents the plot of the cathodic peak current ( $I_{\text{peak}}$ ) vs the square root of scan rate ( $v^{1/2}$ ), the plot of the cathodic peak potential ( $E_{\text{peak}}$ ) vs the logarithm of scan rate ( $\log v$ ), and the plot of  $I_{\text{peak}}$  vs  $\text{Bi}^{3+}$  concentration. All the three plots exhibit an excellent linear relationship, which is characteristic of a diffusion-controlled reaction. The correlation coefficients ( $R$ ) are respectively  $0.9977$  for  $I_{\text{peak}}$  vs  $v^{1/2}$ ,  $0.9988$  for  $I_{\text{peak}}$  vs  $\text{Bi}^{3+}$  concentration, and  $0.9956$  for  $E_{\text{peak}}$  vs  $\log v$ .

### 3.2 Chronoamperometry Study

Chronoamperometry is a very important diagnostic electrochemical technique for electrocrystallization studies. It is well known that Scharifker and Hills<sup>[14]</sup> developed the model for the three-dimensional (3D) multiple nucleation with diffusion-controlled growth.

The expressions for instantaneous and progressive nucleation with 3D growth are given by Eq (1) and Eq (2), respectively.

$$\frac{\hat{I}}{\hat{I}_{\text{max}}} = \frac{1.9542}{t/t_{\text{max}}} \{1 - \exp[-1.2564(t/t_{\text{max}})]\}^2 \quad (1)$$

$$\frac{\hat{I}}{\hat{I}_{\text{max}}} = \frac{1.2254}{t/t_{\text{max}}} \{1 - \exp[-2.3367(t/t_{\text{max}})^2]\}^2 \quad (2)$$

where  $\hat{I}_{\text{max}}$  and  $t_{\text{max}}$  are the current and time coordinates of the chronoamperometric peak. The two equations provide a convenient criterion for distinguishing between these two extreme cases of nucleation kinetics.

Fig 3 is the non-dimensional  $\hat{I}/\hat{I}_{\text{max}}$  vs  $t/t_{\text{max}}$  plots of the data for bismuth electrocrystallization onto GCEs from  $1 \text{ mol} \cdot \text{L}^{-1} \text{HNO}_3$  solutions containing  $20$ , and  $10 \text{ mmol} \cdot \text{L}^{-1} \text{Bi}^{3+}$ , where the solid and dotted lines are the theoretical transients respectively for 3D instantaneous and progressive nucleation with diffusion-controlled growth. The effect of  $\text{Bi}^{3+}$  concentration on nucleation and growth mechanisms can be observed from Fig 3. With the increase of  $\text{Bi}^{3+}$  concentration, the non-dimensional plots lean to the theoretical curve for 3D instantaneous nucleation and growth, suggesting high concentration is helpful for the formation of dense and uniform Bi deposits. Also, the plots corresponding to  $20$  and  $10 \text{ mmol} \cdot \text{L}^{-1} \text{Bi}^{3+}$  show a potential dependence of nucleation and growth mechanism. With the increase of overpotential, the non-dimensional curve approaches closer the limit for 3D instantaneous nucleation and growth. Such a potential dependence was also found in the electrocrystallization of copper on  $\text{Au}(111)$ <sup>[15]</sup>, silver on different carbon substrates<sup>[16]</sup>, and bismuth on fluorine-doped tin oxide-coated conducting glass substrates<sup>[17]</sup>.

For a further analysis of the kinetics mechanism shown by Fig 3, a general equation should be used as

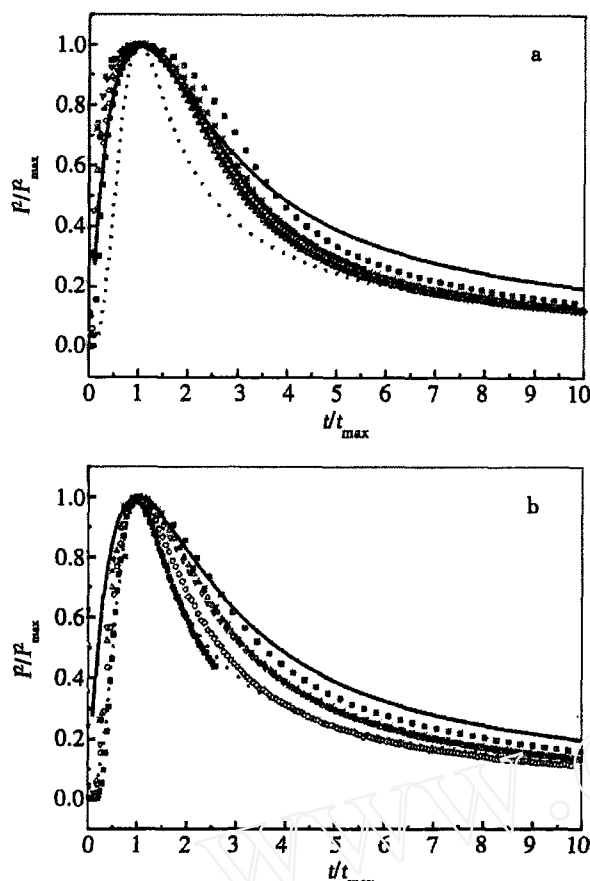


Fig 3 Non-dimensional  $i/i_{\max}$  vs  $t/t_{\max}$  plots of the data for bismuth electrocrystallization onto glassy carbon electrodes from  $1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$  solutions containing (a) 20 and (b)  $10 \text{ mmol} \cdot \text{L}^{-1} \text{ Bi}^{3+}$  the electrode potential was stepped from 0 mV to ( ) - 100, ( ) - 150, ( ) - 200, ( ) - 250, ( ) - 300, and ( ) - 350 mV. The theoretical transients for instantaneous (solid line) and progressive (dotted line) nucleation were calculated according to the Scharifker-Hills model

the theoretical model for the estimation of typical kinetics parameters, nucleation rate constant ( $A$ ) and number density of active sites ( $N_0$ ). Often used is the Scharifker's general equation<sup>[10]</sup> i.e.

$$I_{\text{SD-DC}}(t) = \frac{zFD^{1/2}C}{1/2 t^{1/2}} [1 - \exp(-N_0 k D t)] \quad (3)$$

with

$$= 1 - \frac{(1 - \exp(-At))}{At} \quad (4)$$

where  $zF$  is the molar charge transferred during electrocrystallization,  $D$  is the diffusion coefficient,  $C$  is the bulk concentration of the electroactive species,

$t$  is time. The  $k$  is defined by Equation 4, of which  $M$  and  $\rho$  are the atomic weight and the density of the deposit, respectively.

$$k = \frac{4}{3} \left( \frac{8 CM}{\rho} \right)^{1/2} \quad (5)$$

It should be noted that Heeman and Taralbo<sup>[11]</sup> proposed a modification to the Scharifker general equation:

$$I_{\text{SD-DC}}(t) = \frac{zFD^{1/2}C}{1/2 t^{1/2}} [1 - \exp(-N_0 k D t)] \quad (6)$$

where

$$= 1 - \frac{\exp(-At)}{(At)^{1/2}} \int_0^{(At)^{1/2}} \exp(-x^2) dx \quad (7)$$

Since the function  $F(x) = \exp(-x^2) \int_0^x \exp(-t^2) dt$  can be efficiently approximated with the polynomial<sup>[17]</sup>

$$F(x) = \frac{0.051314213 + 0.47910725x}{1 - 1.2068142x + 1.185724x^2} \quad (8)$$

Eq (7) can be rewritten as

$$= \frac{a - 1.2068142A^{1/2}t^{-1/2} + 1.185724At - 0.051314213A^{-1/2}t^{-1/2}}{1 - 1.2068142A^{1/2}t^{-1/2} + 1.185724At} \quad (9)$$

$$a = 0.52089275$$

The nonlinear parameter estimation was done by fitting Eq (3) and Eq (6) to the experimental data points. A commercial software based on the Levenberg-Marquardt algorithm served as the tool for the nonlinear fitting. Six groups of original experimental current transients obtained at six different deposition potentials (corresponding to Fig 3a) were analyzed. The best-fit kinetics parameters,  $A$ ,  $N_0$ , and  $D$ , were listed in Tab 1. Fig 4 shows a very clear potential dependence of  $A$ ,  $N_0$ , and  $D$ . Whichever model was used,  $A$  and  $N_0$  exponentially grew with the increase of overpotential, while  $D$  decayed in an exponential mode. Similar phenomenon was described by Palmar-Pardave etc. in their study of copper OPD onto Au(111)<sup>[15]</sup>.

Also, Fig 4 provides a direct comparison between the kinetic parameter values obtained from the Scharifker equation and those from the Heeman equation. It can be observed that, the two equations resulted in the very close  $N_0$  and  $D$  values and the distinct  $A$  values (especially at - 300 and - 350

Tab 1 Kinetic parameters of the bismuth OPD from 20 mmol · L<sup>-1</sup> Bi<sup>3+</sup> / 1 mol · L<sup>-1</sup> HNO<sub>3</sub> onto GCEs Estimated by using Eq (3), Scharifker equation and Eq (6), Heeman equation

- E/mV	Scharifker equation			Heeman equation		
	A / 10 <sup>4</sup> s <sup>-1</sup>	N <sub>0</sub> / 10 <sup>7</sup> cm <sup>-2</sup>	D / 10 <sup>-6</sup> cm <sup>2</sup> · s <sup>-1</sup>	A / 10 <sup>4</sup> s <sup>-1</sup>	N <sub>0</sub> / 10 <sup>7</sup> cm <sup>-2</sup>	D / 10 <sup>-6</sup> cm <sup>2</sup> · s <sup>-1</sup>
100	0.00551	0.16458	11.06950	0.00414	0.16007	10.72400
150	0.03130	0.48550	9.90971	0.01964	0.48060	9.76009
200	0.19931	1.26003	9.26057	0.09633	1.26141	9.19914
250	0.84059	2.29023	9.01560	0.31255	2.29961	8.98446
300	3.79127	4.04106	8.78891	0.68042	4.08380	8.76411
350	10.77039	6.46130	8.67057	1.14466	6.53903	8.64899

Tab 2 Linear fitting parameters for the plot of lnA vs E and the estimated N<sub>c</sub> (critical nucleus size)

Models	Section 1			Section 2		
	R	Slope	N <sub>c</sub>	R	Slope	N <sub>c</sub>
Scharifker Equation	0.998 75	33.869 29	0	0.994 57	25.504 55	0
Heeman Equation	0.997 84	29.122 34	0	0.993 49	12.980 96	0

mV). According to the atomistic theory of electrolytic nucleation, the critical size of the nuclei (N<sub>c</sub>) can be estimated using Eq (10).

$$N_c = \frac{KT}{ze_0} \left( - \frac{d \ln A}{dE} \right) - \tag{10}$$

where K is the Boltzmann constant, T is the absolute temperature, z is the number of electrons transferred during the electrochemical reaction, e<sub>0</sub> is the elementary electric charge, and is the kinetic transfer coefficient

With an attempt to judge the kinetic parameter values obtained from the two equations, lnA was plotted as a function of - E (shown in Fig 5). It has been shown that, the lnA vs - E curve should be represented by a cusped line, each sector corresponding to a given number of atoms. Each plot in Fig 5 contains two sections of different slopes. From the slopes and using a transfer coefficient value of 0.5 and a temperature of 298 K, N<sub>c</sub> values were estimated by Eq (10) (see Tab 2). The result N<sub>c</sub> = 0 means that, within the investigated potential interval, the single adsorbed bismuth atoms are strongly bound with GCE surface and form the stable one-atomic "clusters" that can grow irreversibly at the applied potential. Such a phenomenon was ever reported in

the electrocrystallization of rhodium on polycrystalline gold<sup>[19]</sup>. These results suggested that, both the Scharifker and the Heeman equations can be used for describing the electrocrystallization of bismuth on GCEs, at least under the experimental conditions of this work.

### 4 Conclusions

Cyclic voltammograms for bismuth electrocrystallization on GCEs from nitrate solutions showed a couple of well-defined cathodic and anodic peaks and a crossover between the cathodic and anodic branches. The further analysis indicated that the electrocrystallization of bismuth on GCEs is a diffusion-controlled reaction.

The experimental current transients were analyzed with the Scharifker equation and the Heeman equation. With the increase of Bi<sup>3+</sup> concentration, the non-dimensional plots leaned to the theoretical curve for 3D instantaneous nucleation and growth, suggesting high concentration was helpful for the formation of dense and uniform Bi deposits. In the cases of 10 and 20 mmol · L<sup>-1</sup> Bi<sup>3+</sup>, a potential dependence of nucleation and growth mechanism was also be found. With the increase of overpotential, the non-di-

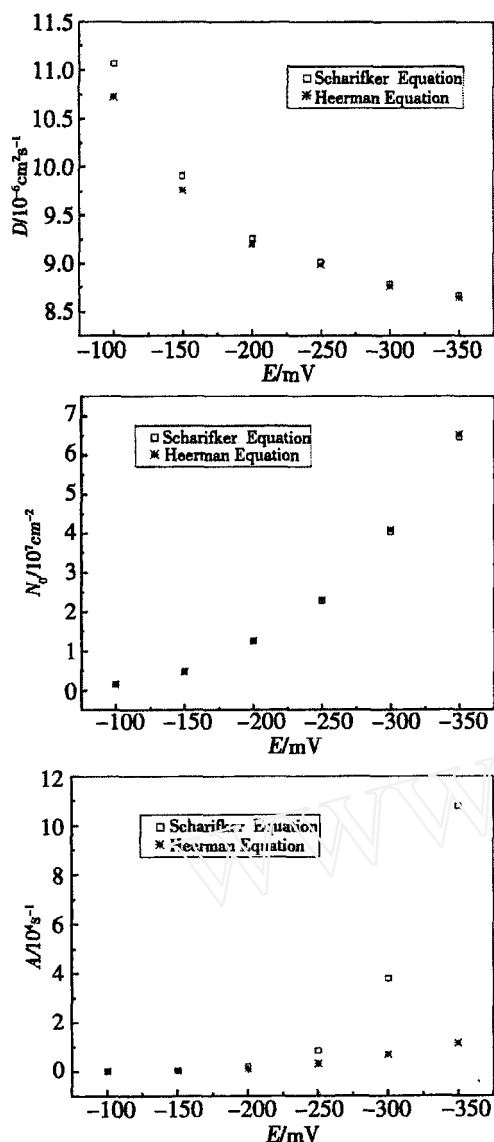


Fig 4 Plots of typical kinetics parameters in Table 1 vs deposition potentials  $A$ ,  $N_0$ , and  $D$  denote the nucleation rate constant, the number density of active sites, and the diffusion coefficient, respectively

mensional curve approaches closer the limit for 3D instantaneous nucleation and growth. A quantitative analysis further showed that  $A$  and  $N_0$  exponentially grew with the increase of overpotential, while  $D$  decayed in an exponential mode.

The kinetic parameter values such as  $N_0$  and  $D$  obtained from the Scharifker equation were very close to those from the Heerman equation, while there were differences between the two groups of  $A$  values

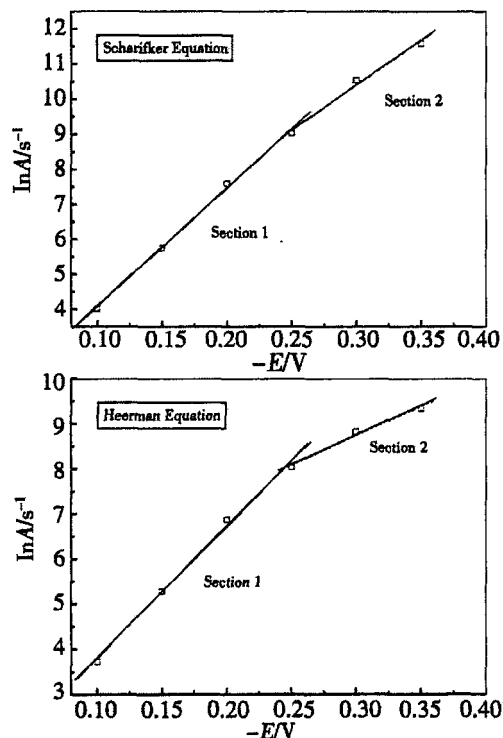


Fig 5 Variation of the  $\ln A$  with electrode potential for bismuth OPD onto GCEs from  $20 \text{ mmol} \cdot \text{L}^{-1} \text{ Bi}^{3+} / 1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$  the  $A$  values (nucleation rate) were obtained from (upper) Eq (3) and (lower) Eq (6), respectively

(especially at  $-300$  and  $-350 \text{ mV}$ ). Under the experimental conditions of this work, both of the equations can be used for describing the electrocrystallization of bismuth on GCEs from nitrate solutions. It was shown that, within the investigated potential interval, the single adsorbed bismuth atoms could be strongly bounded with GCE surface and formed the stable one-atomic "clusters" that could grow irreversibly at the applied potential.

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## 铋在玻碳电极上电化学结晶初步研究

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**摘要:** 应用循环伏安法和计时安培法研究了铋在玻碳电极上的电结晶行为。循环伏安曲线显示了铋在玻碳电极上成核的典型特征, 并表明其于玻碳电极上的电结晶是一个扩散控制过程。根据计时安培法响应曲线分析阐明了铋的浓度和过电势对成核生长机理的影响。进一步的定量测试表明该成核速率常数  $A$  和活化点密度  $N_0$  随过电势增加呈现指数增大规律; 扩散系数  $D$  随过电势增加呈指数衰减。以上实验结果至今未见报道。同时表明: Scharifker公式和 Heeman公式均可用于本实验的理论解释。

**关键词:** 电结晶; 铋; 玻碳电极; 成核; 生长; Scharifker公式; Heeman公式