

Electrodeposition Behaviour of Antimony in $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ Solutions

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The electrodeposition of antimony is first investigated in $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ solutions. In this study, linear scan voltammetry, cyclic voltammetry, chronoamperometry, chronopotentiometry and SEM-EDX techniques were utilized. The results suggested that the Sb^{3+} reduction takes place via a two-step reaction including a pre-conversion process. Linear scan voltammetric technique was used to identify the apparent transfer coefficient, exchange current density and apparent activation energy. The numbers of transfer electrons are calculated to be $n_1=1$ and $n_2=2$. For the first step reaction at 298K, α_1 and i^0_1 are 0.133 and $3.468 \times 10^{-3} \text{ A} \cdot \text{cm}^{-2}$, respectively. The pre-conversion reaction releases two F^- ions and does not affect NH_4^+ ions. A series of cyclic voltammograms were recorded at different scan rates and indicate that the reduction of Sb^{3+} is an irreversible process that is controlled by diffusion. The diffusion coefficients of Sb^{3+} in $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ electrolyte at different temperatures were calculated to be $1.051 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (298K), $1.149 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (303K), $1.257 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (308K), $1.484 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (313K), and $2.120 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (318K). The apparent activation energies of Sb^{3+} reduction at different overpotentials were calculated as $16.932 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.230 V), $16.696 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.240 V), $16.274 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.250 V), $16.195 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.260 V), $15.802 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.270 V), $15.502 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.280 V), $15.244 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.290 V), $14.964 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.300 V), and $14.647 \text{ kJ} \cdot \text{mol}^{-1}$ (-0.310 V).

Keywords: Antimony; Electrodeposition behaviour; $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$; Apparent activation energy; Diffusion coefficient

1. INTRODUCTION

Antimony has attracted considerable attention and industrial interest due to its many desirable properties such as negative thermal expansion [1-2], corrosion resistance and high hardness [3-4]. Antimony is extensively used as a hardening agent to heighten the mechanical strength of lead alloys [5-6] and as an alloying ingredient to improve the mechanical properties, damping capacity, specific capacity and hydrogen storage performance of magnesium alloys [7-13]. Moreover, antimony alloys are semiconductor materials that are used to produce photovoltaic cells and solar panels as a result of their beneficial photoelectric and/or thermoelectric properties [14-17].

During the past few decades, as a useful experimental method to prepare antimony and its alloys, electrodeposition processes have been attempted from various aqueous solutions and high-temperature molten salts [18-19]. Although the electrodeposition from chloride melts contributes to the formation of antimony and its alloys with desired composition, this approach suffers from several drawbacks: much higher operative temperature requirements, increased energy consumption and cost, and the fact that the employed electrolytes are difficult to recycle due to their characteristics volatility and corrosivity [20]. The aqueous electrolytes can be mostly divided into two groups: alkaline electrolytes and acidic electrolytes [21]. The most common constituents of alkaline electrolytes are sodium sulfide and sodium hydrate [22]. Anderson investigated the electrolysis of antimony in purified pregnant solution at 50-55°C, in which a special diaphragm cell was used. Under the best conditions, the Sb concentration was approximately 60 g/L, current density was approximately 320 A/m², and brittle and non-adherent antimony coatings were obtained with cell potentials of 3-5 V [23]. Samuel A. Awe used a non-diaphragm electrowinning cell in which the cathode current density was ten times lower than the anode current density to produce antimony metal from model alkaline sulfide solutions [24-25]. Considering that the electrodeposition of antimony and its alloys without complexing agent usually occurs at relatively high voltages and obtains undesirable morphological and structural cathode surfaces, xylitol (C₅H₁₂O₅), glycerol (C₃H₈O₃), or other polyhydric alcohols have been used as complexing agents to enhance the solubility and stability of Sb(III) [22, 26]. In addition, Zhang Duchao used alkaline xylitol solution as electrolyte for the electrorefining of a gold-bearing antimony alloy [27]. Liu Wei investigated the electrodeposition behaviour of Sb(III) in alkaline solutions containing xylitol by many electrochemical methods such as cyclic voltammetry, linear sweep voltammetry and chronoamperometry [28]. PAN recovered antimony by the electrowinning process from alkaline solutions containing glycerol [29]. However, the alkaline electrolytes used in electrorefining of antimony suffer from drawbacks such as non-adherent coating layer, anodic passivation by lead impurity, and unsuitability for gold-bearing antimony electrorefining because Au could react with sodium sulfide to form Na₃AuS₂, which could ultimately precipitate on the cathode [22, 30-31].

In other work, acidic electrolytes such as chloride [32-34], oxychloride-tartaric acid [35], tartaric acid [36-37], citric acid [22, 38], ethylene glycol [39] and hydrofluoric acid – sulfuric acid [22, 28] have been used in the electrorefining and electrowinning processes of antimony. The electrodeposition of antimony in chloride solutions has been limited due to hydrolysis of antimony (III) in the presence of chloride and due to the formation of explosive antimony [22, 40-41]. Preliminary studies have been with oxychloride-tartaric acid and citric acid. The high costs of tartaric acid and citric acid incur a severe

limitation on the commercial success. Thus far, only hydrofluoric acid-sulfuric acid electrolyte has been commercially used, resulting from its lower price, high stability and effective separation of antimony and lead. However, the electrodeposition of antimony in hydrofluoric acid-sulfuric acid solution is facing increased environmental protection pressure, due to the emission of hydrofluoric acid, which creates poor working conditions and damages the human body [28]. To relieve the harmful effect of hydrofluoric acid-sulfuric acid electrolytes, a new $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ electrolyte system, which could provide high current density, low cost and safety without the inherent disadvantages of the acidic counterparts, has been investigated in this work. Some studies have been conducted to preliminarily analyse the kinetic behaviours of antimony in the $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ system by linear scan voltammetry, cyclic voltammetry, chronopotentiometry and chronoamperometry.

2. EXPERIMENTAL

2.1 Reagents

All electrolytes were prepared with deionizer water and reagents of grade analytical. Hence, Sb_2O_3 (Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd, China, $\geq 99.0\%$), HF (Guangdong Guanghua Chemical Factory Co., Ltd, China, $\geq 40.0\%$), NH_4F (Tianjin Bodi Chemical Co., Ltd, China, $\geq 96.0\%$), H_2SO_4 (Chengdu Kelong Chemical Reagent Factory, China, $95\% \sim 98\%$) were used to prepare electrolytes with the following composition: 120 g/L Sb^{3+} , 50 g/L NH_4^+ , 80 g/L F^- and 360 g/L SO_4^{2-} . The concentration of Sb^{3+} in the electrolyte was changed to the following values: 60, 80, 100 and 120 g/L. The concentration of F^- in the electrolyte was changed to the following values: 50, 65, 80 and 90 g/L. The concentration of NH_4^+ in the electrolyte was changed to the following values: 0, 30, 50 and 70 g/L.

2.2 Electrochemical measurements

The electrodeposition behavior of antimony in $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ solutions was investigated by the analysis of linear scan voltammetry, cyclic voltammetry, chronoamperometry and chronopotentiometry. All the electrochemical measurements were performed in a conventional three-electrode cell using a CHI760C electrochemical workstation (CH Instrument, Inc.). The working electrode (0.071 cm^2 in effective dimension, $\Phi=3\text{ mm}$) and the auxiliary electrode (0.785 cm^2 in effective dimension, $\Phi=10\text{ mm}$) were made of pure antimony rod ($\geq 99.99\%$) which were embedded in ethylene-vinyl acetate (EVA). Glassy carbon electrode was used as another working electrode (0.071 cm^2 in effective dimension, $\Phi=3\text{ mm}$) to determinate the cathodic reaction products. An $\text{Hg}|\text{Hg}_2\text{SO}_4$ electrode (Shanghai Leichi Instrument Factory) with standard electrode potential of 0.616V (vs. NHE) at 298K was used as the reference electrode, which was linked to the electrolytes via the Luggin-capillary.

Linear scan voltammetry were carried out on an antimony electrode at temperature ranging from 298K to 318K in $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ system with different concentrations of Sb^{3+} , F^- and NH_4^+ . The potential was scanned from -0.55V vs. $\text{Hg}|\text{Hg}_2\text{SO}_4$ towards the negative direction to -1.1V vs.

Hg|Hg₂SO₄ with a scan rate of 1mV/s. Chronoamperometry measurements on glassy carbon working electrode at 298K with a constant potential such as -0.8V and -1.0V vs. Hg|Hg₂SO₄) were performed. Chronopotentiometric measurements were performed by stepping the current between $4.93 \times 10^2 \text{ A} \cdot \text{m}^{-2}$ and $4.23 \times 10^3 \text{ A} \cdot \text{m}^{-2}$ on an antimony working electrode at 298K. The cyclic voltammograms were recorded on a pure antimony electrode at 298~318K with various sweeps rates from 50 mV/s to 150 mV/s, respectively. The potential scan is started from 0 V, in the negative potential direction up to -1.1 V, and then reversed to the starting potential. Before each electrochemical measurement, the electrodes were hand-polished with metallographic silicon carbide papers and 0.5~0.7 μm high-purity alumina, cleaned ultrasonically in the alcohols, acetone and deionizer water respectively and finally dried. All potentials reported were referred to the Hg|Hg₂SO₄ electrode. The temperature kept at different constant value using water bath. The elemental composition and surface morphology of the antimony deposit were revealed by scanning electron microscopy (SEM) coupled with energy dispersive analysis (EDS).

3. RESULTS AND DISCUSSION

3.1 Linear sweep voltammetry study

The composition of electrolytes are as follows: 120 g/L Sb³⁺, 50 g/L NH₄⁺, 80 g/L F⁻ and 360g/L SO₄²⁻. Cathodic polarization curves, which was acquired on an antimony working electrode at temperatures ranging from 298K to 318K with a scan rate of 1 mV·s⁻¹, are demonstrated in Fig. 1. The results show that the increase of temperature considerably influences the antimony electrodeposition process. With increasing temperature, the potential of deposition shifts to the positive side (Fig. 1). In the potential region between -0.55 V to -1.1 V vs. Hg|Hg₂SO₄, it is possible to identify two peaks that suggest that the Sb electrodeposition occurs by two steps, which will be explained in detail below.

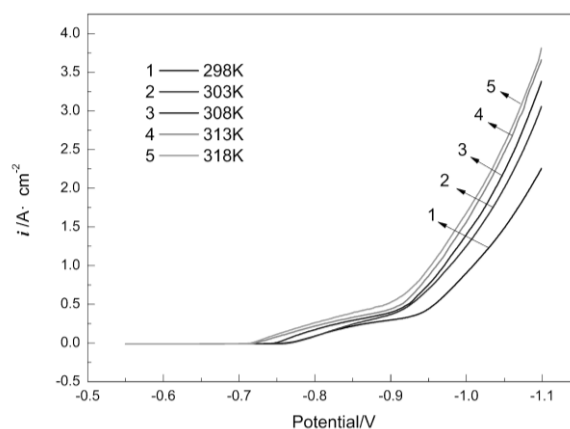


Figure 1. Steady-state polarization curves of antimony electrodeposition at 298K-318K.

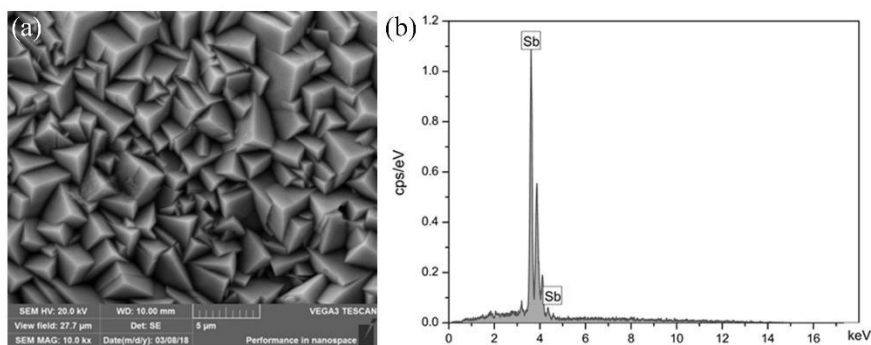


Figure 2. (a) SEM and (b) EDX micrographs of antimony electrodeposits obtained on a glassy carbon substrate at -1.0V vs. Hg|Hg₂SO₄ at 298K.

To identify the chemical species of the cathodic reactions, chronoamperometry measurements were performed on a glassy carbon working electrode at 298K, in which the potential was kept constant (i.e., -0.8 V and -1.0V vs. Hg|Hg₂SO₄). The test conducted at -1.0V shows that antimony was deposited as a silver film, whose thickness increases with time. Nevertheless, no film of deposited antimony was observed at the cathodes when the potential was -0.8 V. For comparison purposes, one of the electrodes that was observed to possess antimony films by chronoamperometry tests was confirmed by energy dispersive spectrometry (SEM-EDX). As shown in Fig. 2, these results confirmed that the antimony metal is deposited on the cathode at -1.0V vs. Hg|Hg₂SO₄.

To determine the value of n_1 , the steady-state polarization curves of antimony electrodeposition with different concentrations of Sb³⁺ at 298K are depicted in Fig. 3. According to the Tafel equation (1), within the potential range from -0.76 V to -0.90V, i^0 of the first step reaction with different concentrations of Sb³⁺ could be respectively evaluated [28].

$$\eta = \frac{2.303RT}{\alpha nF} \lg i^0 - \frac{2.303RT}{\alpha nF} \lg i \quad (1)$$

where n is the number of transferred electrons; F is the Faraday constant; T is the absolute temperature, K; α is the charge coefficient; η is the potential in the polarization curves; i^0 is exchange current density and i is cathodic current density.

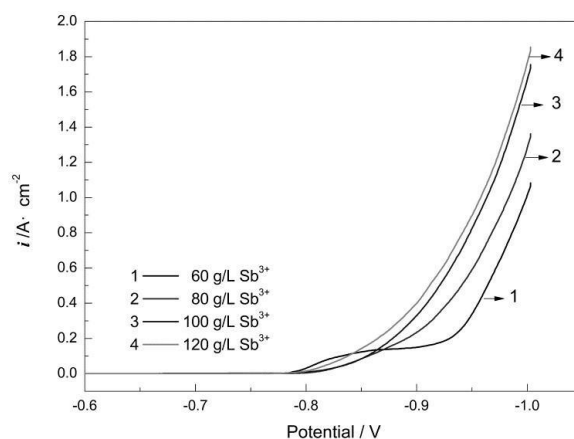


Figure 3. Cathodic polarization curves with different Sb³⁺ concentrations from 60 g/L to 120 g/L at the scan rate of 1 mV/s.

According to Eq. (2), $\log i^0$ and $\log C_{\text{Sb}}$ display a good linear correlation as shown in Fig. 4. The value of $1-\alpha_1$ can be calculated as 0.867, thus α_1 is 0.133.

$$i^0 = \log d_0 + (1 - \alpha) \log C_0 \quad (2)$$

where i^0 is exchange current density; C_0 is the concentration of the oxidation state, which is $\text{C}_{\text{Sb}^{3+}}$; α is the charge coefficient; and d_0 is the exchange current density when the activity of the oxidation state is 1.

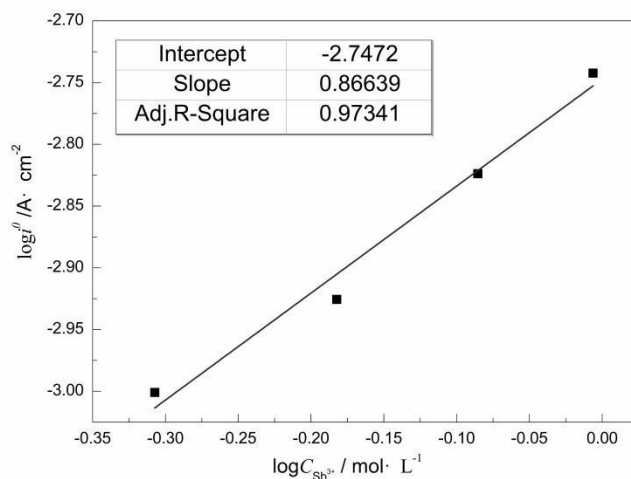


Figure 4. Relationship between $\log i^0$ and $\log C_{\text{Sb}}$.

In addition, the values of the kinetic parameters $\alpha_1 n_1$ and i^0_1 for the first step reaction at 298K can be respectively calculated as 0.138 and $3.468 \times 10^{-3} \text{ A} \cdot \text{cm}^{-2}$ by linear fitting of $\log i$ and η . Since α_1 is 0.133, $n_1 = 1.04$, approaching 1, and $n_2 = 2$.

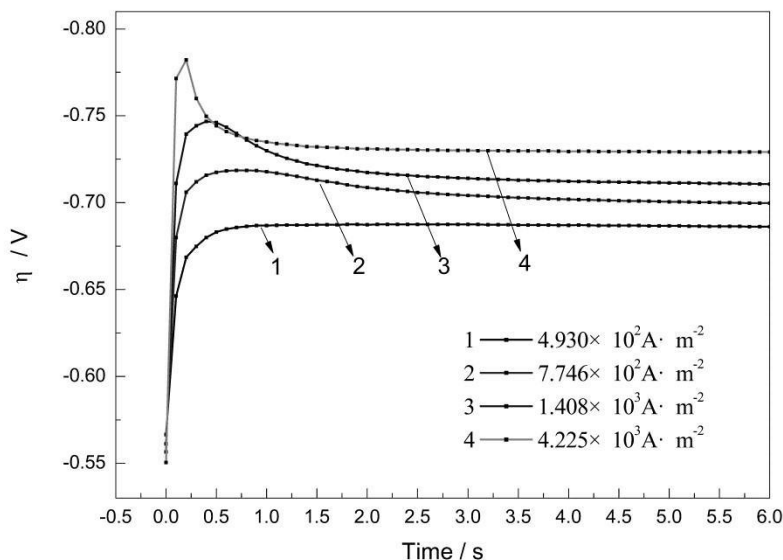


Figure 5. Chronopotentiograms of Sb^{3+} on an antimony electrode at 298K under different current densities from 4.93×10^2 to $4.23 \times 10^3 \text{ A} \cdot \text{m}^{-2}$.

The abovementioned experiments reveal that the Sb^{3+} reduction is a two-step process. To further confirm this, chronopotentiometric measurements were performed by stepping the current between

$4.93 \times 10^2 \text{ A} \cdot \text{m}^{-2}$ and $4.23 \times 10^3 \text{ A} \cdot \text{m}^{-2}$ on an antimony working electrode at 298K. According to the results discovered by Plonski, Xinkuai He et al., two-step reactions exhibit typical characteristics in theoretical η - t curves (η is the overvoltage, while i is the current) measured by chronopotentiometry, from which the following observations were made [42-43]: (1) as a consequence of the competition between the charging of the double layer and the transitory electron transfer process, the η - t curves are peak-shaped within a certain domain of i ; (2) it is generally valid that with an increasing value of i , the time necessary to reach the steady state decreases. Nevertheless, η only monotonously changes with the time for the one step reaction.

As shown in Fig. 5, a series of potential-time transits resulting from chronopotentiometric experiments clearly show the above two similar characteristics of the theoretical curves, which confirms that the antimony electrodeposition occurs by a two-step process, which can be described by Eq. (3).



3.2.2 Voltammetric analysis

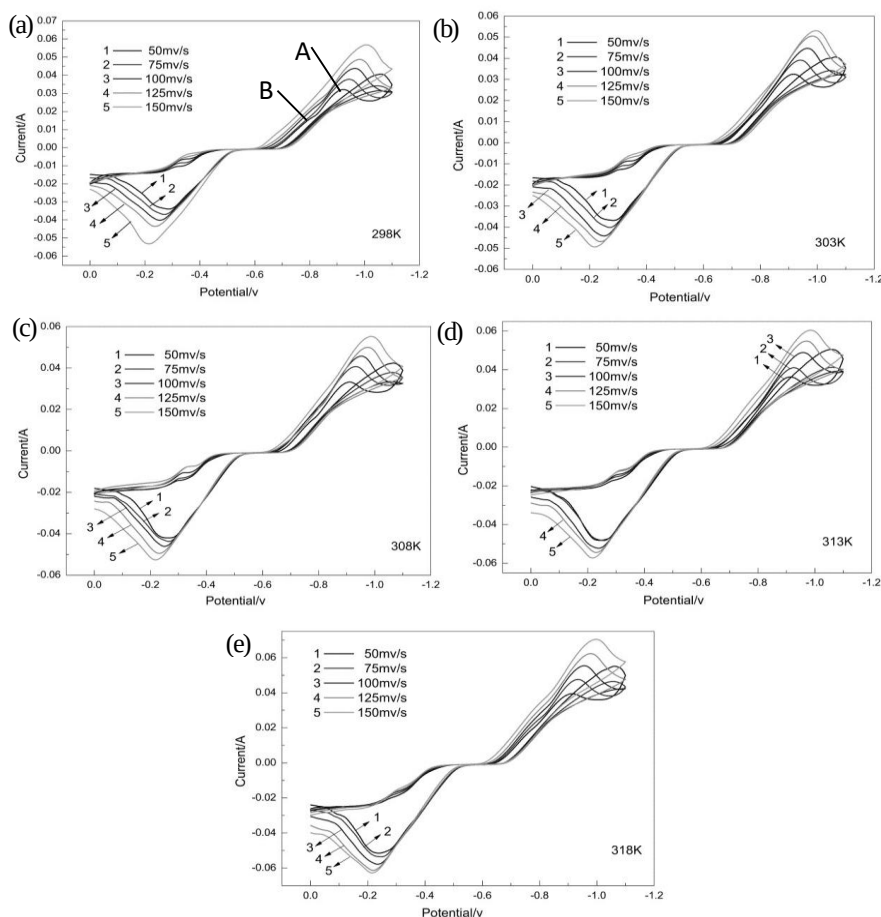


Figure 6. Cyclic voltammograms of Sb^{3+} under different sweep rates from 298-318K with various scan rates from 50 mV/s to 150 mV/s, respectively.

A family of cyclic voltammograms (CVs) of Sb^{3+} recorded on a pure antimony electrode under different sweep rates in the H_2SO_4 - NH_4F - SbF_3 system at 298-318K is shown in Fig. 6. The potential

scan started from 0 V, proceeded in the negative potential direction up to -1.1 V, and then reversed to the starting potential. As seen from Fig. 6, the electrodeposition of antimony exhibits an obvious reduction wave A with a peak potential around -0.90 V to -1.00 V vs. Hg|Hg₂SO₄, as well as a weak reduction wave B located around -0.80 V to -0.85 V. With increasing sweep rate, the reduction wave B becomes more difficult to distinguish, which possibly results from the close reduction potentials of each step to each other.

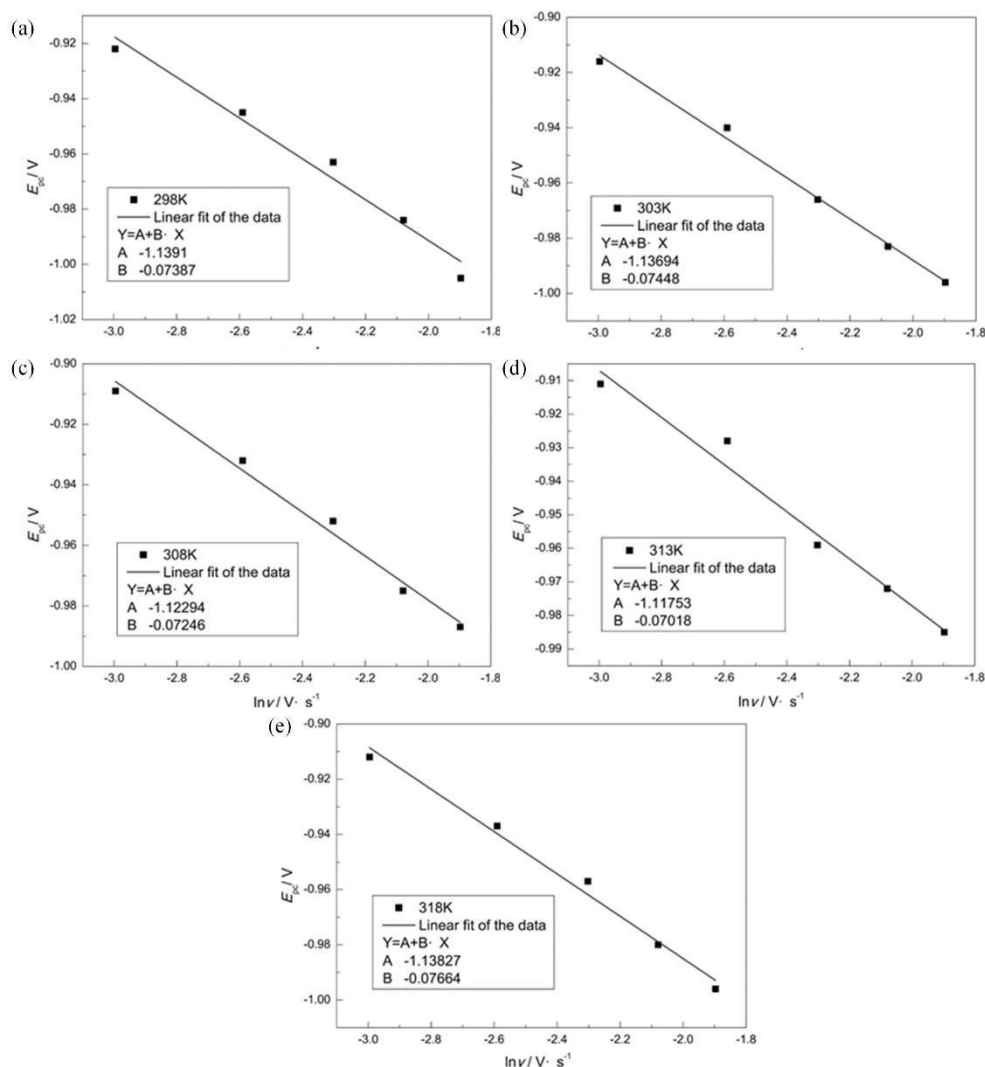


Figure 7. Linear correlation between deposition peak potential (E_{pc}) and $\ln v$ at 298-303K.

These results reveal that the Sb^{3+} reduction occurs via a two-step process, which is essentially in agreement with the results obtained from steady-state polarization curves. In the reverse sweeping, a crossover is observed at the CV, which indicates that an overpotential-driven nucleation/growth electrodeposition process has occurred [44-46].

As illustrated in Fig. 6, the potential of the peak moves more negatively, while the cathodic peak current of reduction wave A increases more sharply when the sweep rate v is increased from 50 mv/s to 150 mv/s. The shapes of all CVs at different temperatures remain almost the same with increasing sweep speed, and all of the polarization peaks are parallel as the potential of the peak shifts towards the negative direction. As shown in the inset of Fig. 7, the cathodic peak potential of reduction wave A, E_{pc} , varies

linearly with the $\ln v$, which indicates that it is an irreversible charge transfer process [47-48]. In case the charge transfer process is irreversible, the transfer coefficient can be calculated by Eq. (4) [49]:

$$\Delta E_p = |E_{p/2} - E_p| = \frac{1.857RT}{\alpha nF} \quad (4)$$

where R is the molar gas constant; T is the thermodynamic temperature; $E_{p/2}$ is the cathodic peak potential; E_p is the cathodic half peak potential; α is the charge transfer coefficient of the rate determining step; n is the electron transfer number, which is 3 for the total reaction; and F is the Faraday constant. The values of I_p , $E_{p/2}$, and E_p can be obtained from Fig. 6 and are listed in Table 1, respectively. The values of α for the irreversible electrode reactions at different temperatures can thus be calculated to be 0.134 (298 K), 0.135 (303 K), 0.131 (308 K), 0.131 (313 K) and 0.128 (318 K), respectively. Compared with the charge coefficient of the first electron transfer ($\alpha_1=0.133$, 298 K), which is obtained from steady-state polarization curves, the total reaction has almost the same charge coefficient ($\alpha=0.134$, 298 K). This outcome indicates that the first step is the rate-controlling process.

Table 1. Cyclic voltammogram data with the potential scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$

T/K	I_p / A	E_p / V	$E_{p/2} / \text{V}$	$ E_p - E_{p/2} / \text{V}$
298	0.03213	-0.922	-0.803	0.119
303	0.03248	-0.916	-0.796	0.120
308	0.03322	-0.909	-0.784	0.125
313	0.03628	-0.911	-0.784	0.127
318	0.03941	-0.912	-0.779	0.133

Fig. 8 shows that a linear relationship exists between the cathodic peak current (I_p) and the square root of the potential sweep rate ($v^{1/2}$) at different temperatures, which indicated that the electrode reaction of Sb^{3+} is a diffusion-controlled process [50-51]. According to the Randles-Sevcik equation, the diffusion coefficient of Sb^{3+} could then be calculated by the slope of $I_p \sim v^{1/2}$ curves [52, 53]:

$$I_p / v^{1/2} = 0.4958 \left(\frac{\alpha F^3}{RT} \right)^{1/2} n^{3/2} A C_0^* D_0^{1/2} \quad (5)$$

where n , A , C_0^* , and D_0 denote the electron transfer number, geometric area of the electrode, bulk concentration of Sb^{3+} , and diffusion coefficient, respectively. According to Eq. (4), the average value of αn has been obtained. Furthermore, the diffusion coefficient of Sb^{3+} in the $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ system is calculated from Eq. (5), which is shown in Table 2.

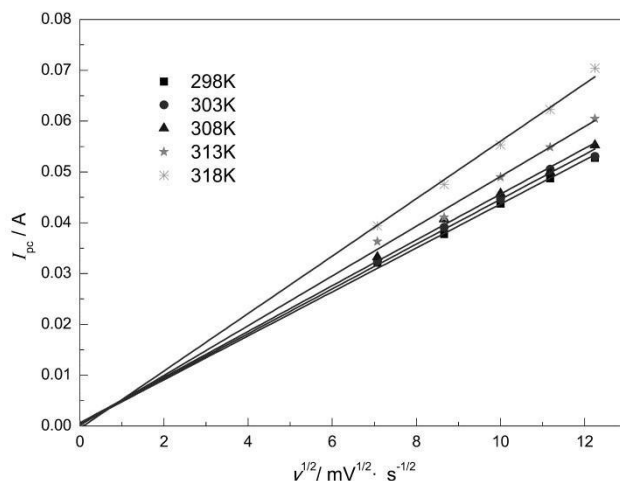


Figure 8. Linear correlations between the cathodic peak current (I_p) and the square root of the potential sweep rate ($v^{1/2}$) at 298-318K

Table 2. Diffusion coefficient of Sb^{3+} at various temperatures

T/K	298	303	308	313	318
D_0 ($\text{cm}^2 \cdot \text{s}^{-1}$)	1.051×10^{-5}	1.149×10^{-5}	1.257×10^{-5}	1.484×10^{-5}	2.120×10^{-5}

3.2.3 Apparent activation energy

At the various overpotentials, the dependence of $\lg i_\eta$ upon $1/T$ is shown in Fig. 9.

The apparent activation energy is calculated by Eq. (6), as shown in Table 3.

$$\ln i_\eta = B - \frac{E}{RT} \quad (6)$$

where i_η is the current density at the overpotential η , A; B is a constant; R is the gas constant, $8.314 \text{ J}/(\text{mol} \cdot \text{K})$; T is the temperature, K; and E is the apparent activation energy in J/mol.

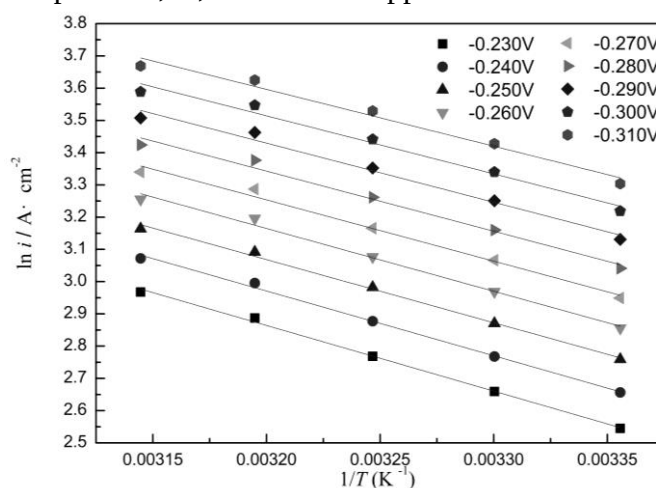


Figure 9. Linear relation of $\ln i - 1/T$ at different overpotentials from -0.23 - -0.31 V.

Table 3. Apparent activation energy of the Sb^{3+} reduction process at different overpotentials

η (V)	-0.23	-0.24	-0.25	-0.26	-0.27	-0.28	-0.29	-0.30	-0.31
slope	-2036.51	-2008.23	-1957.45	-1947.91	-1900.68	-1864.57	-1833.55	-1799.91	-1761.78
E (kJ·mol ⁻¹)	16.93	16.70	16.27	16.20	15.80	15.50	15.24	14.96	14.65

As an important parameter, the value of apparent activation energy of the electrode reaction is commonly used to determine the reaction mechanism. If the electrode reaction is controlled by the charge transfer process, the temperature coefficient of the reaction rate is relatively high, and the apparent activation energy of the electrode reaction is usually larger than 40 kJ/mol. However, if the electrode reaction is a diffusion-controlled process, the temperature coefficient of reaction rate is relatively low, and the apparent activation energy is generally in the range of 12-16 kJ/mol [28]. In this work, the apparent activation energy decreases steadily at more negative potential. According to the lower apparent activation energy, it is confirmed that the deposition rate is determined by a diffusion process, which is essentially consistent with the results obtained from cyclic voltammetry.

3.2.4 Preceding reaction

Considering that various species exist simultaneously in the $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ electrolyte system containing a mixture of Sb^{3+} , SO_4^{2-} , F^- and NH_4^+ , both of the F^- and NH_4^+ species are able to coordinate with Sb^{3+} , either individually or simultaneously, to form various coordination compounds. In addition, no previous studies on the stability constant of $\text{Sb}(\text{NH}_4)_x(\text{F})_\mu$ are found. According to the results of research on the complexation action of F^- and Sb^{3+} , SbF_4^- and SbF_5^- are the primary forms existing in the range of Sb/F molar ratios in the $\text{Sb}^{3+}\text{-F-H}_2\text{O}$ solution. Because negatively charged complex ions are difficult to reduce at the cathode, we speculate that this process occurs via a preceding reaction. To confirm our hypothesis, chronopotentiometry curves are obtained by stepping the current from $8.535 \times 10^2 \text{ A/m}^2$ to $1.057 \times 10^3 \text{ A/m}^2$. As shown in Table 4, the relationship between $i^{1/2}$ and i is calculated.

Table 4. Relationship between current density and transition time

$i \times 10^2$ (A·m ⁻²)	τ (s)	$i\tau^{1/2} i\tau^{1/2} \times 10^2$ (A·m ⁻² ·s ^{1/2})
8.535	586.9	206.769
9.045	340.7	166.953
9.554	80.8	85.880
10.064	60.2	78.085
10.573	37.6	64.832

The relationship between $i^{1/2}$ and i is an effective parameter to determine whether the electrochemical discharge process occurs via a preceding reaction. If the electrode reaction occurs via a preceding reaction, the relationship between $i^{1/2}$ and i conforms to Eq. (7) [54]:

$$i\tau^{1/2} = \frac{nFAC^*\sqrt{\pi D_0}}{2} - \frac{i}{K\sqrt{K_1 + K_{-1}}} \frac{\sqrt{\pi}}{2} \text{erf} \sqrt{(K_1 + K_{-1})\tau} \quad (7)$$

where τ is the transition time, s; i is the current density, A/m²; n is the number of Faradays per mole of reaction; K_1 and K_{-1} are the rate constants of the positive and reverse preceding reactions; K is K_1/K_{-1} ; A is the electrode area, m²; D_0 is the diffusion coefficient of the electroactive species, m²·s⁻¹; C^* is the concentration of the electroactive species, mol/L; and F is the Faraday constant. According to Eq. (7), at a constant concentration of the electroactive species, $i^{1/2}$ is found to vary with current density i . When the current density i is small, there is an approximate linear relationship between $i^{1/2}$ and i . While the current density i is sufficiently large, $i^{1/2}$ is an approximation independent of i . Fig. 10 shows the plot of $i^{1/2}$ vs i , which indicates that the electrodeposition of antimony exhibits typical characteristics of the reduction process via a pre-conversion reaction that could be described by Eq. (8).

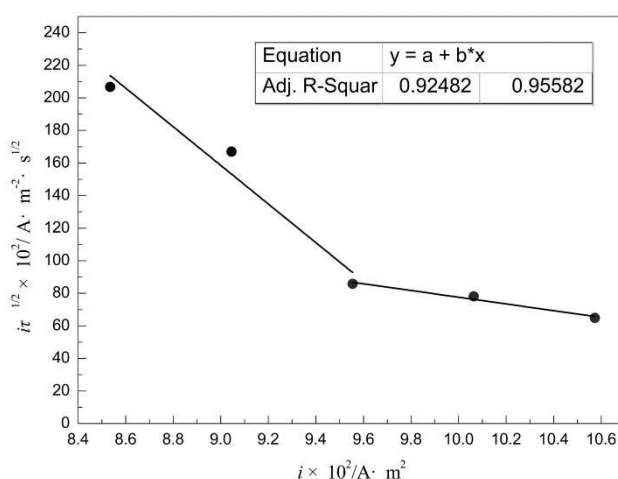
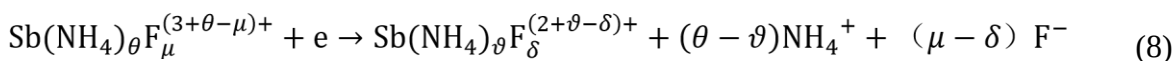
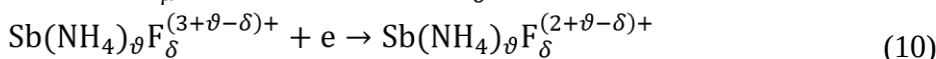
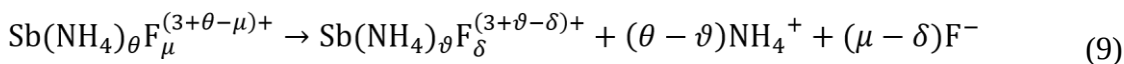


Figure 10. The relationship between $i^{1/2}$ and i after fitting.

According to Eq. (8), the stoichiometric coefficients ν of NH_4^+ and F^- could be given as $\nu_{\text{NH}_4} = -(\theta - \vartheta)$ and $\nu_{\text{F}} = -(\mu - \delta)$. Obviously, Eq. (8) could be divided into a pre-conversion reaction Eq. (9) and an electrochemistry reaction Eq. (10).



From Eq. (9) and Eq. (10), the reaction series Z of NH_4^+ and F^- could be given as $Z_{\text{R,NH}_4} = -(\theta - \vartheta)$ and $Z_{\text{R,F}} = -(\mu - \delta)$. For NH_4^+ and F^- , which participate in the oxidation reaction, we have Eq. (11) and Eq. (12) [55]:

$$\frac{\partial \log i^0}{\partial \log C_{\text{F}}} = Z_{\text{R,F}} + \beta \nu_{\text{F}} \quad (11)$$

$$\frac{\partial \log i^0}{\partial \log C_{\text{NH}_4}} = Z_{\text{R,NH}_4} + \beta \nu_{\text{NH}_4} \quad (12)$$

As $\alpha_1 = 0.133$, $n_1 = 1$, as evaluated by steady-state polarization curves, and Eq. (11) and Eq. (12) can be transformed to Eq. (13) and Eq. (14):

$$\frac{\partial \log i^0}{\partial \log C_F} = -(\mu - \delta) - \beta(\mu - \delta) = -1.873(\mu - \delta) \quad (13)$$

$$\frac{\partial \log i^0}{\partial \log C_{NH_4}} = -(\theta - \vartheta) - \beta(\theta - \vartheta) = -1.873(\theta - \vartheta) \quad (14)$$

To determine the value of $(\mu - \delta)$, steady-state polarization curves of antimony electrodeposition with different concentrations of F^- at 298 K are depicted in Fig. 11. In addition, according to the Tafel equation (1), i^0 of the first step reaction with different concentrations of F^- could be evaluated respectively. At the various F^- concentrations, the dependence of $\log i^0$ upon $\log C_F$ is shown in Fig. 12, demonstrating a linear relationship. The value of $\mu - \delta$ can be estimated from the slope to be 2.07, approaching 2.0.

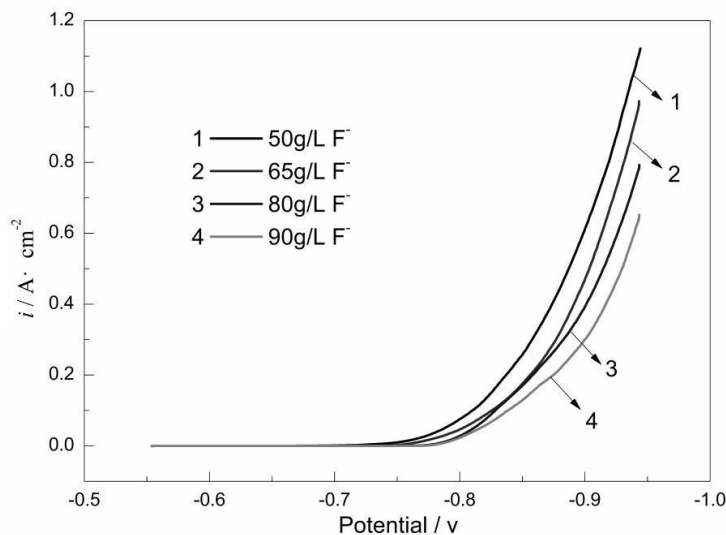


Figure 11. Cathodic polarization curves with different F^- concentrations from 50 g/L to 90 g/L at the scan rate of 1 mV/s.

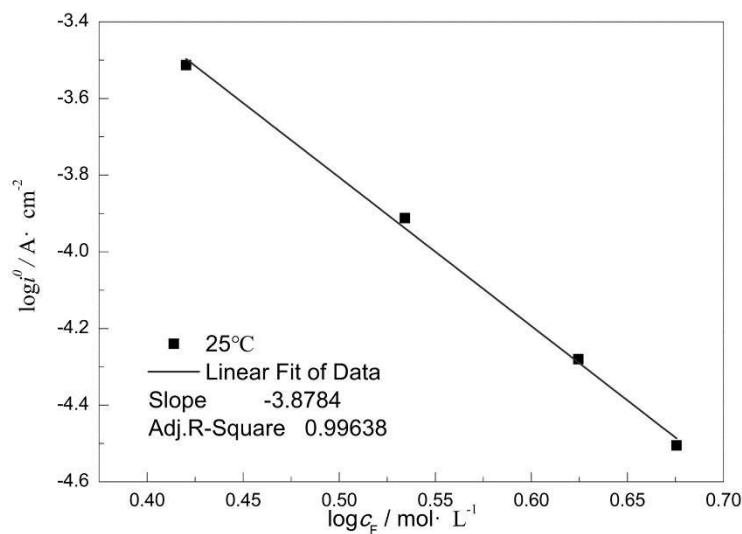


Figure 12. Linear correlation between $\log i^0$ and $\log C_F^-$ after fitting.

The steady-state polarization curves of antimony electrodeposition with different concentrations of NH_4^+ at 298K are depicted in Fig. 13. In addition, according to the Tafel equation (1), i^0 of the first step reaction with different concentrations of NH_4^+ could be evaluated respectively. At the various NH_4^+ concentrations, the dependence of $\log i^0$ upon $\log C_{\text{NH}_4^+}$ is shown in Fig. 14, demonstrating a linear relationship. The value of $\theta - \vartheta$ can be estimated from the slope to be 0.05, approaching 0, which indicates that the electroactive species did not release NH_4^+ ions during the preceding reaction.

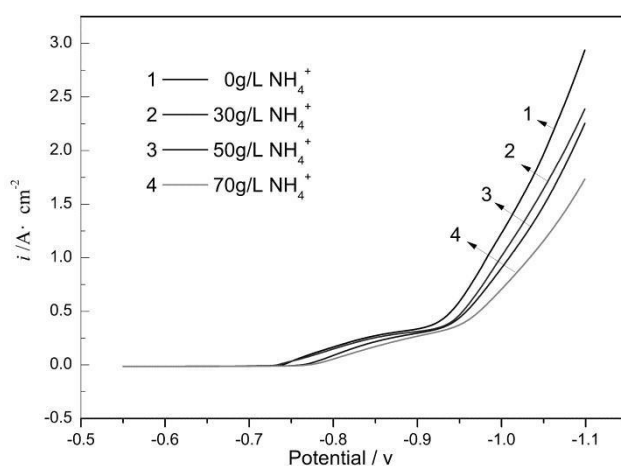


Figure 13. Cathodic polarization curves with different NH_4^+ concentrations of 0-70 g/L at the scan rate of 1 mV/s.

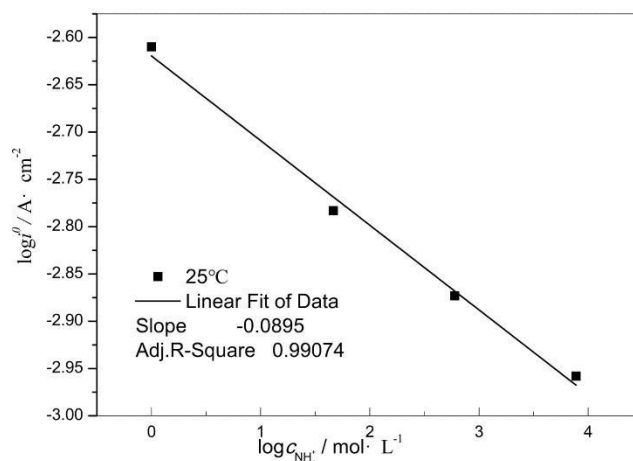


Figure 14. Linear correlation between $\log i^0$ and $\log C_{\text{NH}_4^+}$ after fitting.

4. CONCLUSIONS

The electrochemical reduction of Sb^{3+} in the $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ electrolyte system is investigated. Linear scan voltammetry measurements with different concentrations of Sb^{3+} are recorded. The results show that the Sb^{3+} reduction is a two-step process, which is also verified by chronoamperometry, chronopotentiometry and cyclic voltammetry data. The numbers of transferred

electrons are $n_1=1$ and $n_2=2$. For the first step reaction at 298K, α_1 and i^0_1 are 0.133 and $3.468 \times 10^{-3} \text{ A} \cdot \text{cm}^{-2}$. In addition, the results of cyclic voltammetry show that the reduction of Sb^{3+} is an irreversible process that is controlled by diffusion. The diffusion coefficients of Sb^{3+} in $\text{H}_2\text{SO}_4\text{-NH}_4\text{F-SbF}_3$ solution at different temperatures are calculated as $1.051 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (298K), $1.149 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (303K), $1.257 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (308K), $1.484 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (313K), and $2.120 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ (318K), respectively. Estimated from steady-state polarization curves at different temperatures, the apparent activation energies of Sb^{3+} reduction at different overpotentials (from -0.23 V to -0.31 V) are from 16.932 kJ/mol to 14.647 kJ/mol. The small apparent activation energy value also verified that the Sb^{3+} reduction process is a diffusion controlled process, which has been supported by cyclic voltammetry. The analysis of chronopotentiometry curves and the linear scan voltammetry with different concentrations of NH_4^+ and F^- indicates that the electrodeposition of antimony occurs via a pre-conversion reaction which releases two F^- ions and is completely independent of NH_4^+ ions.

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