



Formation and suppression strategies of by-product in tin oxidative dissolution process

Dongbin Wang^{a,b}, Wenlong Miao^{a,b}, Mingge Fu^{a,b}, Vanduc Tran^c, Liuxin Xiang^{a,b}, Tian Wang^{a,b}, Thiquynhxuan Le^{a,b,*}, Libo Zhang^{a,b,*}

^a State Key Laboratory of Complex Non-ferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, Yunnan 650093, China

^b Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093, China

^c Faculty of Mining, Hanoi University of Mining and Geology, Duc Thang, Bac Tu Liem, Hanoi, Viet Nam

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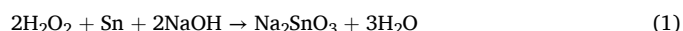
Tin oxidative dissolution
By-products
Stannous oxide (SnO)
Inhibition strategies

ABSTRACT

The formation of black by-products critically limits the efficiency of tin oxidative dissolution in the Sn-H₂O₂-NaOH system. In this work, the occurrence state and effects of these by-products are systematically investigated, confirming that they are a mixture of SnO and SnO₂, with SnO being the dominant phase. Electrochemical and thermodynamic analyses demonstrate that the by-product passivation layer impedes reactant mass transfer and electron transport, while SnO generation alters the reaction pathway and elevates the thermodynamic barrier, collectively reducing the efficiency of tin oxidative dissolution. The effects of temperature, NaOH concentration, NaOH:H₂O₂ volumetric ratio and reaction time on by-product yield and tin oxidative dissolution are thoroughly investigated, leading to proposed inhibition strategies. The optimized process parameters are determined as follows: reaction temperature 20 °C, NaOH concentration 3 mol/L, initial NaOH:H₂O₂ volumetric ratio 30:1, and reaction time 100 min. After process optimization, the efficiency of tin oxidative dissolution reaches 95.25 %, with by-product formation suppressed to 0.03 % of the total tin amount. This work provides fundamental insights into by-product control, significantly improving dissolution efficiency and supporting the green transformation of sodium stannate production.

1. Introduction

Sodium stannate (Na₂SnO₃·3H₂O) is a crucial inorganic functional material extensively utilized in various fields such as electroplating, lithium-ion battery anode materials, flame retardants, and catalyst supports due to its exceptional chemical stability, conductivity, and catalytic properties [1–5]. The increasing demand for high-purity sodium stannate is closely linked to the rapid advancements in the new energy and electronics sectors. The alkali leaching method has emerged as the predominant industrial technique for sodium stannate synthesis because of its favorable attributes including gentle reaction conditions, uncomplicated procedures, energy efficiency, and environmental sustainability. This method relies on metallic tin as the primary raw material, which undergoes oxidative dissolution within a NaOH-H₂O₂ reaction system to generate a sodium stannate solution [6,7]. Subsequent evaporation and crystallization yield the final product. The theoretical reaction pathway is represented as follows [8,9]:



In the industrial production of sodium stannate, the reaction temperature is typically maintained at 70–85 °C with a sodium hydroxide concentration of 4–8 mol/L and a hydrogen peroxide concentration of 15–30 %, where both reagents are dosed at 1.4–2 times the theoretical amount. Under these conditions, the maximum tin oxidative dissolution efficiency can reach 93 %. However, significant side reactions occur under actual operating conditions, primarily generating black insoluble by-products. These by-products typically form an adherent layer covering the tin sheet surface [10–12], and the effects of these by-products on the reaction are as follows: (1) These by-products reduce the conversion rate of tin and the yield of sodium stannate. These particles are difficult to completely remove via conventional filtration and ultimately enter the product during crystallization, causing subsequent deterioration of application performance. (2) When deposited on the tin

* Corresponding authors at: State Key Laboratory of Complex Non-ferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, Yunnan 650093, China.

E-mail addresses: quynhxuanlt@kust.edu.cn (T. Le), zhanglibopaper@126.com (L. Zhang).

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sheet surface, they form a passivation layer that hinders contact between reactants (H_2O_2 , NaOH , and tin) and impedes mass transfer. As the number of by-products increases, the reaction rate and dissolution efficiency decrease, forcing higher reaction temperatures to maintain yield.

The mechanism of by-product formation during the oxidative dissolution of tin is complex and involves the multistep oxidation pathway of $\text{Sn(0)} \rightarrow \text{Sn(II)} \rightarrow \text{Sn(IV)}$. The current understanding of its composition and formation mechanism remains incomplete, as outlined below. Under low oxidation potential, the dominant primary oxidation of $\text{Sn(0)} \rightarrow \text{Sn(II)}$ leads to the formation of by-products (intermediate valence products) such as SnO and Sn(OH)_2 [13]. Electrochemical studies have revealed that tin undergoes a unique pre-passivation process during anodic polarization, sequentially generating various passivation intermediates such as HSnO_2^- or Sn(OH)_3^- , ultimately forming a passive layer composed of SnO and Sn(OH)_2 [14]. Besides, Sn(OH)_2 forms via Sn^{2+} with OH^- , followed by dehydration to SnO [15]. Strong alkaline media promote the electrocrystallization process within a specific active range, making it more prone to form SnO nano-structured microspheres [16]. Another reported by-product is fully oxidized SnO_2 , which may form through further oxidation of incomplete oxides (SnO and Sn(OH)_2) or via direct solid-state passivation process from pure Sn metal to Sn(OH)_4 precursors that readily dehydrate to form by-product SnO_2 [17]. Some researchers suggest that the by-products are non-stoichiometric tin oxides (e.g., Sn_2O_3 , Sn_3O_4) [18,19]. Additionally, non-stoichiometric tin oxides observed that the deep gray to black amorphous by-products result from the co-precipitation of SnO and SnO_2 at varying stoichiometric ratios, and XPS results confirm that they consistently consist of both Sn^{2+} and Sn^{4+} . Therefore, elucidating the by-product formation mechanism and developing control strategies are critical for efficient tin oxidative dissolution in sodium stannate synthesis.

In industrial practice, the prevailing approach involves cyclic oxidative dissolution treatment through mixing by-products with fresh tin feedstock. However, this approach not only prolongs the production cycle and increases specific energy consumption due to repeated unit operations (e.g., heating and mechanical stirring), but also leads to excessive consumption of both sodium hydroxide (NaOH) and oxidants. These factors collectively establish a vicious cycle: by-product accumulation $\rightarrow$ inefficient recovery $\rightarrow$ further by-product generation, ultimately compromising process sustainability. The current improvement strategy centers on increasing the reaction rate and enhancing mass transfer to address by-product control in actual production. Specifically, it involves increasing the amount of H_2O_2 used [20], higher alkali concentrations, and stronger mechanical stirring. Gradual addition of H_2O_2 can alleviate local peroxidation, but excessive cumulative dosage combined with mismatched alkali concentration promotes dense SnO_2 layer formation, hindering further tin oxidation and dissolution. Increasing NaOH concentration promotes the formation of Sn(OH)_6^{2-} complexation, but causes sharp solution viscosity increase, reducing mass transfer efficiency. Excessive NaOH introduces a high concentration of sodium ions, which may cause solid precipitation via the common ion effect, impeding tin dissolution and subsequent production. High-pressure reactors enhance H_2O_2 utilization and tin oxidation dissolution efficiency. Their high energy consumption, equipment costs, and safety risks, however, limit their widespread use [21]. Electrochemical anodic oxidation enables selective tin dissolution [22,23]. Yet, under high tin ion concentrations, however, cathodic reduction deposition ($\text{Sn}^{2+}/\text{Sn}^{4+} \rightarrow \text{Sn}$) reduces the anodic oxidation efficiency, affecting the overall effectiveness of the method.

To address the low efficiency caused by by-products in traditional alkaline tin dissolution, the occurrence forms and inhibitory effects of black by-products on tin oxidative dissolution were investigated in the $\text{Sn-H}_2\text{O}_2\text{-NaOH}$ system. Furthermore, control strategies were developed to reduce by-product generation and enhance tin conversion efficiency during oxidative dissolution. These approaches were designed to achieve efficient tin dissolution and process optimization, thereby

providing new insights for green sodium stannate preparation and advancing non-ferrous metal oxidative dissolution and recovery processes.

2. Materials and methods

2.1. Materials

The NaOH used in this experiment was produced by Tianjin Zhiyuan Chemical Reagent Co., Ltd. High-purity tin sheets were produced by Tengfeng Metal Materials Co., Ltd., with a thickness of 1 millimeter and purity of 99.99 %. The 30 % H_2O_2 used in this experiment was produced by Tianjin Zhiyuan Chemical Reagent Co., Ltd. The distilled water utilized in the experiment was produced in the laboratory.

2.2. Experimental procedure

(1) Experiment on the formation of by-products

To clarify the by-product formation conditions, the effects of temperature (20–70 °C), sodium hydroxide concentration (1–4 mol/L), and initial volumetric ratio between sodium hydroxide and hydrogen peroxide (50:1–10:1) on by-product formation were investigated in the initial stage of the reaction without a stirring field. A 30 % hydrogen peroxide concentration was used in these experiments. After 1 h of reaction involving hydrogen peroxide, sodium hydroxide solution, and tin sheets, the samples were separated, and the solution was vacuum-filtered to determine the tin ion concentration. The tin samples were then soaked in deionized water and ultrasonically cleaned. The mass difference before and after cleaning was measured to evaluate the mass of unreacted tin and surface by-products. The influence of reaction conditions on by-products is demonstrated by the mass of by-products, the mass of tin ions in the solution, and the proportion of unreacted tin sheet mass, with the original tin sheet mass serving as the basis (100 %).

(2) Control of by-product production during oxidative dissolution of tin sheets

Based on actual production conditions, the experiments were conducted at 200 r/min and a total hydrogen peroxide dosage equivalent to 1.5 times the theoretical amount. A 30 % hydrogen peroxide concentration was used in these experiments. At room temperature, the effects of different sodium hydroxide concentrations (2, 3, and 4 mol/L), reaction time (20, 40, 60, 80, 100, and 120 min), and initial volumetric ratios of sodium hydroxide to hydrogen peroxide (50:1, 40:1, 30:1, 20:1, 10:1) on the formation of by-products were studied. In this part of the experiment, hydrogen peroxide was initially added according to the preset proportional ratio, followed by periodic supplementation of 0.5 mL aliquots of H_2O_2 at 10-min intervals until the cumulative amount reached 1.5 times the theoretical requirement, at which point further addition was discontinued. After 120 min of reaction, samples were separated, and the solution was filtered using a vacuum filtration apparatus to determine the tin ion concentration. The tin sheet samples were then immersed in deionized water and subjected to ultrasonic cleaning. The difference in mass before and after cleaning was used to determine the mass of unreacted tin sheets and the by-products covering their surfaces. The yield of the surface by-products ($m_{\text{byproduct}}$) was calculated as Eq. 2 :

$$m_{\text{byproduct}} = m_{\text{total}} - m_1 \quad (2)$$

To evaluate the effect of influencing factors on tin sheet dissolution, the mass loss of tin sheets is employed to calculate the tin dissolution

rate. The calculation formula is shown in Eq. 3. Q represents the oxidative dissolution efficiency of tin, while m_0 (g) and m_1 (g) denote the masses of the tin sheet before and after dissolution, respectively.

$$Q = \frac{m_0 - m_1}{m_0} \times 100\% \quad (3)$$

2.3. Characterization equipment

The morphology and elemental distribution of tin sheets and their surface by-products were analyzed by scanning electron microscopy (SEM ZEISS Sigma 300, Germany). The crystalline phases of tin and by-products were characterized using an X-ray diffractometer (XRD, X'Pert3 powder), and the data were analyzed using Jade software. The concentration of dissolved tin in the supernatant was determined through titration and ICP-OES analysis. The valence states of elements in tin

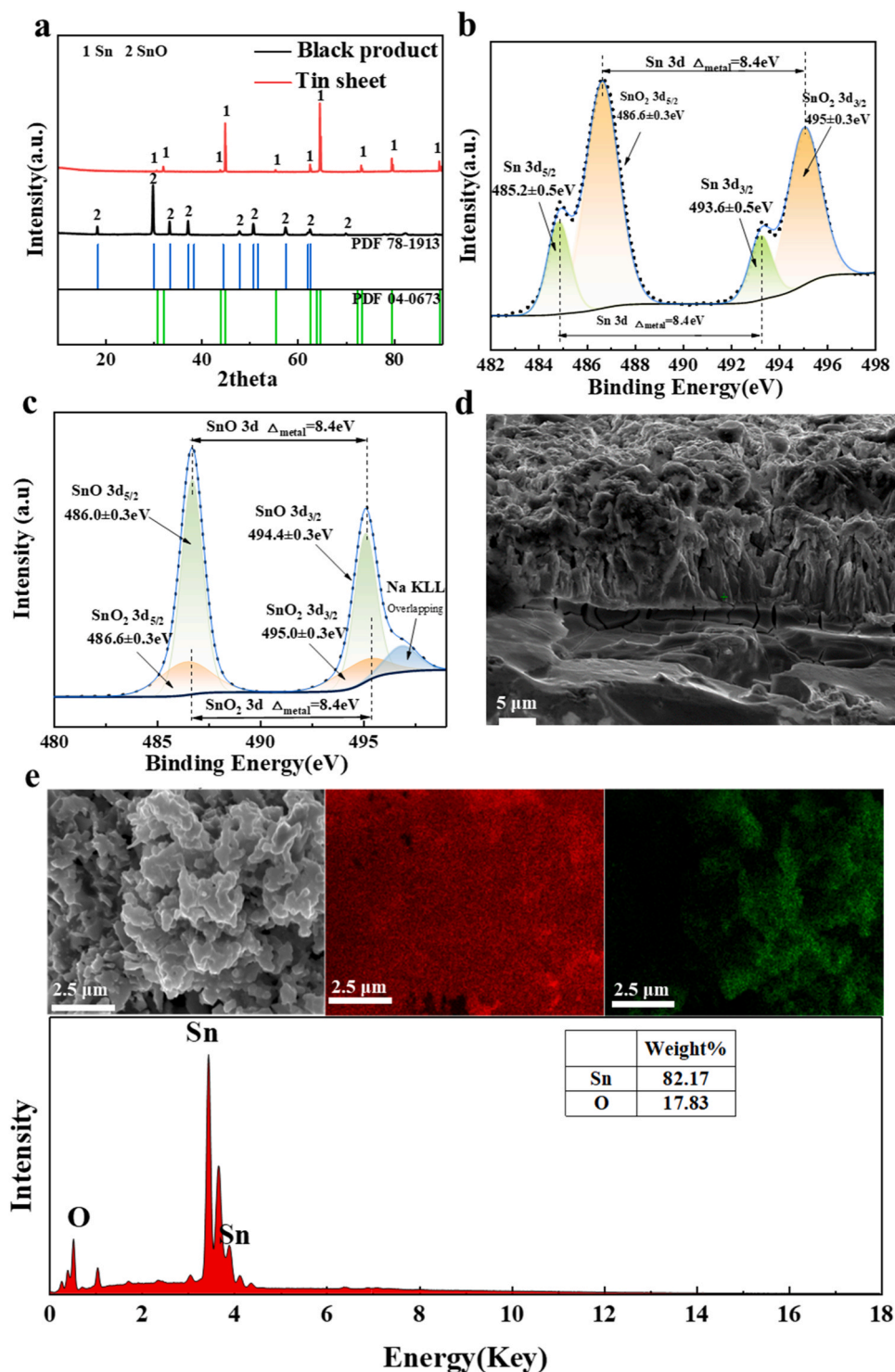


Fig. 1. (a) XRD results of unreacted tin sheet and by-products; (b) XPS analysis of unreacted tin sheet; (c) XPS analysis of black by-products; (d) SEM results of by-products covering the tin sheet surface (cross-sectional view). (e) SEM-EDS results of by-products (Top-view).

sheets and by-products were analyzed by X-ray photoelectron spectroscopy (XPS Thermo Scientific K-Alpha). The electrochemical impedance test was conducted using the Princeton PMC Electrochemical workstation (Princeton Applied Research PMC1000, AMETEK). The purity of tin sheets was determined in accordance with Chinese National Standards GB/T 3260.11–2023 and GB/T 3260.9–2013 through quantification of 12 trace elements (Cu, Fe, Bi, Pb, Sb, As, Al, Zn, Cd, Ag, Ni, Co) by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and sulfur content by high-frequency induction furnace combustion-infrared absorption method, with final purity calculated by subtracting total impurities from 100%. The thermodynamic results were calculated using HSC 6.0 Chemistry software.

The titration of hydrogen peroxide (H_2O_2) was performed following the potassium permanganate (KMnO_4) method specified in the National Standard GB/T 6684–2002 for the determination of H_2O_2 content. The detailed titration procedure is as follows: A v mL (15–20 mL) dropping bottle with a reduction method was used for sample weighing. Approximately m g (0.15–0.2 g) of the sample was accurately weighed (with a precision of ± 0.0002 g) and transferred into a 250 mL conical flask containing 100 mL of sulfuric acid solution (1:15, v/v). The solution was titrated with a pre-standardized KMnO_4 solution until a persistent pink endpoint (stable for ≥ 30 s) was observed. The consumed KMnO_4 solution volume was recorded. The mass fraction of H_2O_2 (W_1 , %) was calculated as Eq. 4:

$$W_1 = \frac{v \times C \times M}{2000m} \times 100\% \quad (4)$$

where: v is the volume of KMnO_4 consumed (unit: mL); C is the KMnO_4 concentration (unit: mol/L); M is the molar mass of H_2O_2 (unit: g/mol); m is the sample mass (g).

3. Results and discussion

3.1. Occurrence state of by-products

To investigate the morphological characteristics of by-products, comparative analyses were performed between unreacted tin sheets and tin sheets with deposited by-products using XRD, XPS, and SEM-EDS. The by-product deposited tin sheets were prepared with NaOH concentration of 3 mol/L, H_2O_2 concentration of 30 %, NaOH: H_2O_2 volumetric ratio of 20:1, and reacted at room temperature for 30 min. Regarding the surface composition analysis of unreacted tin sheets, the XRD results (Fig. 1(a)) show only characteristic peaks of metallic tin without observable oxide peaks, while XPS results (Fig. 1(b)) simultaneously detect characteristic peaks of both metallic tin and SnO_2 . The Sn $3d_{5/2}$ peaks show double peaks at 485.2 eV (Sn^0) and 486.6 eV (Sn^{4+}) [24]. This discrepancy in characterization results stems from the different penetration depths of the two analytical techniques. XRD can penetrate materials to greater depths (micrometer level), whereas XPS has a shallow penetration depth (typically 1–10 nm) and detects only the outermost surface layer. For the black by-products generated during the reaction, XRD analysis (Fig. 1(a)) indicates that stannous oxide (SnO) is the main phase. XPS results (Fig. 1(c)) further confirm that the main component in the black by-products is divalent tin (i.e., SnO , with a characteristic peak at 486.0 eV), and trace amounts of tetravalent tin (with a characteristic peak at 486.6 eV) [25], indicating the presence of trace amounts of SnO_2 in the by-products. The binding energy difference (ΔBE) of 0.6 eV between SnO and SnO_2 , which perfectly matches the established literature range of 0.5–0.7 eV [24–26], confirming the reliability of this differentiation. The SEM result (Fig. 1(d)) reveals that the black by-product exhibits a porous microstructure and conformally covers the tin sheet surface, as observed in cross-sectional view. This dense coating layer directly hinders the solid-liquid reaction, thereby reducing tin dissolution efficiency. Further confirmation by SEM-EDS surface mapping (top-view) demonstrates the compact structure of the

by-products with an atomic ratio of $\text{Sn}:\text{O} = 82.17\%:17.83\%$. This measured composition falls between the theoretical values of SnO ($\text{Sn}:\text{O} = 88.12\%:11.88\%$) and SnO_2 ($\text{Sn}:\text{O} = 78.77\%:21.23\%$), confirming that the by-product is not a single-phase oxide but rather a mixed oxide system comprising both SnO and SnO_2 phases.

In summary, the by-products generated during the oxidative dissolution of tin primarily consist of two components: (1) Primary component SnO , which exists as a black solid. When deposited on the metal surface, it hinders contact between Sn and oxidants. Some SnO particles may detach through mechanical collision and disperse into the solution as fine particulates, leading to darkening of the reaction solution. (2) Trace component SnO_2 . It creates a dense oxide film on tin surface, blocking Sn-oxidant ($\text{H}_2\text{O}_2/\text{OH}^-$) contact, thereby reducing dissolution efficiency.

3.2. Effects of by-product on tin oxidative dissolution process

The tin oxidative dissolution process involves sequential steps, including the oxidant diffusion through the boundary layer, surface oxidation with electron transfer, and mass transfer of oxidation products into the bulk solution [7]. The continuous accumulation of by-products forms a passivation layer, which inhibits hydroxide and oxidant transport to the reactive interface [27], thereby inducing an oxide dissolution-redeposition cycle. The formation of by-products hinders the direct dissolution of tin sheets. Consequently, progressive passivation layer thickening alters the original reaction kinetics. Although partial dissolution occurs through an outer layer reaction with bulk solution, sustained passivation ultimately reduces tin dissolution efficiency [28–30].

The high-frequency (HF) semicircles correspond to the charge transfer process, whereas the low-frequency (LF) linear segment is associated with Warburg impedance, reflecting tin ion diffusion from the electrode surface to the bulk solution [31,32]. The equivalent circuit is shown in Fig. 2(a), where W_s denotes the diffusion impedance. The Warburg impedance (W_s) for tin sheets wrapped with by-products was 3.036Ω , slightly lower than that of bare tin sheets (3.304Ω), indicating stable electrolyte diffusion impedance with negligible influence on the dissolution process. The results show that the R_s values (solution resistance) of the tin sheets wrapped with by-products and pure tin sheets were 0.39Ω and 0.62Ω , respectively, with minor fluctuations. The charge transfer impedance (R_{ct}) serves as an indicator of charge transfer resistance, whose numerical variation directly reflects the state of the passivation layer. A dense and stable passivation layer leads to increased R_{ct} , whereas passivation film rupture results in decreased R_{ct} . The by-product wrapping layer hinders tin ion diffusion through the passivation layer, not only reducing dissolution efficiency but also significantly restricting overall reaction kinetics. This finding provides crucial theoretical insights into the regulatory role of by-products. The R_{ct} value of the tin sheets wrapped in by-products was 3.47Ω , while that of the pure tin sheets was 0.87Ω . Thus, the R_{ct} value of the pure tin sheets was consistently lower than that of the tin sheets wrapped in by-products. Due to their higher resistance value, the same oxidation potential resulted in a lower oxidation current, thereby weakening the electron transfer at the tin sheet surface. Under mass transfer obstruction, the oxidative dissolution of tin was significantly weakened [33–35].

Thermodynamic calculation results obtained using HSC 6.0 software (Fig. 2(b)) further elucidate the influence mechanism of by-products. At 25°C , the oxidation potential of tin indicates that oxidizing tin to $\text{Sn}(\text{OH})_6^{2-}$ requires a potential of 0.262 V. However, when tin generates SnO as by-products during oxidation, converting SnO to $\text{Sn}(\text{OH})_6^{2-}$ requires 0.280 V, significantly increasing the oxidation difficulty. As the reaction temperature increases, the required oxidation potential increases further. The formation of SnO by-products not only increases the system oxidation difficulty but, more importantly, reduces the thermodynamic driving force by altering the reaction pathway.

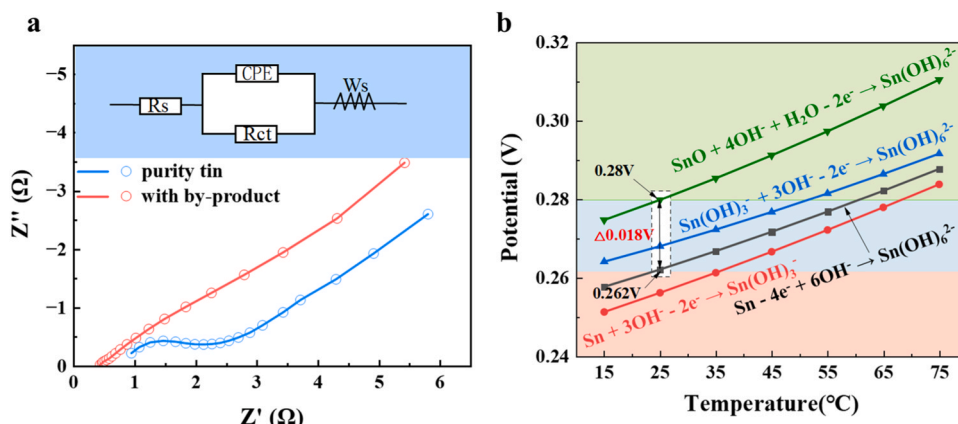


Fig. 2. (a) Nyquist plots of pure tin plates and tin plate electrodes covered with by-products obtained in an open circuit at a frequency of 1 Hz to 10 kHz in a 3 mol/L NaOH solution at room temperature; (b) Thermodynamic analysis of tin oxidation (potential as a function of reaction temperature).

3.3. Formation of by-products

(1) Effect of reaction temperature

Experimental investigations were conducted with NaOH concentration of 3 mol/L, H_2O_2 concentration of 30 %, and NaOH: H_2O_2 volumetric ratio of 10:1 under quiescent conditions. The by-product formation at 60 min in different temperatures (20–70 °C) was investigated by analyzing the mass loss of tin sheets and the Sn^{4+} concentration in the solution. The proportions of tin sheets and by-products and the qualities of by-products under different temperatures at 3 mol/L NaOH are shown in Figs. 3a and 3(b), respectively.

Fig. 3 clearly demonstrates the temperature-dependent deposition behavior of black by-products on tin surfaces. Elevated temperatures not only significantly enhance by-product formation but also induce a progressive color transition from thin dark gray films at 20 °C to dense black coatings at 70 °C. Although the reaction temperature reduces the mass of

unreacted tin sheets, a paradoxical phenomenon emerges: the tin ion concentration remains consistently below 1 %, while the by-product yield increases from 0.1 g at 20 °C to 0.35 g at 70 °C. This discrepancy confirms that the consumed tin primarily transforms into surface-bound byproducts rather than soluble ions.

At elevated temperatures, the spontaneous decomposition of H_2O_2 is significantly accelerated ($2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2\uparrow$), leading to a substantial decrease in the effective oxidant (H_2O_2) concentration. The decomposition efficiency of H_2O_2 is determined by analyzing the

Table 1

Decomposition efficiency of H_2O_2 at different temperatures.

	15 min	30 min	45 min	60 min
20 °C	0.5 %	1.03 %	1.57 %	2.2 %
40 °C	0.62 %	1.45 %	2.01 %	2.48 %
60 °C	11.73 %	23.15 %	39.4 %	42.33 %

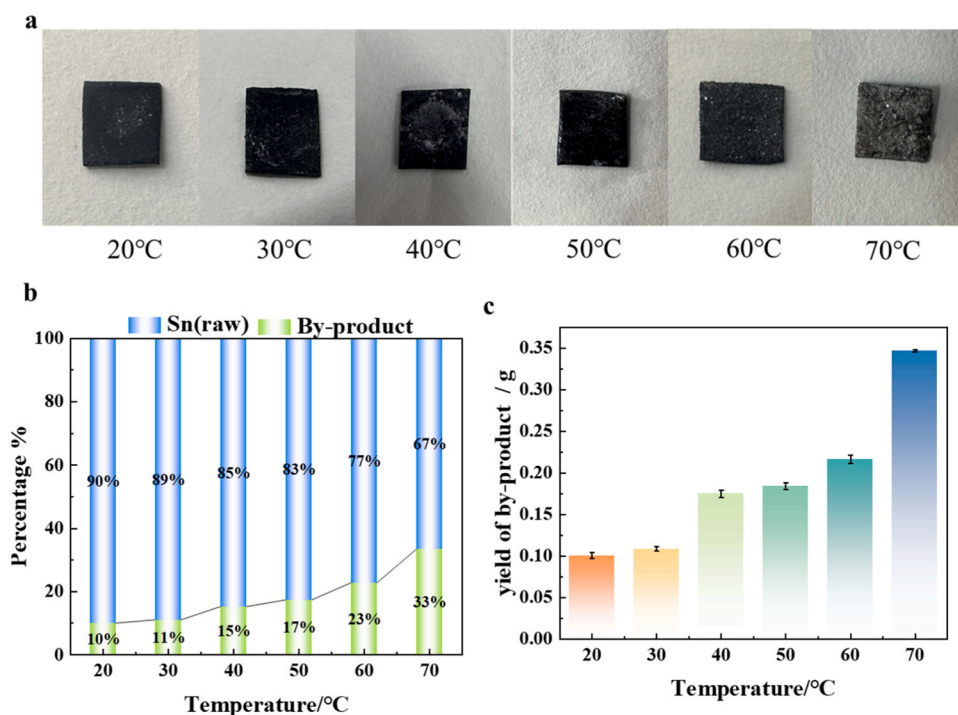


Fig. 3. (a) Macroscopic photographs of black byproduct formation at different temperatures; (b) Proportions of tin sheets and by-products; (c)Yield of by-products under different temperatures.

concentration changes of 30 % H_2O_2 in NaOH solutions (without tin) at different temperatures, as presented in Table 1. The results further demonstrate that elevated temperatures accelerate H_2O_2 decomposition, thereby reducing the effective H_2O_2 concentration in the solution. When the oxidation capacity becomes insufficient, the oxidation reaction of Sn tends to stop at the intermediate Sn(II) state (Reaction 5) rather than proceeding to complete oxidation to Sn(IV) (Reaction 1).



Once formed on the tin surfaces, these by-products exhibit significantly reduced dissolution rates due to diffusion field limitations, leading to their continuous accumulation. This phenomenon becomes more pronounced with increasing temperature [36,37]. To minimize by-product generation, controlling the tin oxidative dissolution process at room temperature (20 °C) is recommended.

(2) Effects of alkali concentration and NaOH: H_2O_2 volumetric ratio

Experimental investigations were conducted at 20 °C for 60 min with a 30 % H_2O_2 concentration under quiescent conditions. The influence of NaOH concentrations (1, 2, 3, and 4 mol/L) and NaOH: H_2O_2 volumetric ratios (50:1, 40:1, 30:1, 20:1, 10:1) on tin dissolution and by-product formation was systematically studied by analyzing tin sheet mass loss and Sn ion concentration in solution. The results are shown in Fig. 4.

At low NaOH concentration (1 mol/L), as shown in Fig. 4(a), tin dissolution efficiency is extremely low, with almost no Sn ions or by-products detected in the solution. The tin sheet surface displays a metallic luster with no observable black by-products, but XPS analysis reveals the formation of a dense SnO_2 passivation layer (Fig. 5). This SnO_2 passivation layer exhibits very low solubility in weakly alkaline

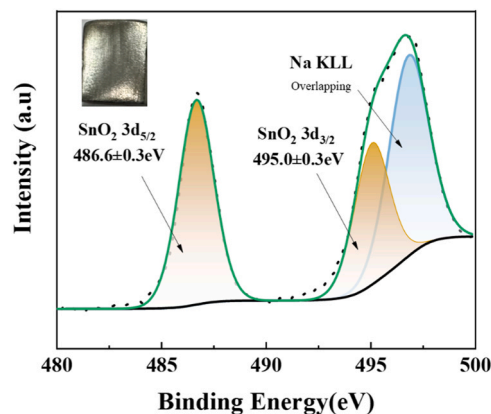


Fig. 5. Actual photographs and XPS analysis of tin sheet at 1 mol/L NaOH concentration and 50:1 NaOH: H_2O_2 volumetric ratio.

environments, effectively blocking contact between the inner metallic tin and the oxidant, causing the reaction to nearly cease.

The higher alkalinity of 2 mol/L NaOH promotes the conversion of tin into tin ions but also leads to a significant increase in by-product formation (Fig. 4(b)). At low oxidant concentration (NaOH: H_2O_2 volumetric ratio of 50:1), insufficient oxidizing capacity results in the preferential formation of intermediate-valence SnO, increasing by-product yield. When the oxidant concentration is increased (NaOH: H_2O_2 volumetric ratio of 40:1–20:1), the mass of by-products decreases, while the amount of Sn ions increases. However, excessively high oxidizing potential (NaOH: H_2O_2 volume ratio of 10:1) exacerbates the formation of

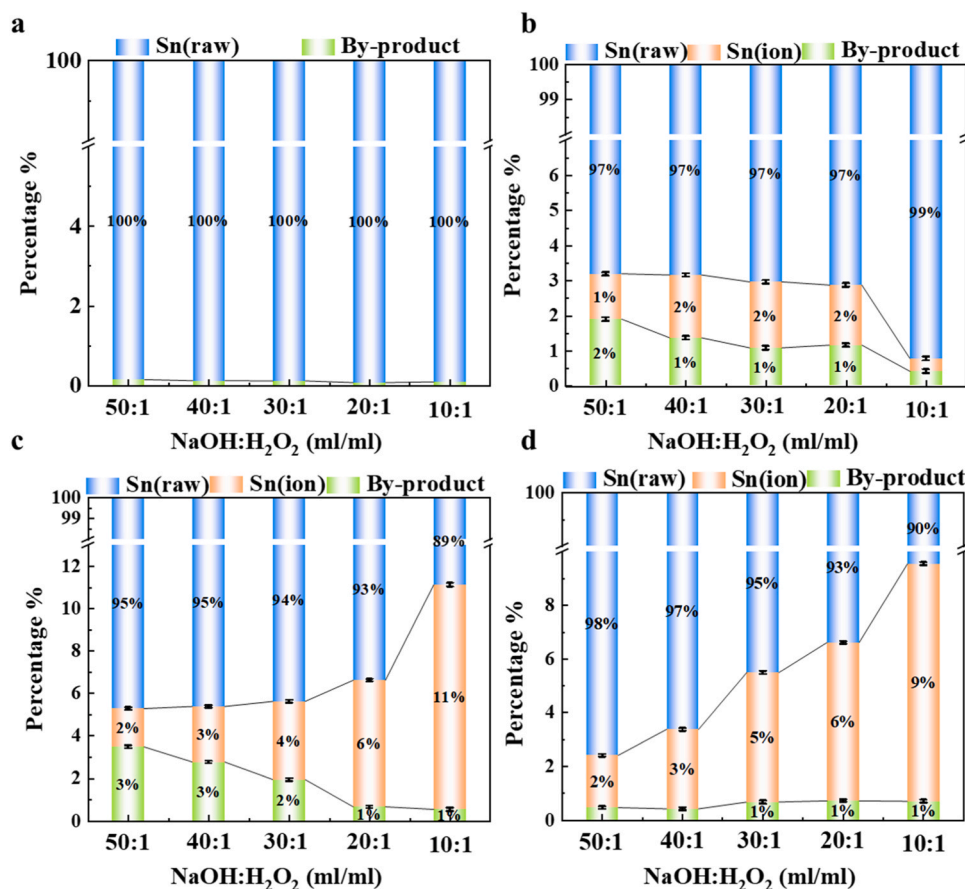


Fig. 4. Proportions of tin sheets and by-products under different NaOH: H_2O_2 volumetric ratios with (a) 1 mol/L NaOH; (b) 2 mol/L NaOH; (c) 3 mol/L NaOH; (d) 4 mol/L NaOH.

an SnO₂ passivation layer, inhibiting the continuous dissolution of tin and the generation of by-products. This indicates that the passivation effect still dominates within this alkalinity range, thereby limiting significant improvement in dissolution efficiency [39,40]. These results suggest that, in practical processes, the initial oxidant dosage must be carefully controlled to avoid excessive passivation.

Under high NaOH conditions (3–4 mol/L) (Figs. 4(c) and 4(d)), the tin oxidative dissolution efficiency increases significantly, while the by-product yield can be maintained at levels comparable to or even lower than those observed at 2 mol/L NaOH. This is attributed to the elevated pH promoting the transformation of the SnO₂ passivation layer into soluble stannate ([Sn(OH)₆]²⁻) [7,8], effectively preventing its accumulation as solid by-products. High-concentration alkaline solutions exhibit elevated viscosity, which may impede the diffusion of reactants (e.g., H₂O₂) and the mass transfer of intermediates, while also potentially affecting the settling behavior of solid particles. Nonetheless, in our experimental system, a pivotal chemical process dominates: SnO₂ rapidly dissolves to form soluble [Sn(OH)₆]²⁻ species. This dominant effect outweighs the adverse impacts associated with increased viscosity, thereby effectively mitigating by-product accumulation. Within this alkaline concentration range, increasing the H₂O₂ amount (decreasing the NaOH: H₂O₂ volume ratio) progressively enhances tin dissolution without inducing the passivation effects observed at lower alkalinities (1–2 mol/L NaOH). This demonstrates that high alkalinity fundamentally alters the reaction pathway, enabling efficient oxidation of both metallic tin and intermediate species directly to [Sn(OH)₆]²⁻.

Through the Pourbaix diagram (Fig. 6), the dissolution behavior of tin is systematically investigated. The Pourbaix diagram shows the stable phase zones under different conditions. In the low alkaline concentration region (pH < 11.2), the oxidation process of tin exhibits distinct stepwise characteristics with increasing oxidation potential, Sn → SnO → Sn(OH)₄ (SnO₂). In the medium alkali concentration region (pH 11.2–13.8), the stepwise oxidation is Sn → SnO → Sn(OH)₆²⁻ (tetraivalent). In the high alkali concentration region (pH > 13.8), tin undergoes complete oxidative dissolution, directly transforming into Sn(OH)₆²⁻. Some studies have shown that the Pourbaix diagram illustrates the formation of Sn(OH)₂ and Sn(OH)₄ hydroxides during tin oxidative dissolution [16,17,38]. However, both Sn(OH)₂ and Sn(OH)₄ are unstable and gradually dehydrate to form SnO_x·nH₂O, ultimately resulting in the black by-products we observed (primarily SnO with minor amounts of SnO₂).

The formation of SnO₂ may occur through two pathways. The first pathway involves the spontaneous formation of a passivation layer. When a tin sheet is exposed to air, a SnO₂ passivation layer forms spontaneously on the surface even in the absence of H₂O₂, as demonstrated by Fig. 1(b). The second pathway involves the oxidation of tin by H₂O₂ under alkaline conditions. In NaOH solution environment, H₂O₂

typically oxidizes tin into soluble tetravalent tin species (e.g., [Sn(OH)₆]²⁻). However, when the H₂O₂ concentration is high or the alkalinity is weak, over-oxidation may occur, leading to the formation of solid SnO₂. The possible intermediate steps include: Sn → SnO → Sn(OH)₄ → SnO₂ (as shown in Fig. 2 and the dehydration of Sn(OH)₄ to form SnO₂), or direct oxidation: Sn + 2 H₂O₂ → SnO₂ + 2 H₂O. Reference [21] confirms that even in a NaOH solution with pH 13, SnO₂ can stably exist in a well crystallized form, indicating its extremely low solubility in alkaline media. The formation of SnO₂ can create a passivation layer on the tin surface due to its dense oxide structure and very low solubility (especially in alkaline environments), significantly inhibiting subsequent reactions.

The formation mechanism of SnO by-products can be attributed to incomplete oxidation of tin under conditions of low pH (<13) and insufficient oxidizing ability of H₂O₂, as shown in Reaction (3). This mechanism aligns with the findings of Li et al. [39], who observed incomplete tin oxidation during SnO thin film prepared via the PLD method provided that under low oxygen partial pressure (0.05 Pa), the Sn 3d_{5/2} peak in the XPS spectra showed double peaks at 484.0 eV (Sn⁰) and 485.4 eV (Sn²⁺), confirming the formation of a Sn-SnO mixed phase and supporting the conclusion of incomplete oxidation. Notably, the rapid generation of black SnO by-products occurs exclusively in alkaline media, whereas no such phenomenon is observed in pure aqueous systems, as shown in Fig. 7. This is primarily because, in pure water, H₂O₂ decomposes sluggishly without catalysis, failing to provide adequate oxidative power. Concurrently, a dense SnO₂ passivation layer forms on the tin surface, inhibiting further reaction. In contrast, OH⁻ ions in alkaline environments not only significantly accelerate H₂O₂ decomposition, enhancing oxidizing capacity, but also effectively dissolve the SnO₂ passivation layer on the tin surface. This continuous exposure of fresh metal surfaces promotes the initial oxidation of Sn to SnO, leading to higher SnO yields. However, the formation of SnO is suppressed when substantial amounts of Na₂SnO₃ ([Sn(OH)₆]²⁻) accumulate in the system. This reduction is attributed to the ability of [Sn(OH)₆]²⁻ to likely coordinate and stabilize H₂O₂, slowing its alkaline decomposition. This stabilization ensures a sustained and effective supply of oxidant, thereby enabling the complete oxidation of Sn(0) and Sn(II) species to Sn(IV) and consequently reducing SnO formation.

In actual production, even under optimized conditions employing strongly alkaline solutions (NaOH concentration >2 mol/L) and excess hydrogen peroxide (typically 1.5 times the theoretical amount) that should theoretically facilitate complete oxidation and dissolution of metallic tin into tetravalent tin species, experimental results still detect residual SnO. The fundamental reason lies in three kinetic barriers hindering the further oxidation of SnO to [Sn(OH)₆]²⁻, including the high activation energy barrier required for the SnO → SnO₂ step, the formation of a dense SnO₂ passivation layer on SnO surfaces that impedes reactant diffusion, and mass transfer limitations of OH⁻/H₂O₂ in the high-viscosity strongly alkaline system.

3.4. Control of by-product production during the oxidative dissolution of tin sheets

The effects of sodium hydroxide concentrations (2, 3, 4 mol/L) and reaction times (20, 40, 60, 80, 100, 120 min) on by-product yields and tin oxidative dissolution efficiency were studied at stirring rate 200 rpm, room temperature (20 °C), NaOH:H₂O₂ volumetric ratio of 30:1. The experimental results are shown in Fig. 8.

As shown in Fig. 8(a), tin oxidative dissolution efficiency increases progressively with extended reaction time, while the by-product yield shows an initial increase followed by a decrease. During the initial reaction stage (0–60 min), sufficient H₂O₂ promotes the oxidative dissolution of tin and had a significant enhancement effect on both steps of tin oxidation, but due to the reaction rate limitation, the oxidation rate of stannous oxide can not match that of Reaction 3, leading to the accumulation of by-products. Notably, by-product accumulation peaks

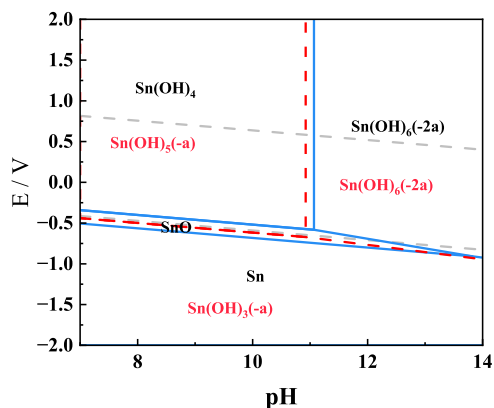


Fig. 6. Phase equilibrium for tin in aqueous solution described by Pourbaix diagram.

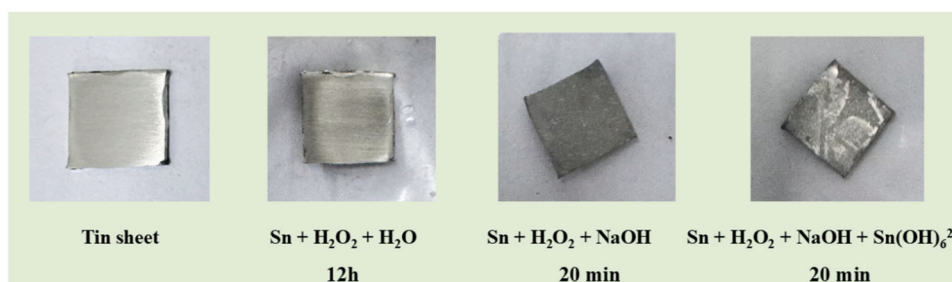


Fig. 7. By-product formation in Sn + H₂O₂ reactions under H₂O and NaOH conditions.

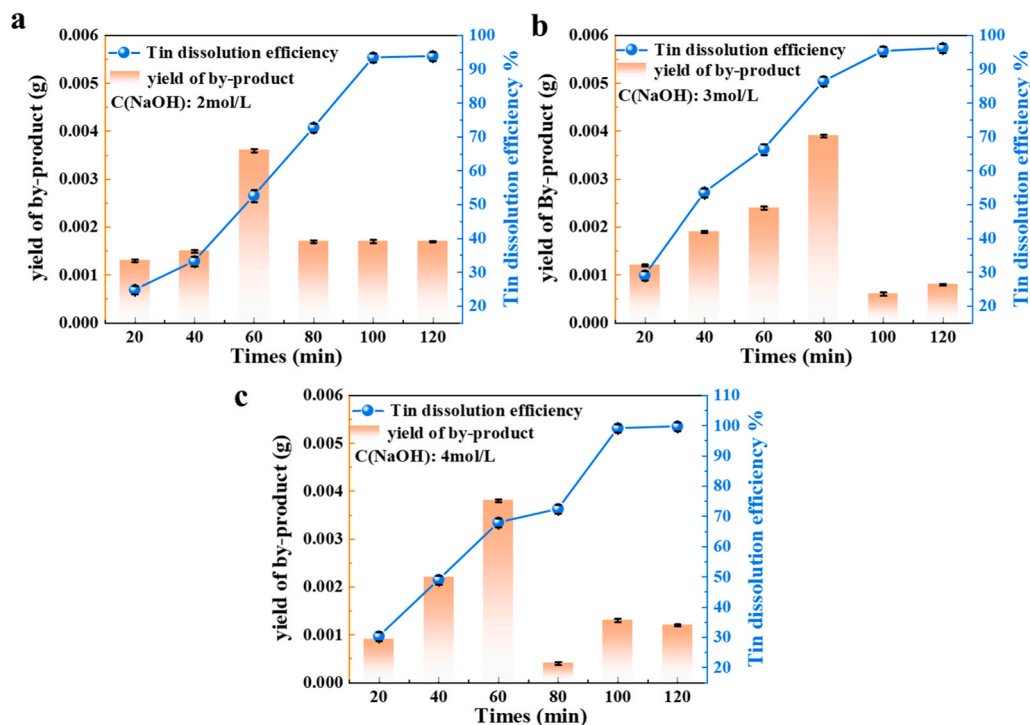


Fig. 8. Yield of by-products and tin oxidative dissolution efficiency with different NaOH concentrations. (a) 2 mol/L; (b) 3 mol/L; (c) 4 mol/L.

consistently within the 60–80 min interval across all alkaline concentrations. As the reaction progresses, the continued consumption of metallic tin and the encapsulation of SnO weaken the reaction of metallic tin with the solution, reducing by-product generation efficiency. Under stable dissolution efficiency conditions, the amount of by-products decreases. Once the tin oxidative dissolution efficiency exceeds 90 %, the reduced concentrations of both oxidant and NaOH limit the oxidative dissolution capacity for residual by-products, causing the by-product mass to stabilize.

Optimal experiments reveal that 3 mol/L NaOH concentration achieves 96.14 ± 0.5 % metallic tin oxidative dissolution efficiency within 120 min, with by-product formation suppressed to 0.0008 g (0.04 % of the initial tin). When NaOH concentration increases to 4 mol/L, although oxidative dissolution efficiency reaches 99.62 %, by-product generation rises to 0.0012 g (0.06 %). This higher concentration has the following limitation: (1) significantly increased solution viscosity hindering ion diffusion; (2) increased reagent consumption raising costs. A comprehensive technical-economic evaluation confirms that the 3 mol/L condition effectively inhibits side reactions while maintaining > 96 % oxidative dissolution efficiency.

Statistical analysis was conducted on the yield of by-products under different NaOH concentrations after 100 min of reaction at a NaOH:H₂O₂ volumetric ratio of 30:1. The results revealed a significant

influence of NaOH concentration on by-product formation ($p < 0.001$). Tukey's post-hoc test confirmed that the 3 mol/L group produced significantly fewer by-products (0.0006 ± 0.0003 g) than both the 2 mol/L group (0.0017 ± 0.00002 g, $p < 0.001$) and the 4 mol/L group (0.00127 ± 0.00007 g, $p < 0.001$).

The effects of the initial NaOH:H₂O₂ volumetric ratios (50:1, 40:1, 30:1, 20:1, 10:1) on by-product yields and tin oxidative dissolution efficiency were studied at reaction times (20, 40, 60, 80, 100, 120 min), stirring rate 200 rpm, room temperature (20°C), with NaOH concentration 3 mol/L. The experimental results are shown in Fig. 9.

Comparative analysis demonstrates that the 30:1 volumetric ratio exhibits optimal process performance, as shown in Fig. 9(a). When NaOH:H₂O₂ volumetric ratio is below 30:1 (e.g., 20:1, 10:1), excessive H₂O₂ causes violent oxygen evolution, reducing oxidant utilization efficiency and increasing by-product residue to 0.15 % of total tin. Conversely, NaOH:H₂O₂ volumetric ratios above 30:1 (e.g., 40:1, 50:1) result in insufficient oxidant, slowing by-product oxidation and dissolution rates. Notably, at 50:1 and 40:1 of NaOH:H₂O₂ volumetric ratios, initial oxidant deficiency leads to significant early-stage by-product accumulation, leading to slow improvement in tin oxidative dissolution efficiency (reaching only 76 % at 100 min), requiring extension to 120 min for satisfactory results. In contrast, at NaOH:H₂O₂ volumetric ratio of 30:1, the tin oxidative dissolution efficiency reaches 95.25 % at

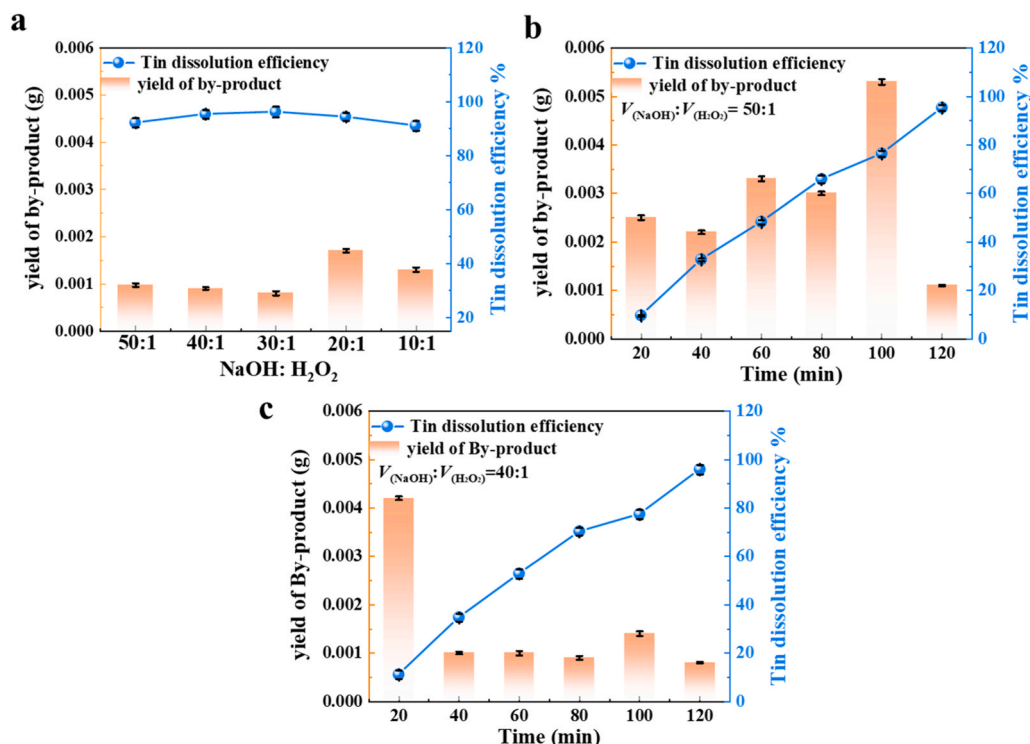


Fig. 9. Yield of by-products and tin oxidative dissolution efficiency under (a) different initial NaOH:H₂O₂ volumetric ratios for 120 min, (b) different time with initial NaOH:H₂O₂ of 50:1; (c) different time with initial NaOH:H₂O₂ of 40:1.

100 min, comparable to 120 min results.

Statistical significance analysis was conducted on the yield of by-products under different NaOH:H₂O₂ volumetric ratios after 100 min of reaction at the NaOH concentration of 3 mol/L, and the results shows no statistically significant differences ($p > 0.05$) in by-product yield among the 50:1, 40:1, and 30:1 conditions, indicating comparable by-product generation. In contrast, the 20:1 ratio exhibited markedly elevated by-product yield (0.0017 g) relative to the 30:1 ratio, with statistical significance confirmed ($p < 0.001$).

Under the conventional industrial production conditions of 70 °C, 1.5 times the theoretical amount of hydrogen peroxide added, and 4 mol/L sodium hydroxide concentration, tin dissolution efficiency reaches 86.56 % after 120 min (Fig. 10). However, under optimized conditions, the efficiency increases to 95.25 % at just 100 min. Additionally, the by-product yield is 0.1304 g after 120 min under conventional conditions but drops to 0.0856 g under optimized conditions,

demonstrating a significant reduction in by-product formation.

Based on these findings, the recommended optimal process parameters are: reaction temperature 20 °C, NaOH concentration 3 mol/L, initial NaOH:H₂O₂ volumetric ratio 30:1, and reaction time 100 min. After optimization, the tin oxidative dissolution efficiency reaches 95.25 %, with by-product formation suppressed to 0.03 % of the total tin amount. This parameter combination ensures efficient tin dissolution while effectively controlling by-product generation, demonstrating significant industrial application value.

4. Conclusions

The occurrence state and effects of by-products during the tin oxidative dissolution process were clarified, and optimized control strategies were proposed in this work. The main results were as follows:

The by-products generated during tin oxidative dissolution consisted mainly of SnO₂ and SnO, with SnO being the dominant component. Electrochemical and thermodynamic analyses revealed that the passivation layer formed by by-products impeded reactant mass transfer and electron transport, thereby reducing tin dissolution efficiency. Meanwhile, SnO formation altered the reaction pathway and increased the thermodynamic difficulty.

The formation and accumulation of SnO relies on two pathways: (1) incomplete oxidation of tin under low oxidation potential and low alkalinity conditions, and (2) oxidation rate limitation resulting in accumulation of by-products. To inhibit the formation of by-products, the optimal process conditions were recommended as follows: reaction temperature 20 °C, NaOH concentration of 3 mol/L, initial NaOH/H₂O₂ volumetric ratio of 30:1, and reaction time of 100 min. After process optimization, the efficiency of tin oxidative dissolution reached 95.25 %, while by-product generation was suppressed to 0.03 % of the total tin content. This study effectively addressed the issues of excessive by-products and low efficiency in traditional alkali dissolution methods, providing technical support for the green preparation of tin salts.

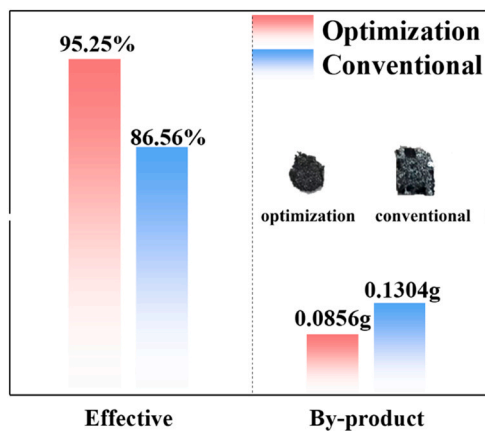


Fig. 10. Tin dissolution efficiency and by-product at optimization and conventional conditions.

CRediT authorship contribution statement

Dongbin Wang: Writing – original draft, Formal analysis, Data curation. **Wenlong Miao:** Writing – review & editing. **Mingge Fu:** Writing – review & editing. **Vanduoc Tran:** Writing – review & editing. **Liuxin Xiang:** Writing – review & editing. **Tian Wang:** Writing – review & editing. **Thiquynhxuan Le:** Writing – review & editing, Supervision, Resources. **Libo Zhang:** Writing – review & editing, Resources.

Declaration of Competing Interest

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

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Data Availability

Data will be made available on request.

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