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Research on the Selective Electrocatalytic Reduction of SO_2 to Recover S^0 by Pb Electrode

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Abstract: Resource utilization of SO_2 from flue gas is a key challenge for the green development of the smelting industry. Recovery of sulfur resources in the form of elemental sulfur (S^0), which has a high market demand and is a current focus in the field of SO_2 treatment, can reduce the solid waste from desulfurization. In this study, it was found that Pb as a cathode material had good catalytic activity for the electrochemical reduction of SO_2 and good selectivity towards elemental sulfur. However, the cathode suffers from sulfur poisoning. The problem was resolved by introducing surfactant, specifically sodium dodecyl benzene sulfonate (SDBS), which significantly lowered the sulfur content ratio on the surface of the electrode from 31.82% to 2.17%. Through the optimization of electrocatalytic parameters, this method enables efficient conversion of SO_2 to S^0, achieving a selectivity of 83% at pH = 0.25 and E = −0.8 *V (vs. SCE)*.

Keywords: Pb; SO_2; S^0; surfactant; sulfur adhesion

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Citation: Liu, X.; Wang, X.; Long, J.; Xie, X.; Wu, L.; Wang, Z.; Fu, Y.; Chen, H.; Xiang, K.; Liu, H. Research on the Selective Electrocatalytic Reduction of SO_2 to Recover S^0 by Pb Electrode. *Metals* **2023**, *13*, 569. https://doi.org/10.3390/met13030569

Academic Editor: Branimir N. Grgur

Received: 13 February 2023
Revised: 28 February 2023
Accepted: 9 March 2023
Published: 12 March 2023

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1. Introduction

Sulfur, comprising more than 30% of all minerals, is one of the essential elements in the geochemical cycle. During high-temperature pyrometallurgical operations, sulfur is oxidized to sulfur dioxide (SO_2) [1–6]. Statistically, the use of these minerals results in the emission of approximately 50 million tons of sulfur dioxide annually, the majority of which is used for the production of high-concentration sulfuric acid. Even though sulfuric acid is widely used in industry and consumed in large quantities, there are numerous safety concerns associated with its storage, transportation, and use. Gypsum, ammonium sulfate, elemental sulfur, and other products are typically used to recover low-concentration sulfur dioxide [7]. In comparison to other desulfurization products such as gypsum, elemental sulfur (S^0) has relatively stable characteristics and is more straightforward to transport and store. Additionally, there is a huge market demand (about 60 million tons per year) for elemental sulfur, which can be used as a raw material to produce other goods that contain sulfur, such as rubber. Consequently, there is a substantial market for the disposal of sulfur dioxide resources through the conversion of sulfur dioxide into elemental sulfur.

Currently, the main methods utilized for the conversion of sulfur dioxide into elemental sulfur encompass gas phase reduction, liquid phase reduction, and electrochemical reduction. The gas phase reduction process involves the introduction of H_2, C, CO, and CH_4 at temperatures exceeding 200 °C [8–10]. In most cases, reaction catalysts are employed to enhance product selectivity and reaction activity. Metal-based materials, including transition metals, precious metals, and non-precious metals, have been extensively studied in this context. Owing to their high density of Lewis acid sites [10], metal-based materials exhibit the capability to efficiently adsorb sulfur dioxide. However, these approaches are not commercially feasible due to their high energy consumption, production of large

quantities of byproducts, reduced sulfur quality, and catalyst degradation resulting from soot formation. Hence, it is imperative to develop a low-cost, energy-efficient sulfur dioxide treatment technology for elemental sulfur recovery. Liquid phase reduction desulfurization (LPRD) is a novel desulfurization technique that exhibits greater reaction efficiency and lower reaction temperatures compared to conventional gas phase catalytic reduction desulfurization technology. However, when reducing sulfur dioxide in liquid phase, the resulting products often contain partially reduced forms of sulfur compounds. As a result, an additional process is needed to separate sulfur product [11,12]. Outotec has proposed another method for obtaining elemental sulfur through liquid phase disproportionation reduction of SO_2. However, this process requires high temperatures. To decrease the reaction temperature, Yang et al. put forward a novel strategy of using selenium (Se) as the catalyst to facilitate the disproportionation of sulfur dioxide alkali absorption solution. As a result, it lowered the disproportionation temperature of sulfur dioxide from 160 °C to 80 °C. Se can be easily regenerated via filtration and can be used repeatedly [11]. However, the theoretical conversion efficiency of the sulfur dioxide disproportionation process is only one-third.

Electrocatalytic reduction of sulfur dioxide is considered an economically viable and eco-friendly approach to recover S^0. Although the electrolytic recovery method has advantages such as the absence of secondary pollution compared to gas phase reduction [8–10] and liquid phase reduction technologies [11,12], the existing sulfur dioxide electrolytic reduction methods suffer from low reactivity and selectivity. Researching and designing electrocatalysts and electrolysis systems are necessary to improve the conversion rate and product selectivity of sulfur dioxide [13]. At the same time, the electro-reduction of sulfur dioxide has a drawback in that the resulting sulfur tends to adhere to the electrode surface, which rapidly deactivates it during the electrolysis process. This has led to a stagnation of electrocatalytic reduction of sulfur dioxide technology in recent years [14,15]. Despite the fact that many studies have focused on finding a solution to the issue of sulfur adhering to the electrode during the electrolysis process, such as the use of a rotating disk electrode and ultrasonic-aided electrolysis [16], the adherence of sulfur on the electrode surface has yet to be resolved fundamentally. Therefore, the breakthrough in sulfur dioxide electro-reduction recovery technology also depends on resolving the issues of sulfur adhesion on electrode.

For the electrocatalytic reduction process, the choice of electrode materials is of paramount importance. Precious metals, such as Au, Ag, and Pt, are the most commonly utilized cathode materials in the electro-reduction process of sulfur dioxide [17–19]. Due to their high price, these electrode materials cannot be used widely. Consequently, the practical application of sulfur dioxide electro-reduction necessitates the screening of inexpensive cathode materials with single-species selectivity, high activity, and good stability for elemental sulfur. The selectivity of electrolytic products during the electrochemical reduction process is often impacted by the hydrogen evolution reaction. Therefore, when choosing electrode materials for SO_2 reduction, materials with superior sulfur dioxide catalytic performance and high hydrogen evolution potential should be taken into consideration. Moreover, the electrolytic reaction of sulfur dioxide typically involves low pH conditions. However, these conditions can cause active metals such as Mg, Al, Zn, and Fe to react with the acid, which limit its effectiveness. Therefore, when selecting materials for electrocatalytic testing and screening, it is important to choose ones with strong acid resistance, such as Pb, Ti, Cu, and glassy carbon.

In this study, material screening was employed to improve the selectivity of elemental sulfur while reducing the side reaction of hydrogen evolution. By adding a surfactant, the primary issue of cathodic sulfur poisoning was resolved. To achieve a balance between current attenuation during the electrolysis process and electrode deactivation during electrolysis, a surfactant that could shield against sulfur poisoning of the electrodes was selected. To determine the effect of the selected surfactant on the electrolysis system, the electrochemical behavior of the surfactant was investigated after being added to the electrolyte.

2. Materials and Methods

2.1. Chemicals and Reagents

The sulfite (Na_2SO_3, AR > 99%) concentration of 0.08 mol/L was used as the reactant. Other chemicals, such as anhydrous sodium sulfate (Na_2SO_4, AR > 99%), acetone, isopropanol, concentrated sulfuric acid (H_2SO_4, AR > 98%), sodium dodecyl benzene sulfonate (SDBS, AR > 99%), polyvinylpyrrolidone (PVP, AR > 99%), and high-purity lead tablets, (AR > 99%), were of analytical grade (Tianjin Kemiou Chemical Reagent Co. of China, Tianjin, China).

2.2. Experimental Procedure

An H-type electrolytic cell (Gaoss Union, Wuhan, China) was used for the electrochemical performance tests. Anode and cathode chambers were divided by using a proton exchange membrane. Pb (1 cm × 1 cm) was used as the working electrode, Pt (1 cm × 1 cm) was used as the counter electrode, and Hg/Hg_2Cl_2 (SCE) was used as the reference electrode for all measurements. A total of 50 mL of the Na_2SO_3/H_2SO_4 solution (0.08 M, pH = 0.5) was placed in the cathodic compartment, and 50 mL of the Na_2SO_4/H_2SO_4 solution (0.08 M, pH = 0.5) was placed in the anode compartment. The pH values of solutions were modulated via the incorporation of 3 mol/L sulfuric acid solution, and the pH was measured by means of a pH meter. Electrochemical activity was measured by using an electrochemical workstation (ZHANER, XPOT). Following 60 min of potentiostatic electrolysis in each group, the solution was filtered, rinsed multiple times, and dried prior to being weighed on an analytical balance (AUY220, Shimadzu) to ascertain the mass of the product. Each set of electrolytic experiments underwent three repetitions, and the resulting average outcomes of the three experiments were considered as the ultimate experimental findings. Determining the electrolytic charge and product quality can be used to calculate the Faraday efficiency of elemental sulfur. The following is the calculating formula:

$$\mathrm{FE} = \frac{nzF}{Q} \times 100\% \quad (1)$$

FE stands for the Faraday efficiency of the elemental sulfur (S^0); n is the number of moles of products; z is the number of electrons exchanged during the reaction; F is the Faraday constant, 96,485.33289 C/mol; Q is the electrolytic charge.

2.3. Analysis and Characterization

Scanning electron microscopy (SEM, JSM-IT300, Tokyo, Japan) with the working current and voltage of 40 mA and 30 kV, respectively, was used in combination with energy dispersive spectroscopy (EDS, Genesis, EDAX. Inc., Mahwah, NJ, USA) to describe the microstructure and elemental distribution of the sample. Prior to the test, the sample was sprayed with gold for around 2 min in order to reduce the excessive volatilization of sulfur in vacuum and improve its conductivity.

X-ray diffraction (XRD, TTRII Rigaku, Tokyo, Japan) was used to identify the phase of products. The precise test parameters are as follows: Cu Kα target (λ = 1.5406 Å), working current of 100 mA, working voltage of 2 kV, scanning angle of 2θ = 10–80°, step length of 0.05°, and scanning speed of 10°/min.

2.4. Electrode Sulfur Poisoning Analysis

To determine the extent of electrode poisoning, the variation in current over time during constant potential electrolysis was monitored using the electrochemical workstation (ZHANER, XPOT). The decay rate of current over time provided an indication of the degree of electrode poisoning. After 60 min of uninterrupted potential electrolysis, the Pb electrode was rinsed with clean water and dried naturally. The surface morphology of the electrode was analyzed using scanning electron microscopy (SEM) to assess the adhesion of elemental sulfur on the electrode surface.

2.5. Screening of Electrode Materials

The electrocatalytic activity and selectivity of the electrode can be partially reflected by comparing the current density and hydrogen evolution potential of different electrode materials at low overpotential. As shown in Figure 1a, Cu has a lower initial reduction potential, but the potential window for the sulfur dioxide catalytic reduction is limited ($E = -0.5 \sim -0.75$ *V vs. SCE*). The initial potential of Pb, Ti, and glassy carbon electrodes were approximately E = −0.4 *V (vs. SCE)*, showing no significant difference among them. However, the reduction peak current in the Pb electrode system was notably higher at a greater negative potential, indicating that Pb has superior catalytic efficiency.

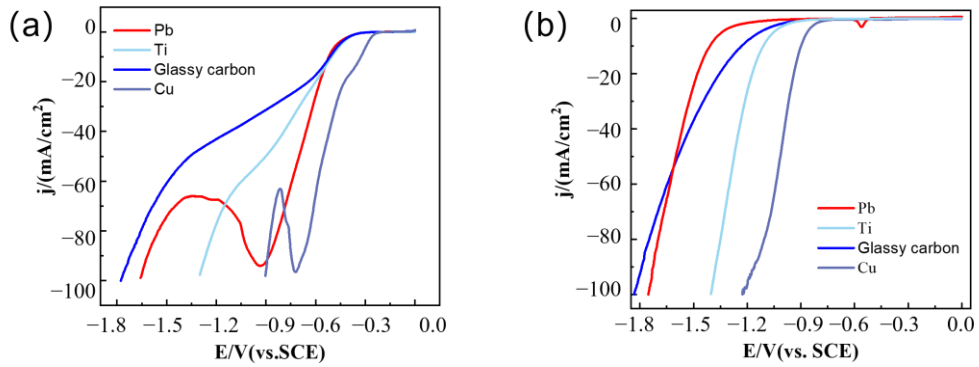


Figure 1. (**a**) The LSV curves of different electrode materials in Na_2SO_3 + H_2SO_4 solution (**b**) The LSV curves of different electrode materials in H_2SO_4 solution.

It is known that the main side reaction during the electrolysis of sulfur dioxide is the hydrogen evolution reaction. Thus, the hydrogen evolution capability of the electrode material is an important factor to be considered when choosing electrodes. Accordingly, in the hydrogen evolution test with 0.5 mol/L H_2SO_4 electrolyte and pH 0.5, Pb was found to have a higher hydrogen evolution potential than other materials, which effectively inhibits the hydrogen evolution reaction and increases the selectivity of the desired product (Figure 1b). Consequently, due to its high catalytic activity and hydrogen evolution potential, Pb was chosen as the cathode material for the electrolytic reduction of sulfur dioxide in this study.

3. Results and Discussion

3.1. Surfactant Inhibition of Cathodic Sulfur Toxicity

3.1.1. Selection Basis of Surfactant

Surfactants, also known as amphiphilic compounds, are composed of two distinct parts: a lipophilic group with an affinity for oil and a hydrophilic group with an affinity for water. This amphiphilic characteristic of surfactants renders them water soluble, as the hydrophilic group attracts water molecules while the lipophilic group repels them. To achieve stability, surfactants must occupy the solid–liquid two-phase interface, extending the lipophilic group to the non-polar group and the hydrophilic group into the water. This is the basis for the selection of surfactants to address sulfur adhesion on the electrode surface.

The surface energy of elemental sulfur is lower than that of the metal electrode, which leads to contact between them during the cathodic reduction of sulfur dioxide to elemental sulfur. Sulfur is easily adsorbed to the electrode surface, thus diminishing its electrochemically active surface area and lowering the electrolysis efficiency and current density. Surface tension at the solid–liquid two-phase contact can be successfully reduced by the surfactant. It is hypothesized that the mechanism of the surfactant promotes the removal of sulfur from the electrode surface in the following manner: In the liquid phase system, the surfactant first adsorbs the electrode, and the sulfur is deposited on the electrode surface before producing a diffusion electric double layer. Due to the identical charge on the electrode and the elemental sulfur surface, they will be effectively isolated from one

another. Furthermore, under the influence of surfactants, elemental sulfur is distributed more evenly and is more stable throughout the solution, as illustrated in Figure 2.

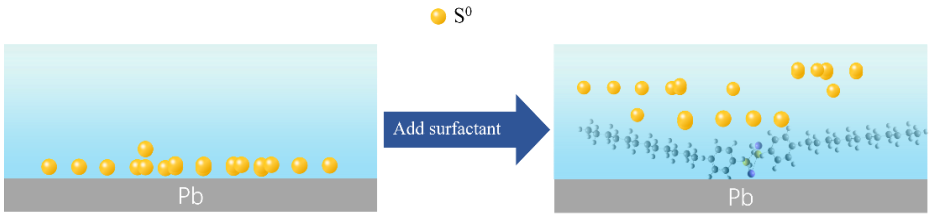


Figure 2. Diagram of the effect of surfactant.

3.1.2. Effect of Surfactant on Inhibition of Cathode S^0 Poisoning

In this study, the effect of surfactant on the inhibition of cathode elemental sulfur poisoning was investigated by using 0.01 mol/L sodium dodecyl benzene sulfonate (SDBS), 0.01 mol/L isopropanol solution (IPA), and 0.3 g/L polyvinylpyrrolidone (PVP) as surfactants. The adherence of elemental sulfur on the cathode surface reduces the electrochemical active surface area of the electrode, which directly leads to a decrease in the electrolytic current. This deactivation of the electrode can be represented by the amount of current attenuation during the electrolysis process. As shown in Figure 3, the current change curve follows a linear relationship (E = −0.8 *V (vs. SCE)*). To calculate the slope, the i–t curve was linearly fitted (Table 1). Results showed that sodium dodecyl benzene sulfonate (SDBS) had stronger inhibitory impact on sulfur poisoning on the electrode surface compared with other surfactants, as the slope of the i–t curve decreased from 0.09 to 0.03. Additionally, due to the surfactant's insulating qualities, as shown in Figure 3, the addition of the surfactant decreased the current density throughout the electrolysis process.

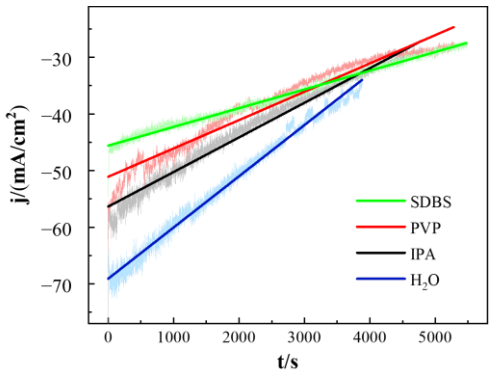


Figure 3. Current density as a function of time with different surfactant.

Table 1. Slope of the i–t curves at constant potential before and after surfactant addition and comparison of sulfur content on electrode surface after electrolysis.

Electrolyte	Slope (Figure 3)	Electrode Surface Sulfur Content (%) (EDS Results)
Na_2SO_3	0.009	31.82
IPA + Na_2SO_3	0.006	16.5
PVP + Na_2SO_3	0.005	4.28
SDBS + Na_2SO_3	0.003	2.17

As shown in Figure 4, in the absence of a surfactant, electrolysis results in a significant number of black material patches developing on the electrode surface, the majority of which are composed of the elemental sulfur. Analysis via Energy Dispersive Spectrometry (EDS) revealed that the sulfur content on the electrode surface after 60 min of electrolysis

without the addition of surfactants was 31.82%. Statistical analysis of the results from the addition of different surfactants (Table 1) indicated that the sulfur content on the electrode surface was dramatically reduced, with SDBS having the most noticeable impact, reducing the sulfur level to 2.17%. It can be concluded that the elemental sulfur is the primary factor contributing to the inactivation of the Pb electrode. Furthermore, the addition of a surfactant can considerably reduce the adhesion of the elemental sulfur on the electrode surface, which is consistent with the inactivation law represented by the slope of the i–t curve. In the follow-up research, SDBS, which had the best anti-deactivation effect, was chosen as an additive to examine the electrolytic reduction of sulfur dioxide in more detail.

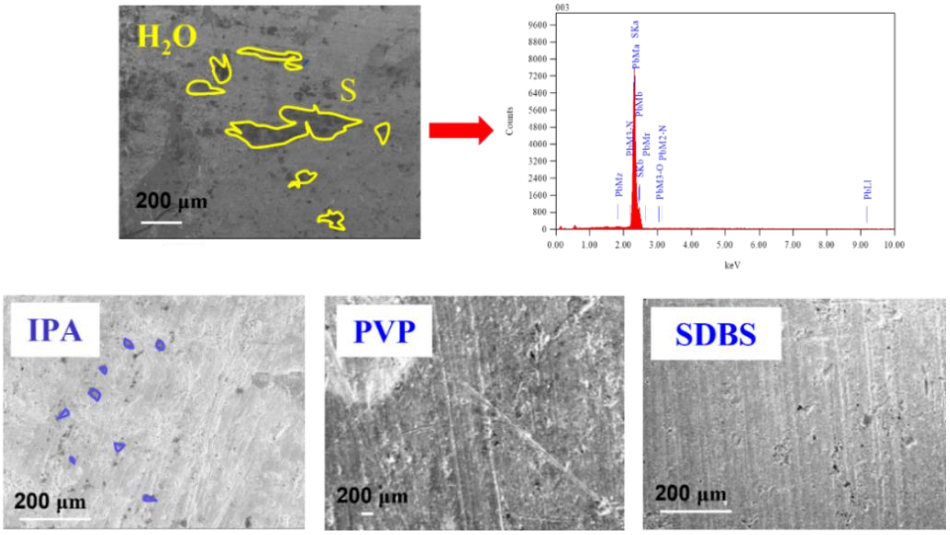


Figure 4. Comparison of SEM images of electrode surfaces before and after surfactant addition.

3.1.3. Effect of Surfactants on Electrochemical Reduction of SO_2

SDBS is an anionic surfactant, which may affect the transmission of electrons during the electrolysis process. As a result, this paper conducted research to analyze the stability of the catalyst and the amount of surfactant applied. To this end, linear voltammetry was employed to assess the effect of sodium dodecyl benzene sulfonate concentrations on the electrochemical reduction of sulfur dioxide by a Pb electrode.

(1) SDBS concentrations

Figure 5 displays the i–t curves for four different sodium dodecyl benzene sulfonate concentrations: 0.01 mol/L, 0.0075 mol/L, 0.005 mol/L, and 0.0025 mol/L. After linear fitting, the slopes were determined to be 0.0056, 0.0053, 0.0055, and 0.0056, respectively. These results suggest that a low concentration of sodium dodecyl benzene sulfonate has a strong inhibitory effect on elemental sulfur adherence to the electrode surface. Thus, sodium dodecyl benzene sulfonate should be controlled at a concentration of 0.0025 mol/L.

The influence of SDBS on the electrolytic reduction performance of sulfur dioxide was studied. Linear voltammetry studies on electrolytes with four SDBS concentrations (0.01 mol/L, 0.0075 mol/L, 0.005 mol/L, and 0.0025 mol/L) were conducted. As depicted in Figure 6, the results showed that as SDBS concentrations increased, the reduction current of sulfur dioxide decreased. This can be attributed to the low solubility of SDBS in acidic solutions, which caused some SDBS to precipitate in the solution as crystals, thus impeding electron transmission and resulting in a drop in current. Additionally, the reduction potential steadily diminished as the SDBS concentration increased. Moreover, the relationship was observed to be non-linear, likely due to the high concentration of SDBS hindering electron exchange and lowering the electrode potential.

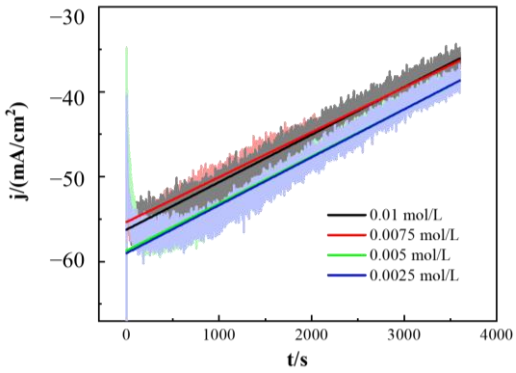


Figure 5. Current density as a function of time for different SDBS concentrations.

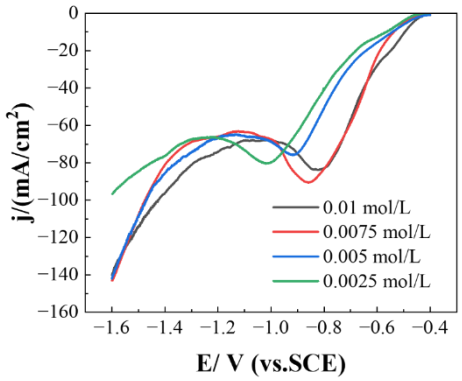


Figure 6. The LSV curves at different SDBS concentrations.

(2) Electrochemical reduction behavior of SO_2 in SDBS solution

In addition, the electrochemical reduction behavior of sulfur dioxide in sodium dodecyl benzene sulfonate (SDBS) solution was studied by linear voltammetry in three different electrolytes (Figure 7) 0.5 mol/L H_2SO_4, 0.5 mol/L H_2SO_4 + 0.0025 mol/L SDBS and 0.5 mol/L H_2SO_4 + 0.0025 mol/L SDBS + 00.08 mol/L Na_2SO_3. According to the test results, the addition of SDBS significantly decreased the reduction peak current at E = −0.6 *V (vs. SCE)*, demonstrating that SDBS can effectively prevent the reaction between Pb and dilute sulfuric acid. Moreover, an adsorption layer was produced on the lead electrode by SDBS to improve the stability of the electrode material. After adding Na_2SO_3, a significant reduction peak appeared near E = −0.8 *V (vs. SCE)*, indicating that sulfur dioxide could be reduced in the presence of SDBS, and thus it can be inferred that sulfur dioxide reduction is the dominant reaction in this potential range.

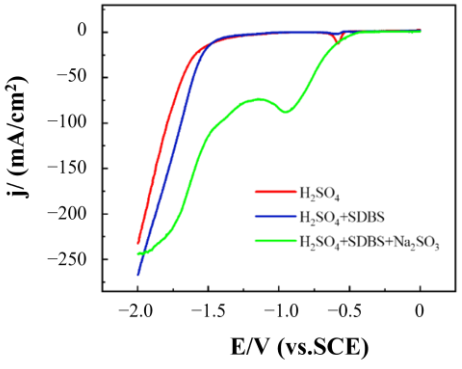


Figure 7. The LSV curves in different electrolytes.

(3) Effect of SDBS on the morphology of the product

In order to investigate the impact of sodium dodecyl benzene sulfonate (SDBS) on the morphology and purity of the product, electrolytic products were examined by SEM-EDS (Figure 8a–d). It was observed that the surface of the product was flocculent and rough without the addition of surfactant (Figure 8a), with spherical particles that had considerable adherence and poor dispersion. After the addition of SDBS, the product's particle form changed to an elliptical shape, and the surface smoothened (Figure 8c), making it more difficult to aggregate and deposit on the electrode surface. The EDS results (Figure 8b,d) revealed that the electrolytic products before and after the addition of SDBS essentially only contained S, indicating that elemental sulfur is of high purity and SDBS can be entirely separated from elemental sulfur. Figure 8e depicts the XRD of the product, which indicated that all diffraction peaks of the product could be indexed to the elemental sulfur (S_8) (JCPDS card No. 08-0247) single phase without impurities. It can thus be concluded that SDBS can effectively enhance the dispersion of the product without compromising its purity.

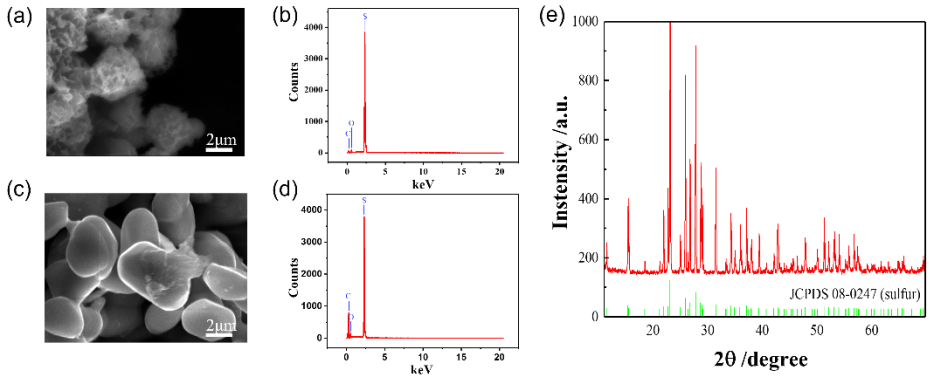


Figure 8. (**a**) Product morphology before adding SDBS; (**b**) EDS spectrum of product composition before adding SDBS; (**c**) product morphology after adding SDBS; (**d**) EDS spectrum of product composition after adding SDBS; (**e**) XRD of the product.

3.2. Selectivity and Activity

It is essential to investigate the selectivity and electrode reaction activity of the elemental sulfur in the electrolytic process at varying potentials and pH levels. This experiment was conducted using a 0.08 mol/L Na_2SO_3, 0.0025 mol/L SDBS, and 0.5 mol/L H_2SO_4 mixed solution. The voltage was set at $E = -0.6 \sim -1.2$ *V (vs. SCE)*, pH = 0.5, and the electrolysis time was 60 min. As shown in Figure 9a, an increase in voltage leads to an increase in current density, indicating a faster ion exchange rate on the electrode surface. At $E = -0.8$ *V (vs. SCE)*, the selectivity of elemental sulfur reached its peak (FE = 78%) (Figure 9d). As the voltage increased further, the selectivity of elemental sulfur decreased. Combined with the CV results obtained under the same experimental conditions, the reduction potential of sulfur dioxide was 0.88 V, and the increase of voltage-triggered side reactions diminished the selectivity of elemental sulfur.

The reactivity of sulfur dioxide is highly dependent on pH. To investigate the impact of pH on the various forms of sulfur dioxide in solution, the electrolyte's pH was adjusted to 0, 0.25, 0.50, 0.75, 1, and 2. As depicted in Figure S1, the reduction in peak current of sulfur dioxide diminishes with increasing pH. Furthermore, when pH > 1, no reduction peak of sulfur dioxide is observable, indicating that sulfur dioxide reduction is more probable at lower pH levels. This phenomenon can be attributed to the electrolytic reactants being sulfur dioxide or H_2SO_3 molecules in such conditions, and the proportion of sulfur dioxide in the solution diminishing as the pH rises. It is well-known that lower pH conditions promote the hydrogen evolution reaction in the solution, and conducting sulfur dioxide electrolysis in a highly acidic environment may lead to a higher electrolysis current while also accelerating the hydrogen evolution reaction. As demonstrated in Figure 9b, the current

density increases notably with decreasing pH. The Faraday efficiency of the elemental sulfur was evaluated at different pH levels ($E = -0.8$ *V (vs. SCE)*), and the results, as presented in Figure 9c, indicate that the Faraday efficiency of elemental sulfur reaches a maximum of 83.5% at pH = 0.25. This can be ascribed to the increased concentration of H^+ in the solution at low pH levels, promoting the occurrence of the hydrogen evolution reaction during the electrolysis process. However, the Faraday efficiency of elemental sulfur decreases dramatically when pH < 0.25. Thus, pH is a critical factor influencing the hydrogen evolution reaction during sulfur dioxide electrocatalytic reduction.

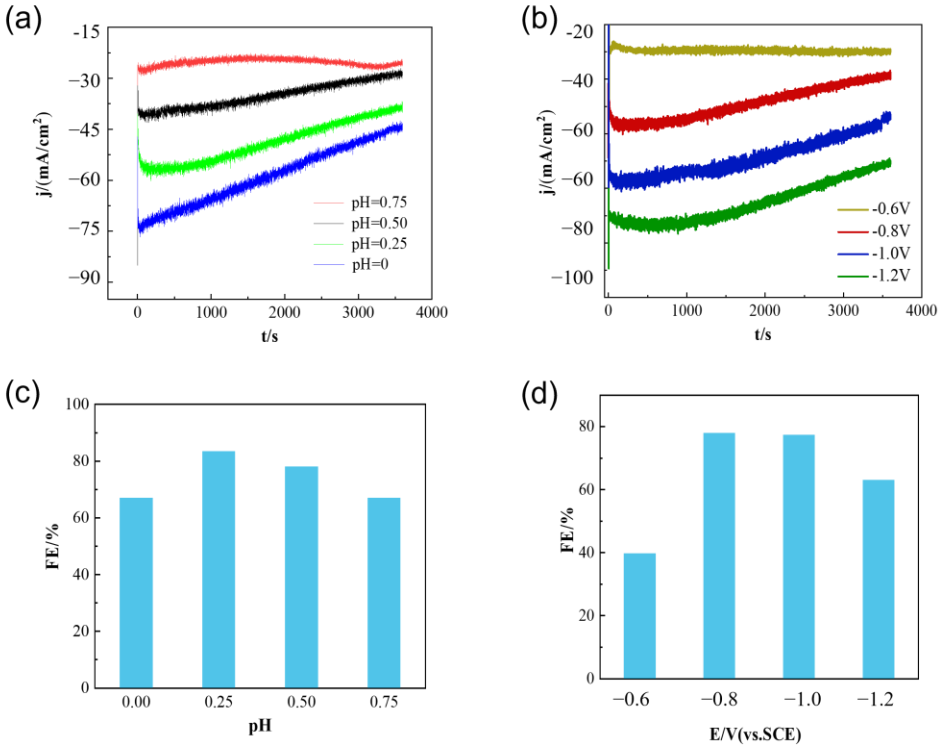


Figure 9. (**a**) Current density as a function of time at different pH; (**b**) current density as a function of time at different potentials; (**c**) Faraday efficiency of elemental sulfur at different pH (E = −0.8 *V (vs. SCE)*); (**d**) Faraday efficiency of elemental sulfur at different potentials (pH = 0.25).

4. Conclusions

In order to address the issues of low elemental sulfur selectivity and sulfur poisoning during the electrochemical conversion of sulfur dioxide, this paper explored the electro-reduction performance of a range of cathode materials. The addition of surfactants effectively resolve the problem of cathode sulfur poisoning. The main conclusions of the study are as follows:

(1) Pb possess a good catalytic activity and high hydrogen potential for sulfur dioxide electro-reduction, which effectively inhibited the occurrence of hydrogen evolution side reactions and increased the selectivity of elemental sulfur.

(2) The use of surfactants in the sulfur dioxide electrolysis system was reported for the first time. SDBS had the most notable inhibitory effect on cathode sulfur poisoning, which can reduce the content of sulfur on cathode from 31.82% to 2.17%.

(3) A novel system for the electrolytic reduction of sulfur dioxide was developed. The Pb electrode was found to have high selectivity for elemental sulfur, good stability during prolonged electrolysis, and high catalytic activity for sulfur dioxide electro-reduction. The Faraday efficiency of elemental sulfur was optimized to 83.5% at pH = 0.25, E = −0.8 *V (vs. SCE)*.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/met13030569/s1, Figure S1: (a) The LSV curves at different pH conditions (b) The relationship between acidity and reduction potential of pH in the range of 0–0.75.

Author Contributions: X.L.: Investigation, Formal analysis, Writing—original draft, Writing—review and editing; X.W., J.L. and X.X.: Writing—review and editing; L.W., Z.W., Y.F. and H.C.: Formal analysis; K.X.: Formal analysis, Writing—review and editing, Funding acquisition; H.L.: Formal analysis, Writing—review and editing, Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Innovative Research Group Project of the National Natural Science Foundation of China (No.52121004), National Key Research and Development Program of China (No.2022YFC3901100), and National Natural Science Foundation of China (No.52234011, No.51974378, No.52200138).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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