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Electro-oxidation of Sulfide on Ti/RuO_2 Electrode in an Aqueous Alkaline Solution

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The electro-oxidation processes of sulfide at Ti/RuO_2 anode in alkaline solution are investigated. The experiment results indicated that the electro-oxidation process of sulfide is irreversible, and the control step is mass diffusion. The final electro-oxidation product is mainly SO_4^{2-} (95.8%), while $S_2O_3^{2-}$+ SO_3^{2-} is 3% and sulfur is 1.2% under the experiment conditions (0.023M Na_2S, 25mA·cm^{-2}, pH 13, 20℃). The SEM results show that the sulfur deposit on the surface of anode with porous structure, and the XRD results confirm that the sulfur is α-S_8. Michaelis-Menten equation can be used to describe the electro-oxidation process, and the values of V_{max} (0.011 mol·L^{-1}·h^{-1}) and K_m (0.010 mol·L^{-1}·h^{-1}) are put forward.

Keywords: electrochemical methods; sulfur oxides (SO_x); electrolysis; pollutants; process optimization

1. INTRODUCTION

Hydrogen sulfide is one of the common components in malodorous gases with severe neurotoxicity and low odor threshold [1]. It usually presents in the processes of natural gas purification, wastewater treatment, and petroleum or mining industry. The traditional methods as combustion or adsorption can remove hydrogen sulfide. However, due to the secondary pollution and high treatment cost, the traditional processes are difficult to achieve the desired results [2,3].

Hydrogen sulfide can be removed from aqueous solutions by electrochemical oxidation process. The anodes as Graphite [3], platinum [5], gold [6] and the mixed metal oxides (MMO) [7] have been applied in the processes of sulfide degradation. When S^{2-} is oxidized at the graphite anode, the main oxidation products are S^0 and S_x^{2-}, and only one oxidation peak appears on the voltammetry curve (-0.8 to +1.5 V) [8]. However, When S^{2-} is oxidized at the platinum anode, two oxidation peaks are observed on the voltammetry curve (-0.8 to +1.5 V), which indicates the possibility of the further oxidation of sulfur and polysulfide [5,9]. Nathan S. Lawrence reported that sulfide can be converted to sulfate directly with boron doped diamond (BBD) anode, and the potential is close to oxygen evolution potential [10]. Katie Waterston confirmed the results with BBD anode. Furthermore, they find the main oxidation products are SO_4^{2-} and the removal rate of S^{2-} coincide to the zero-order kinetics [11]. Chen A. and Miller B. reported the electrochemical oscillations of sulfide oxidation on $Ti/Ta_2O_5–IrO_2$ electrodes and they speculated that the phenomena are caused by the periodic formation/removal of sulfur from the electrode surface [12,13]. Similar behavior occurs at platinum anodes [14,15]. It has been found that potential oscillations play a detrimental impact on the electrode lifetime [13]. The electro-oxidation process of $S^{2-}\rightarrow S$ is a way for us to recovery sulfur [16], but the sulfur will deposit on the surface of the anode quickly. The passive film of sulfur can make the cell potential increase sharply, and then put the process into trouble. In this case, the electro-oxidation process of $S^{2-}\rightarrow SO_4^{2-}$ comes to be an effective way to remove sulfide, especially for the wastewater treatment with low S^{2-} concentration.

The Ti/RuO_2 electrode can be used as dimension stable anode (DSA) which has the advantages for the long lifetime and good stability. Just like boron doped diamond (BDD) and β-PbO_2 [17], RuO_2 anode can generate hydroxyl radicals by oxidizing water, which can do help for sulfide oxidization. In this paper, the electro-oxidation processes of sulfide at Ti/RuO_2 anode in alkaline solution are investigated.

2. MATERIALS AND METHOD

2.1Material

The plate Ti/RuO_2 anode is prepared by thermal decomposition technique. The pre-treatment of titanium substrate and the preparing process of anode are described as reference [18]. The final RuO_2 loading is 2 ± 0.2 $mg\cdot cm^{-2}$.

The sulfide solution is prepared with sodium sulfide nonahydrate ($Na_2S\cdot 9H_2O$). All the reagents are analytical grade and from Sinopharm Chemical Reagent Co., Ltd. All solutions are prepared with deionized water (<10 $\mu s\cdot cm^{-1}$) and deaerated with ultrapure nitrogen (99.9995%, 10 min) to remove dissolved oxygen. The sulfide solution must be used within one hour after preparation to minimize losses due to air oxidation.

2.2 Cyclic voltammetry and experiment system

Cyclic voltammetry (CV) is measured by electrochemical workstation (CHI600D, Shanghai Chen Hua Co., Ltd.) with a three-electrode cell [12]. The anode is Ti/RuO_2 electrode with surface area $1cm^2$ and should be cleaned by carbon disulfide, ethanol and distilled water successively before being used. The anode is activated in 0.1 M NaOH by cyclic voltammetry and then to be test. The cathode is a plate electrode (Pt, 1.0 cm^2), which is cleaned by flame annealing and quenched with pure water. The reference electrode is a saturated calomel electrode (SCE) which is connected with the investigated solutions by a salt bridge.

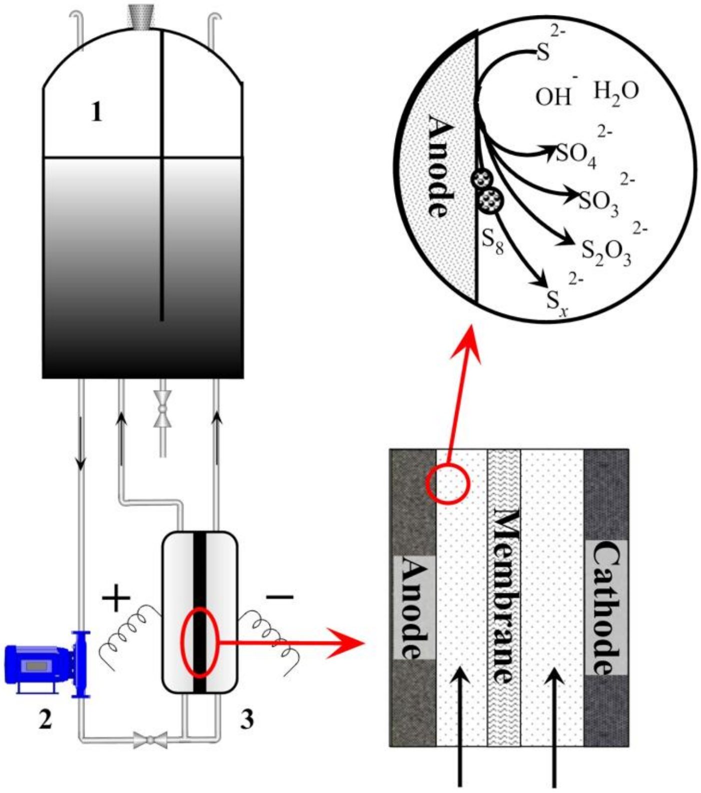

Figure 1. The schematic of the experiment system (1, Feed tank; 2, Pump; 3, Electrochemical reactor)

Figure. 1 shows the schematic of the experiment system of electrochemical oxidation. The two-chambered electrochemical cell with two parallel plate electrodes (∅14cm, 154 cm^2, Ti/RuO$_2$ anode and stainless steel cathode) is separated by a microporous membrane (average pore size1.2 μm). The microporous membrane has been dipped in the solution and the conductivity of the membrane is nearly the same as the solution. The space between the electrode and the membrane was 1mm. The total volume of feed tank is 2 L. The solution in feed tank is introduced into the electrochemical reactor by pump. The sulfide in the solution is oxidized at porous Ti based RuO$_2$ (Ti/RuO$_2$) anode and then return back to the feed tank. The feed flow in the anode chamber is maintained at 80 L·h^{-1}(except the experiment of fig. 7). The DC power is supplied by potentiostat/galvanostat (WYJ50A30V, Hangzhou Apple Instrument Co., Ltd.).

2.3Analytical measurements

The concentrations of sulfide, sulfite and thiosulfate ion are measured according to GB10500-2009 [19]. The concentration of sulfate is measured by precipitation method [20]. The amount of sulfur is detected by plasma emission spectrometer (Vista-AX, USA Varian Inc.).

3. RESULTS AND DISCUSSION

3.1. CV curves under different S^{2-} concentration

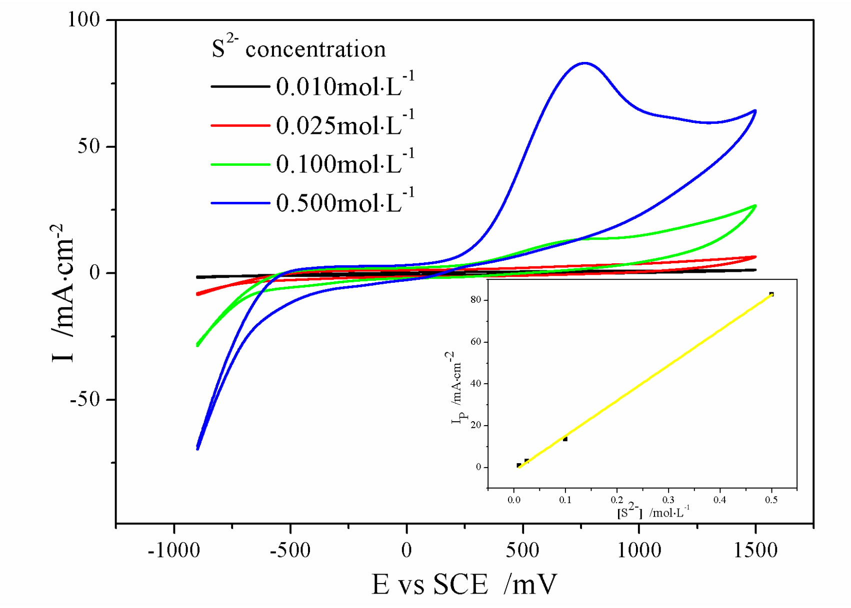

Figure 2. CV curves under different S^{2-} concentration (Ti/RuO_2 anode, 50 mV/s, 20℃)

The CV results (50mV/s, 20℃) of Na_2S solution with different concentration of S^{2-} (0.01M, 0.025M, 0.1M and 0.5M) are shown in Fig. 2. The open circuit potential is about -0.43V in 0.5M sulfide solution. In the range of -1V/SCE to -0.5V/SCE, hydrogen bubbles formed on the surface of Ti/RuO_2 electrode. In the range of -0.5V to 2V, the bubbles are inconspicuous. The oxidation potential of sulfide is lower than that of oxygen. However, all the curves show the same U_p (potential at the peak of the CV curves) as approximately 750mV/SCE, which is different from that of Pt anode [9]. There are only Na^+, HS^-, S^{2-}, OH^- and H^+ in the solution, which indicates that the peak corresponds to HS^-/S^{2-} oxidation.

One weak reduction peak can be observed in the CV curves at approximately -0.2V/SCE. However, the oxidation peak is far from symmetry with the reduction peak, which indicates that the electro-oxidation of sulfide at the Ti/RuO_2 anode is an irreversible process. Moreover, as shown in Fig.2, the current at peak (I_p, U=750mV/SCE) is linearly increased with the increasing of S^{2-} concentration.

3.2. Reactions in the electro-oxidation process

Since sulfur shows different valence as -2, 0, +4 and +6, the oxidation process of sulfide may obtain sulfur, polysulfide or sulfur oxyanions under the experiment conditions. The relevant oxidation reaction equations of S^{2-} removing are shown in Table 1 with its Gibbs free energy $\Delta_r G_m^{\Theta}$ and standard electric potential E^{Θ}.

Table 1. The oxidation reaction equations of S^{2-}

Reaction equation	$\Delta_r G_m^{\Theta}$ / kJ mol^{-1}	E^{Θ} vs SCE/V*	Equation NO.
$S^{2-}=S+2e$	-85.69	+0.20	(1)
$2S^{2-}+6OH^{-}=S_2O_3^{2-}+3H_2O+8e$	-461.60	+0.36	(2)
$S^{2-}+6OH^{-}=SO_3^{2-}+3H_2O+6e$	-339.96	+0.35	(3)
$S^{2-}+8OH^{-}=SO_4^{2-}+4H_2O+8e$	-520.45	+0.43	(4)
$2S+6OH^{-}=S_2O_3^{2-}+3H_2O+4e$	-290.22	+0.51	(5)
$S+6OH^{-}=SO_3^{2-}+3H_2O+4e$	-254.27	+0.42	(6)
$S+8OH^{-}=SO_4^{2-}+4H_2O+8e$	-434.76	+0.51	(7)
$\frac{1}{2}S_2O_3^{2-}+3OH^{-}=SO_3^{2-}+\frac{3}{2}H_2O+2e$	-109.16	+0.33	(8)
$SO_3^{2-}+2OH^{-}=SO_4^{2-}+H_2O+2e$	-180.49	+0.70	(9)

*Saturated calomel electrode (SCE), +0.2444V (25℃).

On the surface of RuO_2/Ti electrode, the radicals with strong oxidant capacity (as ·OH) are generated, which can be used to remove contaminants effectively in the process of hydroxylation [21]. As shown in Fig. 2, the peak value of the oxidation potential is 750mV/SCE, which means all the reactions could happen according to table 1. So it can be speculated that the wide peak is generated due to multi-parallel reactions.

In order to clarify the oxidation process, the further experiments are developed (experiment conditions: Ti/RuO_2 anode, 0.023M Na_2S, 25mA·cm^{-2}, pH 13, 20℃), and the mass balance of the ions (S^{2-}, SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$) are shown in Fig. 3 according to the operation time.

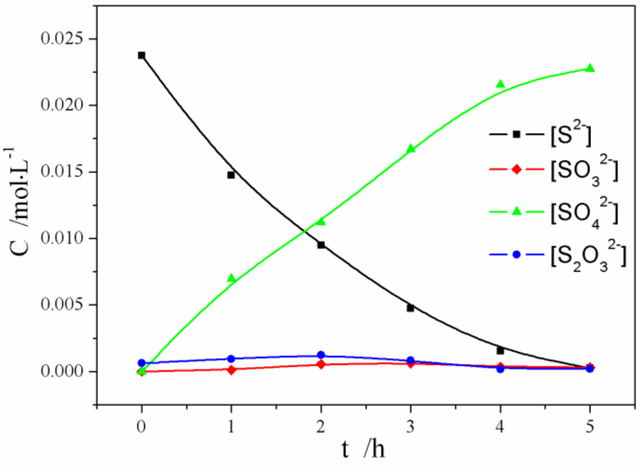

Figure 3. Relationships between the ions and the operation time in the oxidation process (Ti/RuO_2 anode, 0.023M Na_2S, 25mA·cm^{-2}, pH 13, 20℃)

As shown in Fig. 3, although SO_3^{2-} and $S_2O_3^{2-}$ appeared in the solution, but the final oxidation product of S^{2-} is mainly SO_4^{2-}. At the end of the electro-oxidation process, the proportion of SO_4^{2-} in total sulfur is 95.8%, while the proportion of $S_2O_3^{2-}+SO_3^{2-}$ is 3% and the proportion of sulfur is only 1.2%.

3.3. Effect of pH on the electro-oxidation process

It can be seen from the equations in Table 1 that OH^- can promote all the reactions to generate sulfur oxide except Eq. 1. Fig. 4 shows the CV curves with different pH (Ti/RuO_2 anode, 0.5M Na_2S, 50mV/s, 25℃). As shown in Fig. 4, the values of I_p are basically the same, while the U_P are different under different pH values.

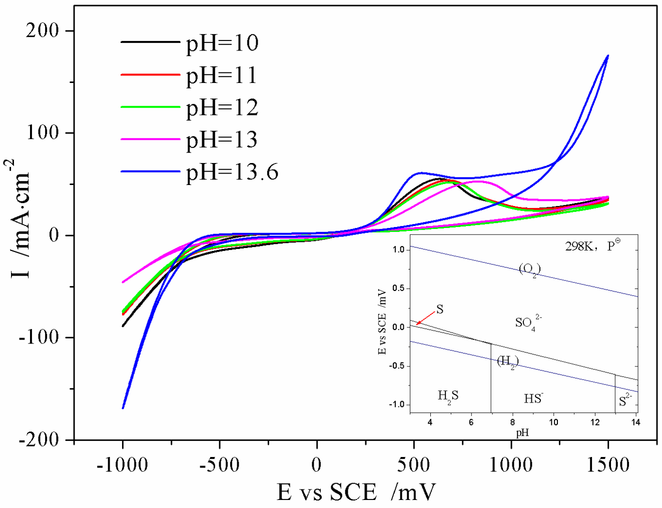

Figure 4. Effect of pH on the electro-oxidation process of sulfide (Ti/RuO_2 anode, 20 mV/s, 0.5M Na_2S, 20℃)

As shown in Fig. 4 (E-pH), HS^- and S^{2-} are generated from the hydrolysis of Na_2S, while the dominant species are upon the value of pH (HS^-, pH 11-13; S^{2-}, pH>13) [21]. Depending on the special characters, the electro-oxidation processes led by HS^- or S^{2-} are different. For example, the thermodynamic values ($\Delta_rG_m^{\Theta}$=-526.64kJ·mol^{-1}, E^{Θ}=+0.44 V/SCE) for HS^- oxidation according to Eq.11 are different from that of Eq.4. In this case, the difference of the electrode potentials at oxidation peaks promoted by pH will be strengthened.

$$HS^-+9OH^-=SO_4^{2-}+5H_2O+8e \qquad (10)$$

Moreover, Lawrence et al. [10] reported that the oxidation potential of sulfide is electrode-dependent and the values (vs. SCE) are +0.36 V, +0.45 V, +0.76 V, +1.30V for Pt, glassy carbon, Au and BDD, respectively. The oxidation product relevant sulfide is mainly S^0 and S_x^{2-} with Pt or glassy carbon anode, while the oxidation product is mainly SO_4^{2-} with BBD anode [11].The oxidation potential of Ti/RuO_2 in sulfide solution is close to Au, but higher than Pt or glassy carbon. It can be seen from Fig. 4 (E-pH) that SO_4^{2-} is the most stable one in alkaline solution [22], which is coincided with the results in Fig. 3.

3.4. Effect of scan rate on the electro-oxidation process

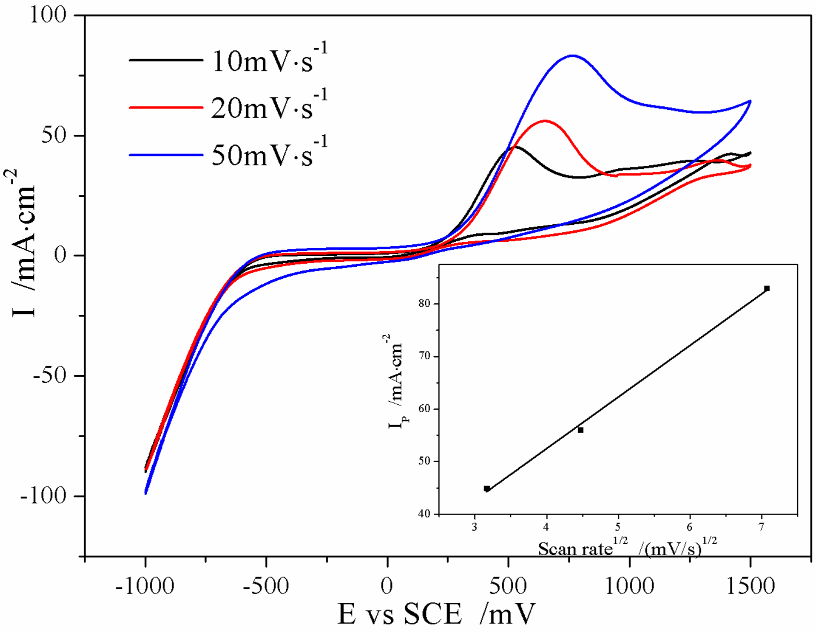

Figure 5. Effect of potential scan rate on the electro-oxidation process of sulfide (Ti/RuO_2 anode, 0.5M Na_2S, 20℃)

As shown in Fig. 5, the potential scan rate shows a significant effect on the values of U_p and I_p. When the scan rate increases from 10mV to 50mV, the width of the oxidation peak, both values of I_p and U_p all increase, which indicates that the oxidation reaction is irreversible. Moreover, the relationship between I_p and the square root of scanning rate coincide with the equation Y=9.81X+13.25, and the Adj.R-Square of the fitting equation is 0.995, which indicates that the relationship between I_p and the square root of scanning rate is linear and the control step during the oxidation process is mass diffusion [23].

3.5. The kinetics of sulfide electro-oxidation process

As discussed before, the electro-oxidation of sulfide at Ti/RuO_2 anode in alkaline solution is a complex and irreversible process. Under the experiment conditions (Ti/RuO_2 anode, 25mA·cm^{-2}, pH 13, 20℃), the relationship between the concentrations of S^{2-} and operation time is investigated and the results are shown in Fig. 6.

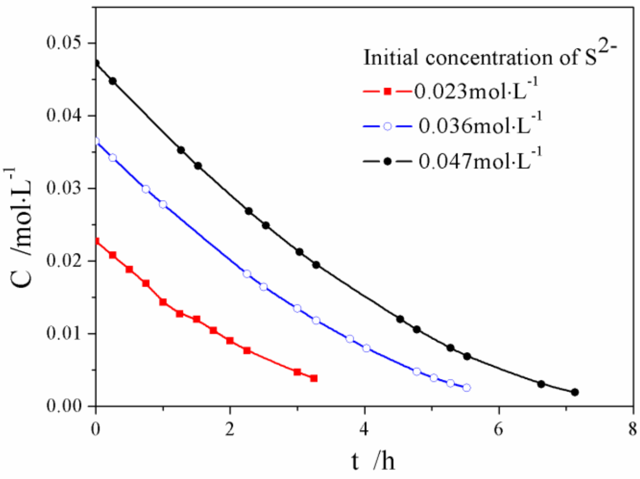

Figure 6. Relationships between the concentration of S^{2-} and operation time under different initial concentration of the sulfide (Ti/RuO_2 anode, 25mA·cm^{-2}, pH 13, 20℃; the symbols are from the experiment results and the lines are from the theoretical results)

As shown in Fig. 6, the slope of the curves is nearly constant under the high concentration of S^{2-}, while the removal rate of sulfide coincide with the first-order kinetics under the lower concentration of S^{2-}.

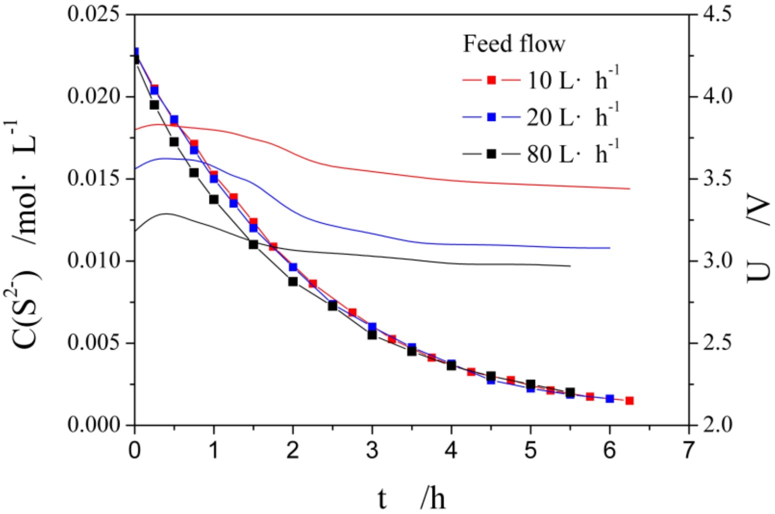

Figure 7. Effect of feed flow on the electro-oxidation process of sulfide (Ti/RuO_2 anode, 0.025M Na_2S, 25mA·cm^{-2}, 20℃, pH12.8)

In this case, the Michaelis-Menten equation [24], which is approved to describe the relationship between the concentration of the substrate and the rate of substrate conversion by an enzyme, is an appropriate model for the electro-oxidation process. The classical Michaelis-Menten equation can be revised as Eq. 11 after integral, and the fitting curves are shown in Fig. 6.

$$t = \frac{1}{V_{\max}}\left(K_m \ln\frac{C_0}{C} + C_0 - C\right) \qquad (11)$$

Where t is the operation time; C is the concentration of S^{2-}; C_0 is the initial concentration of S^{2-}; K_m is the Michaelis constant; V_{max} is the maximum rate of S^{2-} conversion achieved by the system.

It can be seen from Fig. 6 that the experiment results coincide with the theoretical results very well, and the fitting values of V_{max} (0.011 $mol \cdot L^{-1} \cdot h^{-1}$) and K_m (0.010 $mol \cdot L^{-1}$) in different experiments agree with each other. This confirms that Michaelis–Menten kinetics is suitable for describing the electro-oxidation process of S^{2-} removing. Furthermore, the value $V_{max=}$0.011 $mol \cdot L^{-1} \cdot h^{-1}$ indicates that the maximum removal rate of sulfide is 40.57$g \cdot m^{-2} \cdot h^{-1}$ under the experiment conditions.

Under the same experiment conditions (Ti/RuO_2 anode, 0.025M Na_2S, 20℃, pH 12.8), the effect of the feed flow on the electro-oxidation process of sulfide is investigated and the results are shown in Fig. 7. The migration effect in the cell can be strengthened by the feed flow. It can be seen from fig. 7 that the cell voltage decreases with the increasing of feed flow. However, the curves of $C(S^{2-})$ vs. t with different rate of feed flow in fig. 7 are nearly the same, and the experiment results coincide with Eq. (11), which indicates that the feed flow has little effect on the electro-oxidation process of sulfide. In this case, the mechanistic scheme of the electro-oxidation process is simply similar to that proposed by Michaelis and Menten.

3.6. Effect of sulfur on the electro-oxidation process

Sulfide can be oxidized, which will generate sulfur during the process of electro-oxidation. Furthermore, part of the sulfur can be dissolved into the solution and then turn into soluble polysulfides (Eq.12) in alkaline solution [4], and the appearance of the solution will turn yellow.

$$(x\text{-}1)\mathrm{S} + \mathrm{S}^{2-} = \mathrm{S}_x^{\ 2-} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (12)$$

However, other sulfur will still attach on the surface of the anode. Comparing with the new electrode (Fig. 8a), there are porous material deposits on the surface of the used electrode (Fig. 8b), and Fig. 8c confirmed the new material on the surface of Ti/RuO_2 electrode is α-S_8.

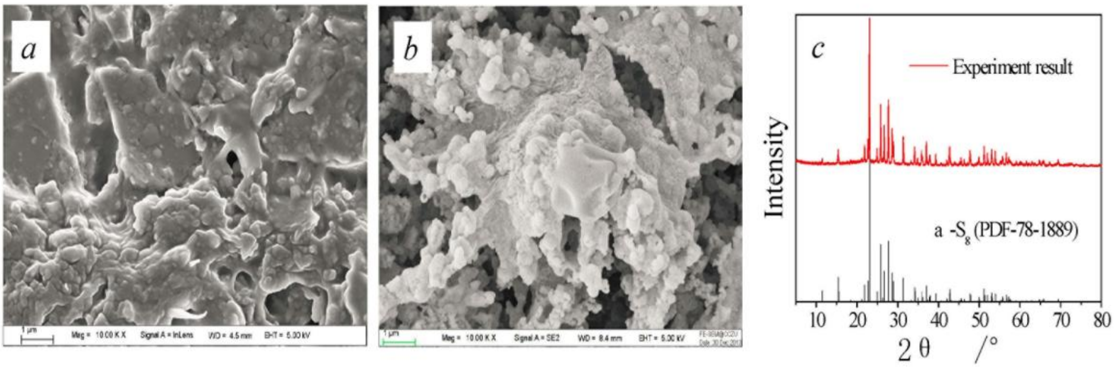

Figure 8. Morphology and XRD pattern of Ti/RuO_2 electrode surface (a, new; b, used; c, XRD pattern)

Sulfur covering the active surface as a contaminant of electrode, which will degrade the performance of the electrode. Under the experiment conditions (Ti/RuO_2 anode, 0.025M Na_2S, 20℃), Fig. 9 shows the U-I curves of the regenerated anode and contaminated anode. Under the same current density, the cell potential of contaminated electrode is higher than that of the regenerated electrode, and the potential difference is more than 0.6V at I=35mA·cm^{-2}.

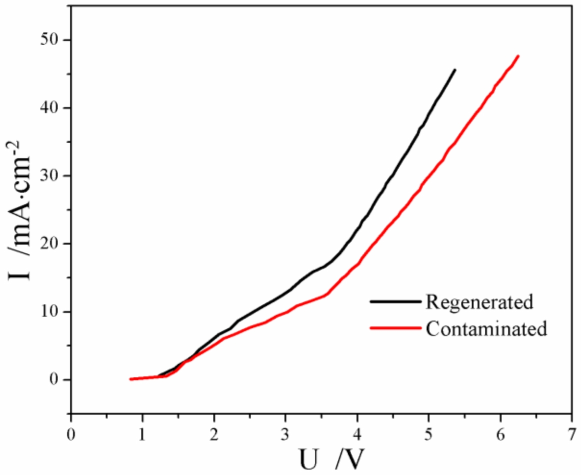

Figure 9. U-I curves of regenerated electrode and contaminated electrode (Ti/RuO_2 anode, 0.025M Na_2S, 20℃)

Moreover, the sulfur cannot be removed from the surface of the Ti/RuO_2 anode in the further electro-oxidation process (0.5M NaOH, 3V, 50mA·cm^{-2}, 25℃, 3h). It can be inferred from the experiment results that the oxides are generated mainly upon aquatic reactions (Eq.2-4 or Eq.8-9) rather than the further oxidation of sulfur (Eq.5-7). Generally, the performance of the electrode will degrade if the sulfur was deposited on the surface of the electrode. The electrode can be refreshed after sponge scrubbing or CS_2 cleaning in the process of applications.

4. CONCLUSIONS

The sulfur deposit on the surface of anode with porous structure, and the XRD results confirm that the sulfur is α-S_8. The electro-oxidation process of sulfide at Ti/RuO_2 anode is irreversible, and the control step in the process is mass diffusion.

Michaelis-Menten equation can be used to describe the electro-oxidation processes (V_{max}=0.011 mol·L^{-1}·h^{-1}, K_m=0.010 mol·L^{-1}·h^{-1}). The final electro-oxidation products are SO_4^{2-} (95.8%), $S_2O_3^{2-}$ +SO_3^{2-}(3%) and sulfur (1.2%) under the experiment conditions (Ti/RuO_2 anode, 0.023M Na_2S, 25mA·cm^{-2}, pH 13, 20℃).

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