Electrochemical reaction mechanism of aqueous polysulfide solution[①]

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[**Abstract**] Cyclic voltammetry and choronopotentiometry studies on aqueous polysulfide solution at graphite anode have been reported . The experiments show that the anode oxidation of the polysulfide , which consists of several parallel electrode reactions and following chemical reactions , is an irreversible process , and that the potential peak in time − potential curves for constant current steps indicates a self-catalysis process in the electrochemical oxidation of the polysulfide solution . It is found from further analysis for the cyclic voltammetry and choronopotentiometry that the number of electrons transferred in rate-determining process of the anode oxidation is close to 1 , and that the reaction rate constant of self-catalysis is large . These results indicate that interreactions of the polysulfide are quick processes . The potential peak in the potential − time curve disappears with the increase of the current .

[**Key words**] polysulfide ; voltammetry ; electrolysis

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1 INTRODUCTION

When alkaline hydrogen sulfide solution , represented by Na_2S , is electrochemically oxidized , polysulfide ions are firstly formed and the polysulfide ions are finally transited into elemental sulfur . This process is a new method used to treat H_2S waste gas and it has some economic advantages over the conventional Claus process in recovery of resources , removal efficiency of H_2S waste gas and energy saving[1~6] . The polysulfide ions have also been applied in pulp and paper industry . It is reported[7] that if the white liquor , i .e . the alkaline Na_2S solution , contains polysulfide ions which can be produced by electrochemical oxidation of the aqueous Na_2S solution , the production of the suspension or pulp would increase .

Unfortunately , little electrochemical investigation about the polysulfide solution has been reported . Lessener et al[8] reported the theory of coupled electrochemical and chemical reactions , response to a little potential step for aqueous polysulfide solutions . The results for the two homogeneous kinetic models obtained were qualitatively similar but differed quantitatively . Detailed reviews for the electrolysis of the sulfide solution can be found from work of Behm et al[7] . In this paper , an investigation of cyclic voltammetry and responses to current steps for aqueous polysulfide solutions will be reported , whose purpose is to obtain a better understanding of the anode oxidation of the polysulfide ions and to supply some fundamental data both for the electrolysis of aqueous H_2S solution and electrochemical production of the polysulfide .

2 EXPERIMENTAL

All chemicals were reagent-grade materials and not purified before experiments . Anode was made from high-density graphite and Pt cathode was from pure Pt whose purity is 99 .9 % . During N_2 gas was continuously bubbled into the solution , solid sulfur was dissolved in the aqueous Na_2S solution , and its concentration was titrated by a standard iodine solution . The polysulfide solution was preserved in a closed vessel . All experiments were carried out in a constant temperature water bath . Potentials of working electrode were monitored by HDV-7B potentiostat with KS-1 signal scanning producer . Both relationships of currents with potentials and potentials with times were recorded on a Yew-Model 3086 $XY_1 Y_2$ function recorder . Before experiments , both anode and cathode were polished carefully using emery papers , following washed by acetone and deionized water , finally dried in air . The glass electrolytic cell consists of two compartments separated by a cation-selective membrane , which can be crossed freely by cations but hinders both the polysulfide ions S_x^{2-} and sulfur produced at anode to migrate into cathode compartment where they are to be reduced . Before experiments were carried out , nitrogen gas was bubbled

through the anolyte so that dissolved oxygen gas was removed. All experiments were finished in static solution. The potentials reported in this paper were on the SCE scale. Catholyte was always 1 mol/L NaOH solution.

3 RESULTS AND DISCUSSION

3.1 Voltammograms of polysulfide solution

A wider anodic potential peak will be obtained when an anode potential scanning is applied with the polysulfide solution, which is similar to the aqueous Na_2S solution[4]. This is because of the complexity of the polysulfide solution containing more electro-active species[8]. Therefore, the anodic oxidation process may consist of several continuous reactions, and the electrode potentials about interreactions of the poly-sulfide ions have little difference, which leads to a wider anodic peak. The phenomenon that Fig.1 shows an obvious shoulder peak A_0 at lower potential for the polysulfide solution is similar to that of the following potential scan of the sulfide solution[9], which indicates that, during the cyclic potential scan for the first time, anodic oxidation of the Na_2S solution or the following chemical reaction produces the polysulfide ions which will be oxidized at anode in the following potential positive-scan.
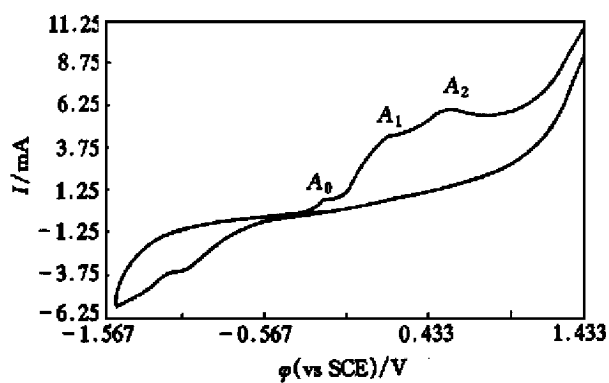

Fig.1 Cyclic voltammogram of aqueous polysulfide solution

Molar ratio S^{2-} : S = 1 : 1, total sulfur 0.3 mol/L,

V = 200 mV/s, 10 ℃, anode area 0.078 cm²

Fig.1 shows that anodic peaks and cathodic peaks are separated with larger potentials and that cathodic peaks are not obvious. Therefore, the anode process transferring electrons does not keep balance. Further research for the system shown in Fig.1 indicates that the shoulder peak (A_1) at lower potential becomes more obvious with the decrease of the scan rate and the peak will weaken or even disappears with the increase of the scan rate. Dependences of the potentials of peaks A_1 and A_2 on the scan rates, respectively, are shown in Fig.2, and their slopes are approximately the same,
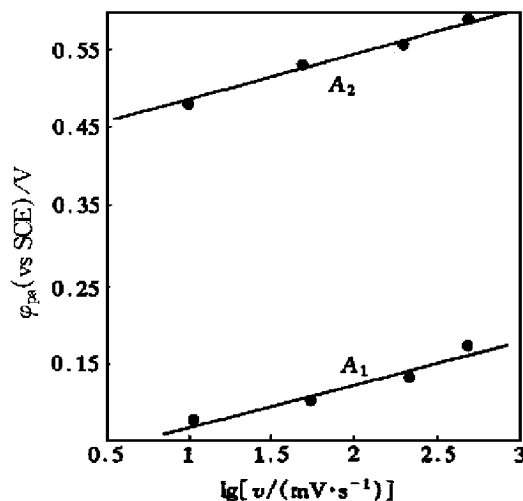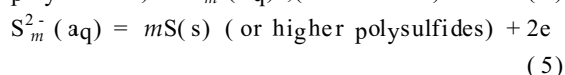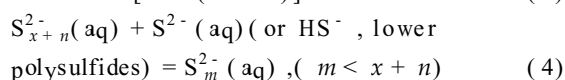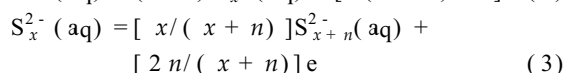

Fig.2 Relationship between φ_{pa} and lg V

Other conditions are the same as Fig.1

A_1 : d(φ_{pa})/d(lg V) = 52,

A_2 : d(φ_{pa})/d(lg V) = 59.

If charge transfer coefficient a_a is 0.5, the transferred electrons of the rate-determining process in the anode reactions will come close to 1 according to d(φ_{pa})/d(lg V) = 30(na_a) in the irreversible system. Possible anode reactions or chemical reactions for the polysulfide ions are

$$HS^-(aq) = (1/x)S_x^{2-}(aq) + H^+(aq) + [2(x-1)/x]e \qquad (1)$$

$$S^{2-}(aq) = (1/x)S_x^{2-}(aq) + [2(x-1)/x]e \qquad (2)$$

$$S_x^{2-}(aq) = [x/(x+n)]S_{x+n}^{2-}(aq) + [2n/(x+n)]e \qquad (3)$$

$$S_{x+n}^{2-}(aq) + S^{2-}(aq)(\text{or } HS^-, \text{lower polysulfides}) = S_m^{2-}(aq), (m < x+n) \qquad (4)$$

$$S_m^{2-}(aq) = mS(s) \text{ (or higher polysulfides) } + 2e \qquad (5)$$
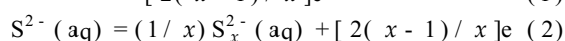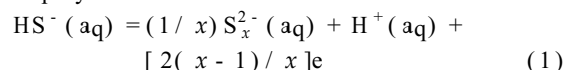
where reactions (1), (2) and (3) are electrode reactions of the initial species in the polysulfide solution. These reactions are similar to those taking place in the sulfide solution[9,10]. Because S_m^{2-}(aq) formed by the reaction (4) may be the same as S_x^{2-}(aq) formed in electrochemical reactions, the system has a self-catalytic characteristic[4]. The dependence of the potential peak A_1 on the scan rate V shows that the mechanism of the reaction corresponding to the anode peak A_1 may belong to EC reaction. When the anode potential increases, the current increases too, but concentrations of the electro-active species near the electrode surface decrease. After the top of the anode peak, if the scan rate decreases, the products by anode oxidation have sufficient time to react with the electro-active species transferring from bulk solution to the electrode surface. Therefore, the more the anode reactants are consumed, the more obvious the anode peak A_1 becomes with the decrease of V. The

reduction process for negative-scan is that of the absorbed sulfur or S_m^{2-} (aq) into lower polysulfide ions even sulfides , such as S^{2-} (aq) , HS^- (aq) , or H_2S (aq) .

It can be concluded that the electrochemical reaction process of the polysulfide system is similar to that of the sulfide system , except their initial reaction species .

3 .2　Time⁻potential curves of polysulfide system

Responses to current steps for the polysulfide solution are shown in Fig .3 . When the current step is a smaller value , i .e . 35 .7 mA/cm², the response curve is similar to that of the Na_2S solution[10]. After getting to a maximum value , the anode potential decreases , then it gradually increases . At initial stage of electrolysis main electro-active species are S^{2-} (aq) , HS^- (aq) and polysulfide ions S_x^{2-} (aq) . However, reaction (4) results in increasing concentrations of the electro-active species , i .e . polysulfide ions , in reaction (3) , so that the anode potential decreases . When the lower polysulfide ions are consumed , the potential rises and the higher polysulfide ions formed from these lower ones at larger anode over-potentials continue to be oxidized . Then the potential in time - potential curve increases steadily .
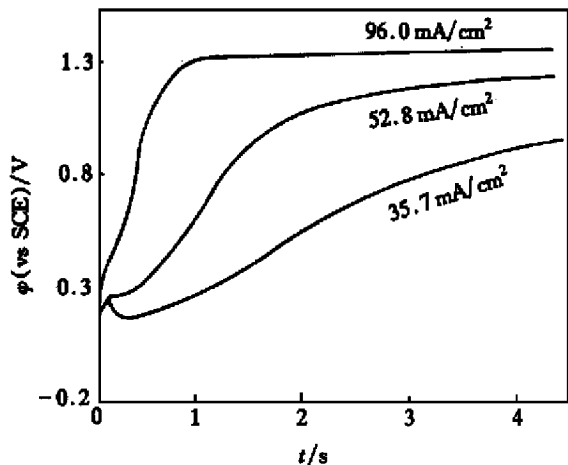

Fig .3　Choronopotentiometric curves for graphite electrode
Conditions : 0 .1 mol/L Na_2S , 0 .2 mol/L NaOH at 10 ℃

3 .3　Self-catalytic process

Fig .3 shows a short platform when the current density is 52 .8 mA/cm². From the above-mentioned cyclic voltammogram , electrochemical oxidation of the sulfide or polysulfide system is an irreversible electron-transferring process . Therefore , the dependence of the anode over-potential η_a on time t can be expressed by following Eqn .(6)[11] :

$$\eta_a = \frac{RT}{\alpha_a nF} \ln \frac{J_a}{J_0} - \frac{RT}{\alpha_a nF} \ln(1 - \sqrt{\frac{t}{\tau}}) \qquad (6)$$

where　J_a is a current step and τ is transient time .

Because it is not easy to determine the equilibrium potential of the system , Eqn .(6) is changed into Eqn .(7) :

$$\varphi_a = (Z + \frac{RT}{\alpha_a nF} \ln \frac{J_a}{J_0}) - \frac{RT}{\alpha_a nF} \ln(1 - \sqrt{\frac{t}{\tau}}) \qquad (7)$$

where　φ_a is electrode potential on the SCE scale , Z expresses the equilibrium potential . According to J_a = 52 .8 mA/cm² and the linear relationship of φ_a and $\ln(1 - (t/\tau)^{1/2})$ shown in Fig .4 , one gets $\alpha_a n$ = 0 .60 , which agrees with the result from cyclic voltammograms .
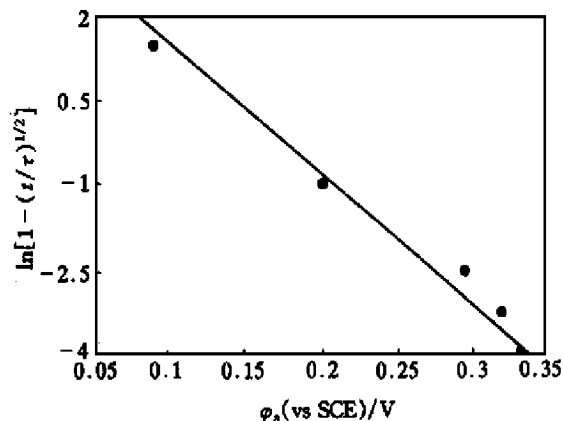

Fig .4　Relationship between φ_a and $\ln(1 - (t/\tau)^{1/2})$
Conditions are the same as Fig .3

If the steady potential of the system was its equilibrium potential , the exchange current density J_0 was calculated to be $5 .28 \times 10^{-4.2}$ A/cm² from Eqn .(7) .
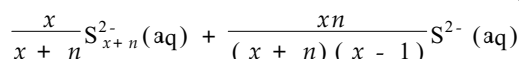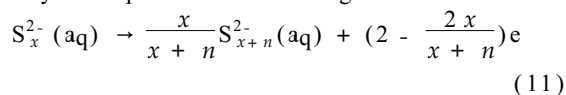
Whether the peaks in time against potential curve appear or not is dependent upon the current value . The time at the top of peak corresponds to that the concentration of the catalyst in the self-catalytic process becomes minimum at electrode/electrolyte interface . According to general reactions of the self-catalytic process[11],

$$R \rightarrow bO + ne \qquad (8)$$
$$bO + Z^* (excess) \rightarrow (1 + f) R + Y^* (excess) \qquad (9)$$
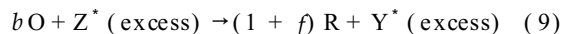
where　R and O are the catalyst and its oxidized product respectively , Z^* or Y^* represents a species in the system , one gets the time t when concentration of the catalyst R becomes minimum at the top of the peak[11] :

$$t = \frac{1}{k_s} \ln(1 + \frac{1}{f}) \qquad (10)$$

The self-catalytic process for the polysulfide system may be expressed as following reactions[10] :

$$S_x^{2-} (aq) \rightarrow \frac{x}{x+n} S_{x+n}^{2-}(aq) + (2 - \frac{2x}{x+n})e \qquad (11)$$

$$\frac{x}{x+n} S_{x+n}^{2-}(aq) + \frac{xn}{(x+n)(x-1)} S^{2-} (aq)$$

$$\rightarrow (1 + \frac{n}{x^2 + xn - x - n}) S_x^{2-} (aq) \qquad (12)$$
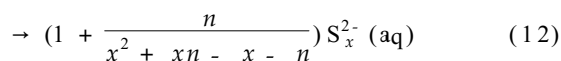
According to the time corresponding to the peak in Fig .3 , the rate constant k_s of the electrode reaction can be figured out from Eqn .(10) :

$$k_s = 20.03 \lg(1 + 1/f)$$

where $f = n/(x^2 + xn - x - n)$. The possible rate constants k_s under different x and n values are listed in Table 1 .

Table 1　Possible rate constants k_s in self-catalytic process for polysulfide solution

x	2	2	2	3	3	4
n	1	2	3	1	2	1
k_s/s^{-1}	12.059	9.557	8.532	19.113	15.586	24.118

The calculated rate constants show that reaction (9) or (12) is faster . Occurring of the peaks in choronopotentiometric curves may be related to both the self-catalytic process and the dissolution of elemental sulfur in the solution . The two fast processes result in increasing the concentration of S_x^{2-} (aq) , thereafter leading to the decrease of anodic potential one time in choronopotentiometric curves .

4　CONCLUSIONS

1) The polysulfide solution consists of more electro-active species and its anode oxidation includes several parallel electrode reactions , which leads to a wider anode peak in its voltammogram .

2) The anode oxidation of the polysulfide ions is an irreversible electron-transferring process and the transferred electron in rate-determining process is close to 1 .

3) At a lower current density , a potential peak is present in time － potential curve because of the self-catalytic process of the system including interreactions of polysulfide ions and dissolution of elemental sulfur in the solution . When the current density increases , the potential peak disappears , which can be seen from the time － potential curve that the potential sharply increases at the initial stage of electrolysis , then increases slowly .

[REFERENCES]

[1]　Szynkarczuk J , Komorowski P G and Donini J C . Redox reactions of hydrosulphide ions on the Pt electrode II : An impedance spectroscopy study and identification of the polysulphide intermediates [J] . Electrochim Acta , 1995 , 40 : 487 - 494 .

[2]　Szynkarczuk J , Komorowski P G and Donini J C . Redox reactions of hydrosulphide ions on the Pt electrode I : The presence of intermediate polysulphide ions and sulphur layers [J] . Electrochim Acta , 1994 , 39 : 2285 - 2289 .

[3]　Anani A A , Mao Z , White R E , et al . Electrochemical production of hydrogen and sulfur by low-temperature decomposition of hydrogen sulfide in an aqueous alkaline solution [J] . J Electrochem Soc , 1990 , 137 : 2703 - 2709 .

[4]　Mao Z , Anani A A , White R E , et al . A modified electrochemical process for the decomposition of hydrogen sulfide in an aqueous alkaline solution [J] . J Electrochem Soc , 1991 , 138 : 1299 - 1303 .

[5]　YI Qing-feng , CHEN Qi-yuan and ZHANG Ping-min . Anodic depassivation study of sulfide electrolysis in presence of surfactant [J] . J Xiangtan Mining Institute , (in Chinese) , 1996 , 11(3) : 53 - 58 .

[6]　LIU Chang-qing , WEI Qing , ZHANG Ping-min , et al . Effective factors of oxido-absorption of hydrogen sulfide and recovery of hydrogen and sulfur [J] . The Chinese Journal of Nonferrous Metals , (in Chinese) , 1998 , 8 (4) : 687 - 690 .

[7]　Behm M and Simonsson D . Electrochemical production of polysulfides and sodium hydroxide from white liquor (Part I) : Experiments with rotating disc and ring-disc electrodes [J] . J Appl Electrochem , 1997 , 27 : 507 - 517 .

[8]　Lessner P , Winnick J , Mclaarnon F R , et al . Kinetics of aqueous polysulfide solutions II : Electrochemical measurement of the rates of coupled electrochemical and chemical reactions by the potential step method [J] . J Electrochem Soc : Electrochem Sci and Technology , 1986 , 133(12) : 2517 - 2522 .

[9]　YI Qing-feng . Fundamental studies on direct electrolysis for the decomposition of hydrogen sulfide in an aqueous solution to produce sulfur and hydrogen gas , (in Chinese) [D] . Changsha : Central South University of Technology , 1997 .

[10]　YI Qing-feng . Investigation of anodic oxidation mechanism of aqueous Na_2S solution at graphite electrode [J] . Acta Physico-Chimica Sinica , (in Chinese) , 2000 , 16 (3) : 263 - 268 .

[11]　TIAN Zha-wu . Research Methods of Electrochemistry , (in Chinese) [M] . Beijing : Science Press , 1984 . 151 - 160 .

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