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Electrochemical production of polysulfides and sodium hydroxide from white liquor Part I: Experiments with rotating disc and ring-disc electrodes

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Electrochemical oxidation of white liquor in a membrane cell is a process of great potential for the pulp and paper industry. The process produces polysulfide-containing white liquor in the anode chamber, and pure sodium hydroxide solution in the cathode chamber. The anode reaction has been investigated using cyclic voltammetry at temperatures between 25 and 90 °C on rotating disc and ring-disc electrodes. It was further investigated using chronoamperometry on rotating disc electrodes at 90 °C. The experiments, which were mainly run in dilute alkaline sulfide solutions, using platinum electrodes, show that the electrochemical production of polysulfide ions, at lower anode potentials (−0.1 to +0.1 V vs SCE), proceeds via formation of elemental sulfur on the electrode surface. The sulfur is dissolved by hydrosulfide and polysulfide ions producing (longer-chain) polysulfide ions. The rate of dissolution, and thus the overall reaction rate, increases strongly with temperature. Polysulfide ions have an autocatalytic effect on the anode reaction due to their ability to dissolve adsorbed sulfur. At higher anode potentials (≥ 0.2 V vs SCE), a change of reaction mechanism is observed. In this region the reaction rate depends on electrode potential and is not catalysed by polysulfide ions.

1. Introduction

In the pulp and paper industry's Kraft pulping process, so called white liquor is charged together with wood chips, into the digester, at high pressure and temperatures up to 170 °C. The composition of a typical white liquor is 3 M NaOH, 0.7 M Na_2S and 0.25 M Na_2CO_3. Within the digester, lignin from the wood is removed by action of the hydroxide (OH^-) and hydrosulfide (HS^-) ions producing a suspension of cellulose fibres. This suspension is the pulp. White liquor that contains polysulfide ions is known to increase the process' yield [1]. Pure sodium hydroxide solution is used in a number of situations in the pulping mill. Electrochemical oxidation of white liquor in a membrane cell, producing polysulfide-containing white liquor in the anode compartment, and pure sodium hydroxide solution in the cathode compartment, is therefore an interesting process.

The electrode and consequent cell reactions are:

anode :

$$(n+1)HS^- + (n+1)OH^- \longrightarrow S_nS^{2-} + (n+1)H_2O + 2ne^- \qquad (1)$$

cathode :

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2 \qquad (2)$$

cell reaction

$$(n+1)HS^- + (n-1)H_2O \longrightarrow S_nS^{2-} + (n-1)OH^- + nH_2 \qquad (3)$$

The process can be integrated into the pulp mill's chemicals recovery cycle. Therefore, in addition to the generation of oxidized white liquor and sodium hydroxide, the process can control the sodium and sulfur balance within the white liquor. This is made possible due to the migration of sodium ions out of the white liquor, by way of the cell's ion-selective membrane. Such separation processes, or 'kidneys', are increasing as important tools within moves toward a closed pulp mill.

An already existing method, for generation of polysulfide ions within white liquor, is the MOXY process. This partially oxidizes the sulfide with air, in the presence of a catalyst, according to the equation:

$$(n+1)HS^- + n/2O_2 \Longleftrightarrow S_nS^{2-} + (n-1)OH^- + H_2O \qquad (4)$$

MOXY and similar methods have been reviewed by Dorris [2]. The advantages of the electrochemical method over MOXY are the separate generation of pure NaOH solution, the possibility of a higher product selectivity by controlling the electrode potential, and the separation of sodium ions from the white liquor. To date the electrochemistry of the S^{-II}/S^0 system has been studied at different pH's and concentrations by a number of authors and for a wide variety of reasons. These include improved understanding of hydrometallurgical reactions [3, 4], the use of aqueous polysulfide solutions in batteries and photoelectrochemical cells [5–8] and cleaning of hydrogen sulfide from natural and process gases [9–19]. Furthermore, adsorbed sulfide/sulfur on noble metal electrodes, significantly enhances the electrocatalytic activity for the anodic oxidation of carbon monoxide, formic acid and methanol; while in other cases it acts as a catalyst poison [20].

A number of experimental techniques have been used to study the reactions. These include traditional electrochemical [3, 4, 9–11, 20–30] and radiotracer methods [26, 31], SERS [32], STM [33], modulated reflectance spectroscopy [34], electron diffraction [27] and ESCA [4]. It is clear that when hydrosulfide ions are oxidized, a layer of elemental sulfur is formed at the electrode surface. Yet the nature of the deposited sulfur, and the mechanisms of sulfur deposition and formation of soluble polysulfide ions, are still not completely understood. Further complicating the issue is that at high electrode potentials, oxyanions of sulfur, such as thiosulfate and sulfate, can also be formed.

When sulfide solutions are anodically oxidized to produce polysulfide ions, passivation of the anode, due to the thickness of the sulfur layer, is reported to be a major problem. Different ways of avoiding this problem have been suggested. These include the use of indirect electrolysis [16, 17], continual removal of the sulfur with an organic solvent [18], and using a rotating wiper-blade electrode [19]. In general, the degree of passivation of the anode should depend upon the choice of electrode material and upon the solubility of sulfur in the solution. In aqueous sulfide solutions it has been shown that the solubility of elemental sulfur increases with pH, temperature and sulfide concentration [35]. High current densities and efficiencies have also been reported when using carbon electrodes at high concentrations of OH^- and HS^-, and temperatures around 80 °C [12, 14]. Nygren *et al.* [15] reported high current densities even at room temperature, but with an activated glassy carbon electrode.

In this paper the anodic oxidation of hydrosulfide ions to polysulfide ions, in alkaline solution, is investigated at temperatures between 25 and 90 °C, on platinum rotating disc and ring-disc electrodes. Additional experiments were also run using a rotating disc electrode of mixed iridium–tantalum oxide coated titanium. The aim of the paper is to establish better knowledge of the anode reaction as part of the overall aim of moving towards a future full-scale industrial process. Dilute solutions were mainly used in the experiments, but it is believed that the general drawn conclusions will be of relevance to the real process of more concentrated liquor. A following paper is to be presented [39], that investigates the process using synthetic white liquors, at 90 °C, in a laboratory scale flow cell.

2. Experimental details

The experiments were run using either a Pine Instrument Company AFRDE5E bipotentiostat or a PAR 273 potentiostat. Data from the bipotentiostat were recorded on BBC Goerz Metrawatt model 790 X–Y recorders, whereas a Macintosh computer with LabView software was used to control and collect data from the PAR 273 potentiostat.

A PARC model 636 rotating ring-disc electrode system was used in an ordinary three-electrode glass cell, thermostated to the desired temperature. The potentials were measured against a saturated calomel electrode (SCE) from Radiometer A/S, Copenhagen, at 25 °C, and a platinum cage served as a counter electrode. The rotating ring-disc electrode ($r_1 = 2.50$ mm, $r_2 = 2.65$ mm, $r_3 = 3.65$ mm) was made by KS Elektronik, Göteborg, Sweden and epoxy resin was used as the sealing material. Experiments with the rotating disc electrode at elevated temperatures used an electrode with an yttria stabilized zirconia shroud to prevent leaks between the disc and the PTFE sealing. This electrode was supplied by Pine Instruments. The disc diameter was 5 mm. The surface roughness of the platinum electrodes was estimated to be 2.2 from analysis of the hydrogen adsorption/desorption peaks of cyclic voltammograms in 0.5 M H_2SO_4 solution. The mixed iridium–tantalum oxide coated titanium rotating disc electrode was made from an 11 mm OD titanium cylinder. A 4 mm diameter circle, on the base of the cylinder, was coated with an active noble metal oxide, while the rest of it was covered with epoxy resin.

The chemicals were analytical grade NaOH, $Na_2S.xH_2O$ and Na_2CO_3 from Merck, and extra pure sulfur from Riedel-de Haën. The water was purified in a combined Milli-RO 15 and Milli-Q water purification system from Millipore. A concentrated sodium sulfide stock solution was prepared by dissolving $Na_2S.xH_2O$ in carefully deoxygenated water. The sulfide concentration was measured using potentiometric titration with $AgNO_3$, and a sulfide-ion selective electrode. The experiments involving polysulfide solution used elemental sulfur dissolved in the stock solution, to give the desired polysulfide excess sulfur concentration. The electrolyte was deaerated with nitrogen during the running of the experiments.

Before each new experiment on platinum, the following procedure was repeated. The electrode was polished with either 3 μm oil based diamond suspension or 1 μm water based alumina suspension, cleaned in acetone, in an ultrasonic bath, and rinsed with water. Before the concentrated hydrosulfide/polysulfide stock solution was added to the 0.1 M sodium hydroxide solution, the electrode was first subjected to 10 s of hydrogen evolution at -1.05 V vs SCE followed by 50 cycles between hydrogen and oxygen evolution at 500 mV s^{-1}. The electrode was then left at open circuit and the stock solution was added to give the desired concentration. After two minutes the sweeps were started again. In the rotating ring-disc electrode experiments, the ring was held at −1.0 V, which is of a sufficient negative potential to detect polysulfide ions formed at the disc while disturbing currents from hydrogen evolution can still be avoided. However, the potential was not negative enough for the reduction of polysulfide to occur under pure diffusion control. This meant that quantitative evaluation of the results using the collection efficiency could not be used. The experiments with mixed iridium–tantalum oxide coated titanium electrode were performed directly in the synthetic white liquor, without any electrochemical pretreatment in pure sodium hydroxide solution.

3. Results

3.1. *Cyclic voltammetry*

Cyclic voltammetry experiments were run on rotating disc and ring-disc electrodes in a 0.1 M NaOH, 0.03 M Na_2S solution at 25, 50, 70 and 90 °C with a 3000 rpm rotation rate. The curves are shown in Figs 1–6. The obtained curves stabilize at a constant shape after around ten sweeps. It can be seen that anodic currents, that are due to the oxidation of hydrosulfide ions, increase strongly with temperature, while the cathodic reduction peaks, that are due to reduction of sulfur on the electrode, vary to a much lesser extent. Hydrogen evolution decreases gradually with increasing number of sweeps and occurs at more positive potentials as the temperature rises.

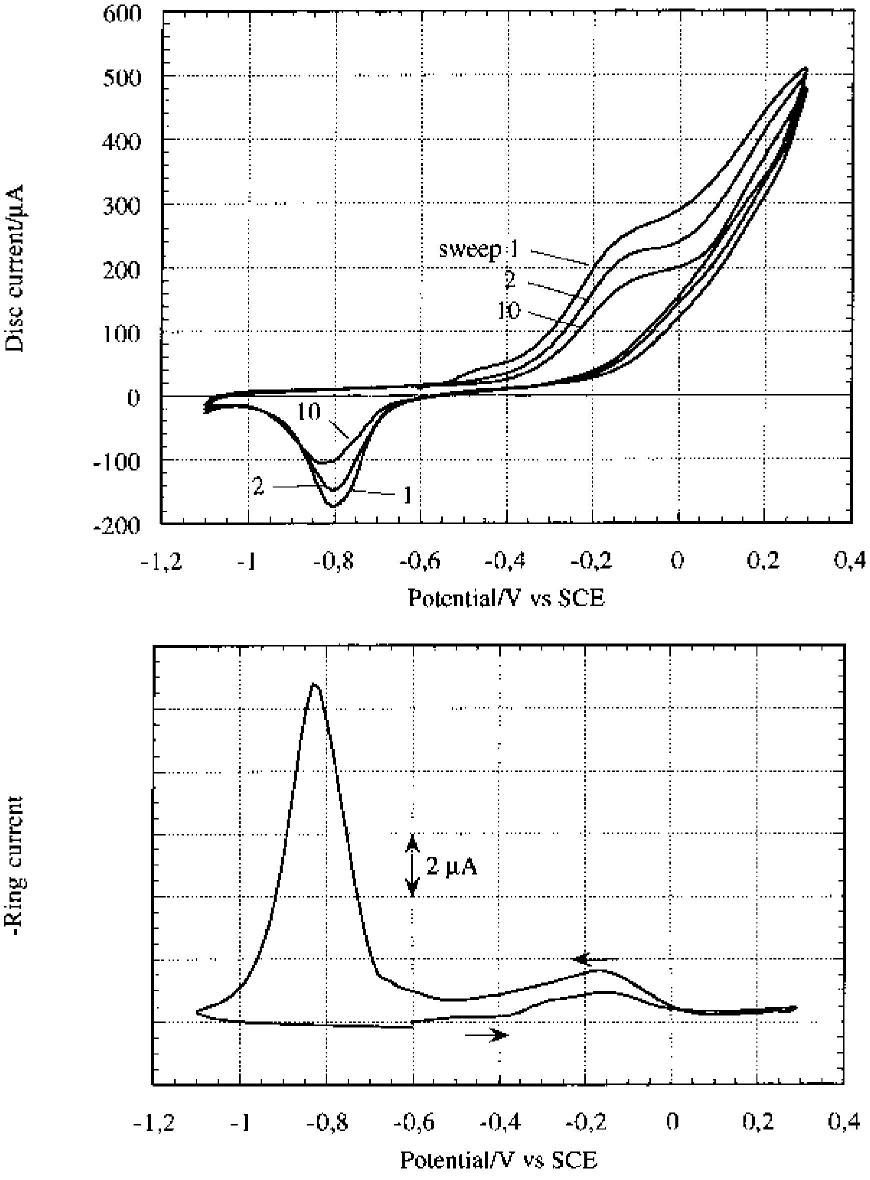

Fig. 1. Cyclic voltammetry for a platinum rotating ring-disc electrode in 0.1 M NaOH and 0.03 M Na_2S at 25 °C. Disc area: 0.196 cm^2. Sweep rate: 100 mV s^{-1}. $E_{ring} = -1.0$ V vs SCE. Rotation rate: 3000 rpm. (a) Disc electrode, sweeps 1, 2 and 10. (b) Ring electrode, sweep 1.

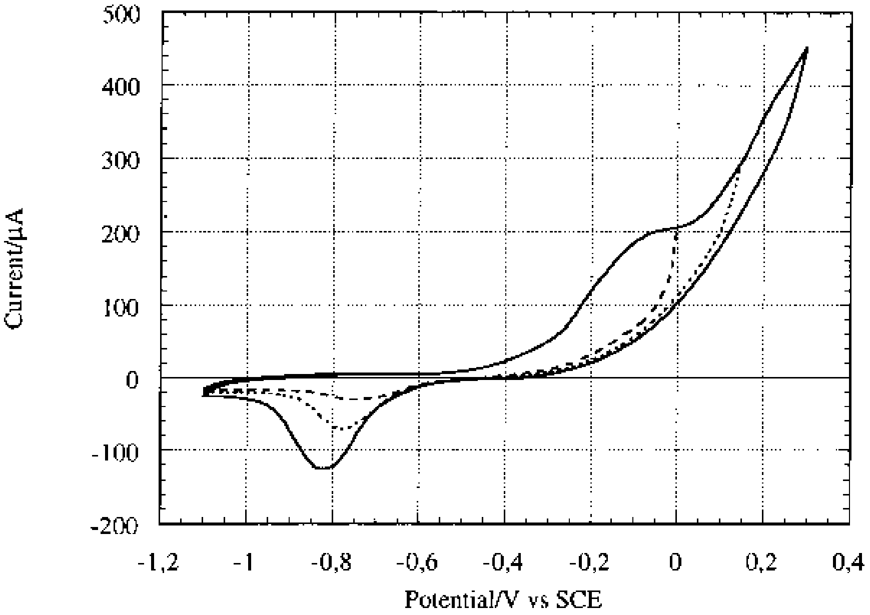

Fig. 2. Cyclic voltammetry for a platinum rotating disc electrode in 0.1 M NaOH and 0.03 M Na_2S at 25 °C. Electrode area: 0.196 cm^2. Sweep rate: 100 mV s^{-1}. Rotation rate: 3000 rpm. Recorded after 10 sweeps between −1.1 and +0.3 V. Anodic sweep limits 0, 0.15 and 0.3 V.

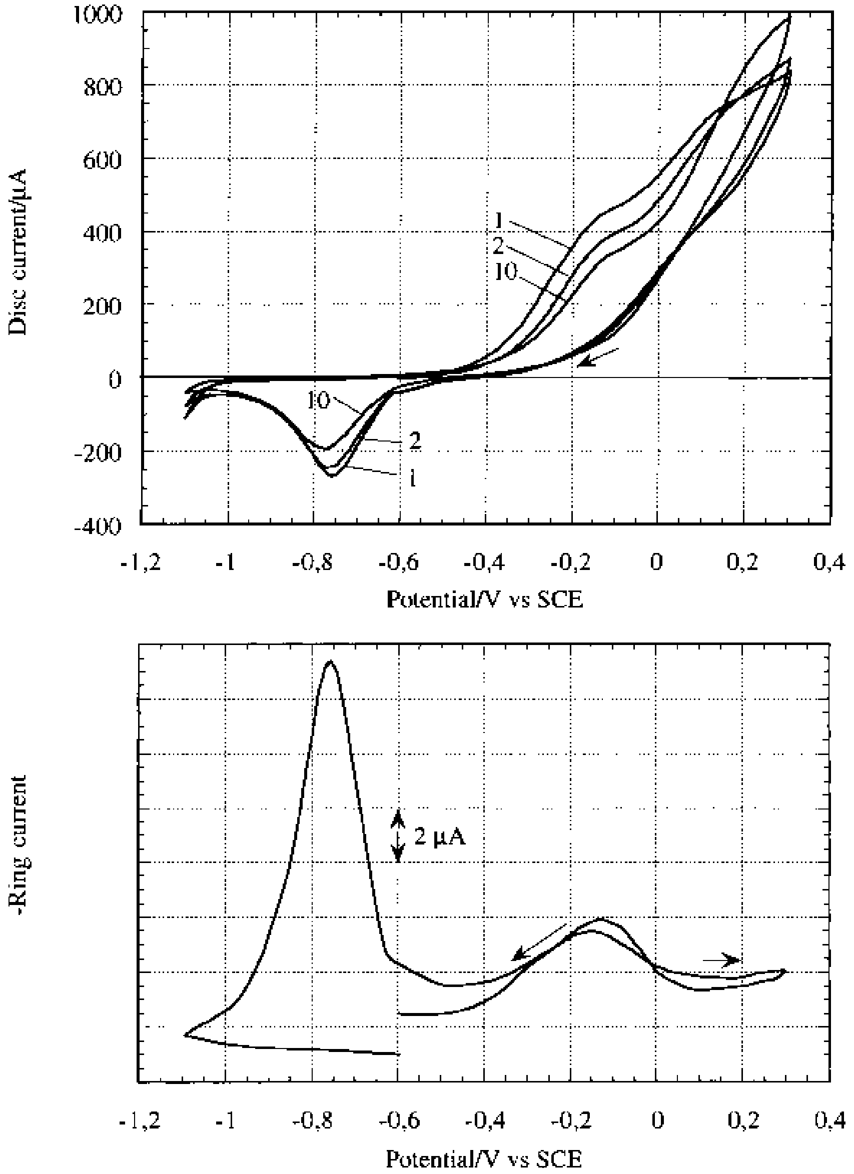

Fig. 3. Cyclic voltammetry for a platinum rotating ring-disc electrode in 0.1 M NaOH and 0.03 M Na_2S at 50 °C. Disc area: 0.196 cm^2. Sweep rate: 100 mV s^{-1}. $E_{ring} = -1.0$ V vs SCE. Rotation rate: 3000 rpm. (a) Disc electrode, sweeps 1, 2 and 10. (b) Ring electrode, sweep 1.

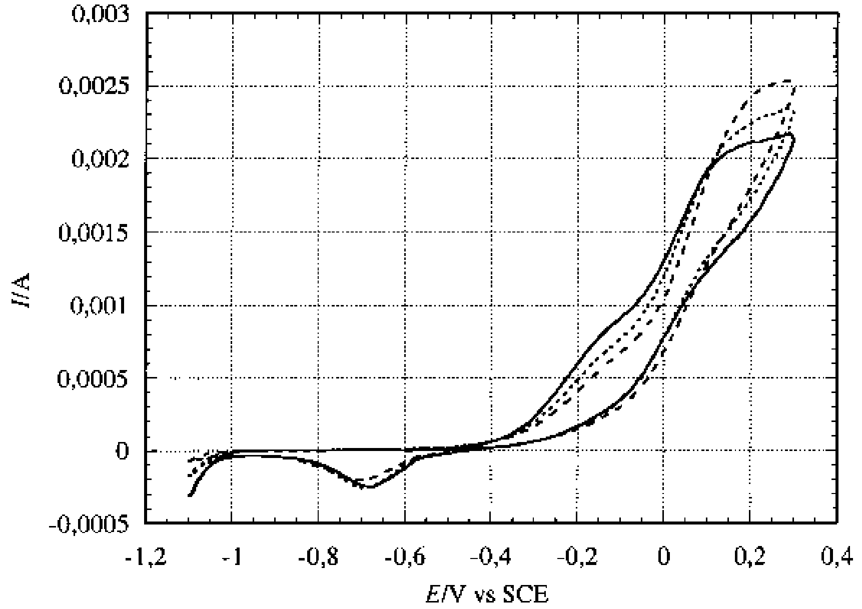

Fig. 4. Cyclic voltammetry for a platinum rotating disc electrode in 0.1 M NaOH and 0.03 M Na_2S at 70 °C. Electrode area: 0.196 cm^2. Sweep rate: 100 mV s^{-1}. Rotation rate: 3000 rpm. Sweep 1 (——), 2 (- - - -) and 10 (– – – –).

There are two anodic waves in the positive-going direction, at 25 and 50 °C. Surprisingly, there is no maximum that would indicate passivation due to deposition of a sulfur layer on the electrode. The anodic waves are less pronounced at 70 and 90 °C, and at 90 °C the current reaches a maximum before the anodic sweep limit is reached. In Fig. 2, that was run at 25 °C, the upper potential limit was lowered in two steps, and resulted in smaller reduction peaks in the negative-going scans. Estimations of the passed anodic and cathodic charges show that the ratios are in the same range for all upper potential limits, that is, 6.1, 6.4 and 7.4 for 0, 0.15 and 0.3 V, respectively. From this it can be concluded that sulfur is deposited on the electrode surface in both the anodic waves.

If it is assumed that no side reactions occur and that the formation of a monolayer of sulfur requires 2.3 C m^{-2} [3], then it can be calculated that for the sweep that was reversed at 0.3 V more than twenty monolayers of sulfur (based on the real surface area) were formed. As pointed out for the case of gold, by Kelsall and Thompson [11], the imbalance between anodic and cathodic charge can be firstly due to anodic charge being spent on forming soluble sulfur oxidation products, such as polysulfide ions and oxyanions, in parallel with sulfur formation. Secondly, the imbalance can be due to the formation of

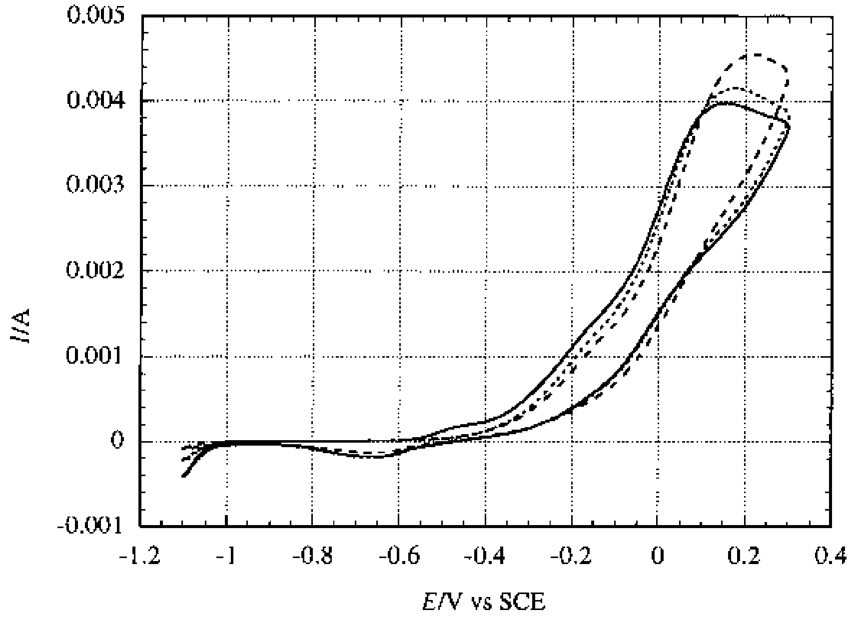

Fig. 5. Cyclic voltammetry for a platinum rotating disc electrode in 0.1 M NaOH and 0.03 M Na_2S at 90 °C. Conditions and legend as for Fig. 4.

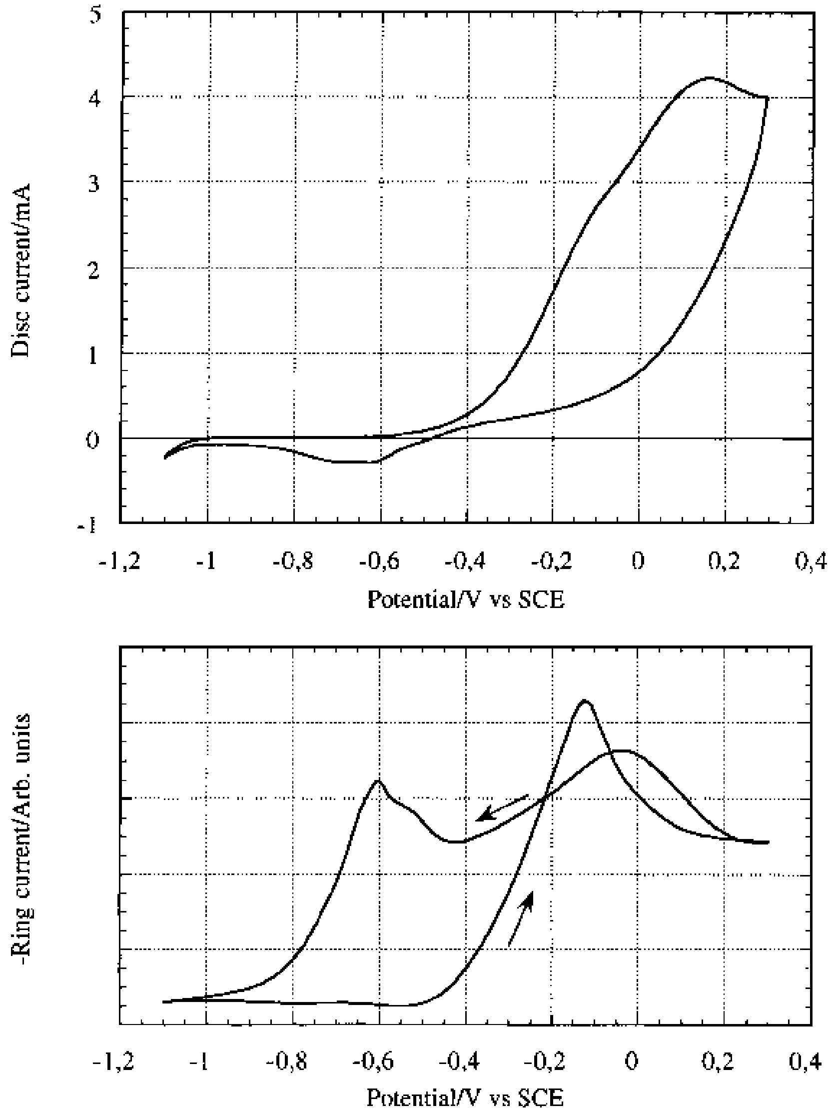

Fig. 6. Cyclic voltammetry for a platinum rotating ring-disc electrode in 0.1 M NaOH and 0.03 M Na_2S at 90 °C. Disc area: 0.196 cm^2. Sweep rate: 100 mV s^{-1}. $E_{ring} = -1.0$ V vs SCE. Rotation rate: 3000 rpm. Recorded after ten sweeps. (a) Disc electrode. (b) Ring electrode.

polysulfide ions rather than hydrosulfide ions in the reduction peak, which requires less cathodic charge. The experiments show that this imbalance increases with temperature.

The ring currents of the ring-disc experiments at 25, 50 and 90 °C (Figs 1, 3 and 6) exhibit peaks between −0.2 and 0 V in both sweep directions and between −0.6 and −0.85 V in the negative-going scan. This means that polysulfide ions are formed both in the anodic and cathodic peaks. The relative amount of the polysulfide ion formation in the anodic process increases with temperature. At 90 °C the polysulfide ions, formed from the cathodic reduction of deposited sulfur, are only a minor part of the total amount of polysulfide ions detected on the ring. It should be noted that the ring current below −0.45 V, in the negative-going scan, is probably due to two types of polysulfide formation. The first is formation, as an inclined baseline, from chemical dissolution, whilst the second occurs simultaneously and comes from cathodic reduction of the sulfur. The higher anodic production rate of polysulfide ions should depend upon a higher solubility of elemental sulfur and faster kinetics of dissolution. Yet, it is interesting to note that from the size of the reduction peaks, there is no indication that the sulfur layer on the electrode is thinner at 90 °C than it is at 25 °C.

The above results have shown that the highest reaction rates are obtained at 90 °C. For this reason 90 °C was chosen as the temperature for future experiments. This temperature is also technically suitable with respect to a possible integration into the Kraft pulping process.

In the voltammograms of Figs 7–9, effects of variation of rotation rate, increased hydrosulfide ion concentration and additon of elemental sulfur to the electrolyte are demonstrated. Figure 7 shows that when the rotation rate is decreased from 3000 to 300 rpm, a beneficial effect on the anodic current is observed. A stationary electrode also gives higher anodic currents, but only up to 0.05 V in the positive-going scan, where the lower transport rate of hydrosulfide ions to the surface probably affects the

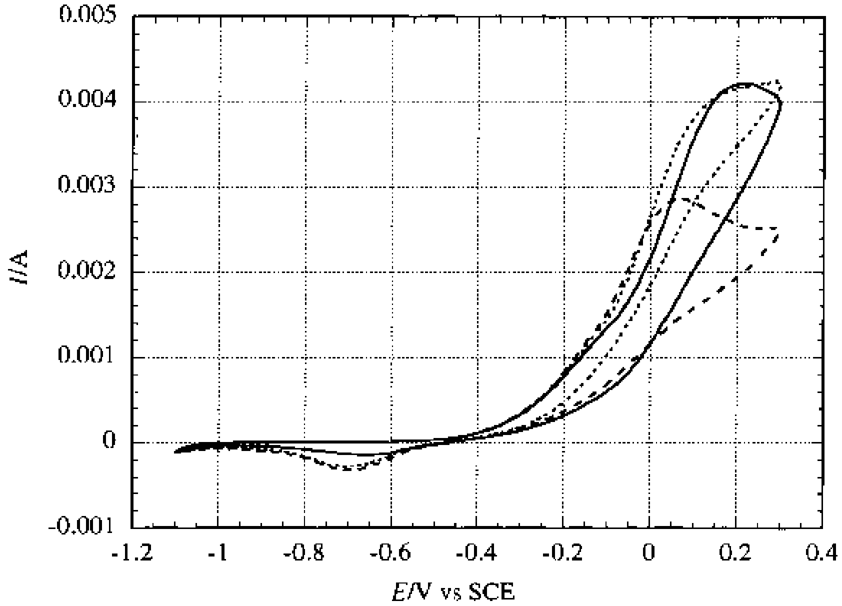

Fig. 7. Cyclic voltammetry for a platinum rotating disc electrode in 0.1 M NaOH and 0.03 M Na_2S at 90 °C. Electrode area: 0.196 cm^2. Sweep rate: 100 mV s^{-1}. Rotation rates: 3000 (——), 300 (- - - -) and 0 (– – – –) rpm. Recorded after 10 sweeps at 3000 rpm.

reaction rate. In the negative-going scan, the size of the reduction peak is likewise increased by a lower rotation rate. The larger reduction peaks at low rotation rates could occur because the sulfur layer is thicker when the potential of the reduction peak is reached. They could also occur because the sulfur is further reduced to hydrosulfide ions, due to the slow diffusion away from the surface of the polysulfide ions that were formed as intermediates. The slower diffusion and consequently higher concentration of polysulfide ions, at the surface, can also explain the different responses of anodic currents to changes in rotation rate. This will be discussed in more detail below.

Figure 8 shows the first, second and tenth sweeps of an experiment where HS^- concentration was twice as high as in earlier experiments, that is, 0.06 M. The rotation rate has remained constant. On comparison with Fig. 5, it is seen that the anodic part has roughly the same shape but the current peaks are twice as high. Conversely, the cathodic peak is considerably smaller.

The voltammograms in Figure 9 were recorded in a 0.1 M NaOH, 0.03 M Na_2S, 0.015 M S^0 solution, i.e. both hydrosulfide and polysulfide ions are present, as in the case of a partially converted solution. Compared to the experiment in polysulfide-free solution, shown in Fig. 5, the anodic currents are higher and

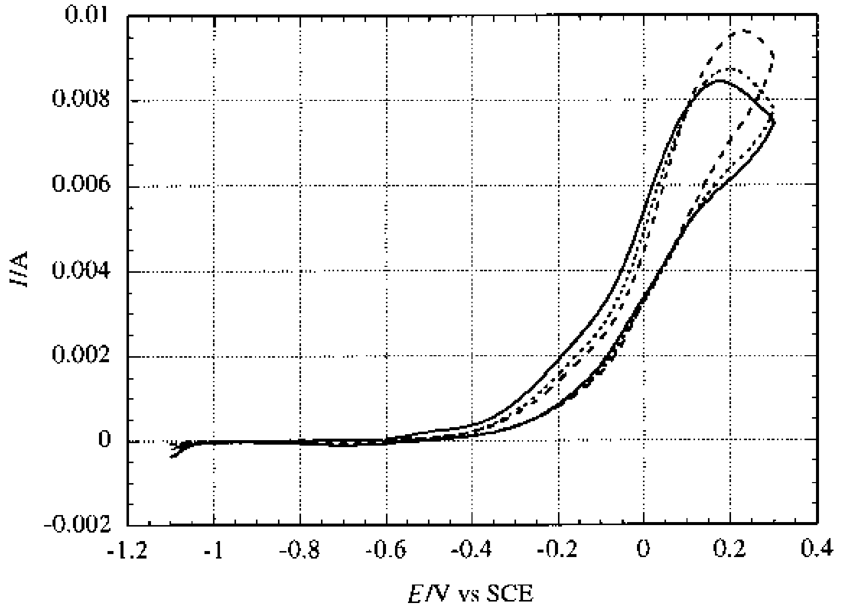

Fig. 8. Cyclic voltammetry for a platinum rotating disc electrode in 0.1 M NaOH and 0.06 M Na_2S at 90 C. Electrode area: 0.196 cm^2. Sweep rate: 100 mV s^{-1}. Rotation rate: 3000 rpm. Sweeps 1 (——), 2 (- - - -) and 10 (– – – –).

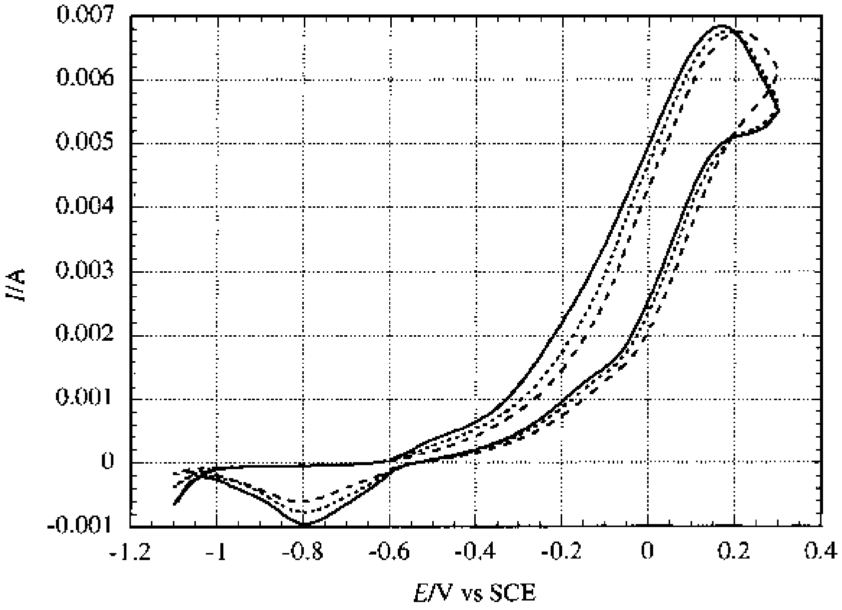

Fig. 9. Cyclic voltammetry for a platinum rotating disc electrode in 0.1 M NaOH, 0.03 M Na_2S and 0.015 M S^0 at 90 °C. Conditions and legend as for Fig. 8.

the cathodic peak remarkably larger. In addition, the maximum in the cathodic peak is shifted from the region of −0.65 to −0.8 V.

3.2. *Chronoamperometry*

In order to follow the development of current, at a fixed potential and on a longer time scale than a cyclic sweep, chronoamperometric experiments were run. This was done after the electrode had first been cycled ten times between −1.1 V and 0.3 V. In the eleventh cycle the potential was swept to a final value where it was held constant for 20 mins. Current–time curves, such as those shown in Figs 10 and 11, were recorded.

Figure 10 shows the current–time curves for five different potentials where the rotation rate was held constant at 3000 rpm. Initially the current falls with time for all potentials, probably because a deactivating sulfur layer is formed. After 5 to 10 mins the current reaches a steady-state value, irrespective of the electrode potentials of −0.1, 0 and 0.1 V. Conversely, current subsequently increases against electrode potential at the higher potentials. Similar experiments were also run in a polysulfide solution (0.1 M NaOH, 0.03 M Na_2S, 0.015 M S^0). These experiments showed that the electrode process was catalysed by the presence of polysulfide ions. In the range of −0.1 to 0.1 V, currents were two to three

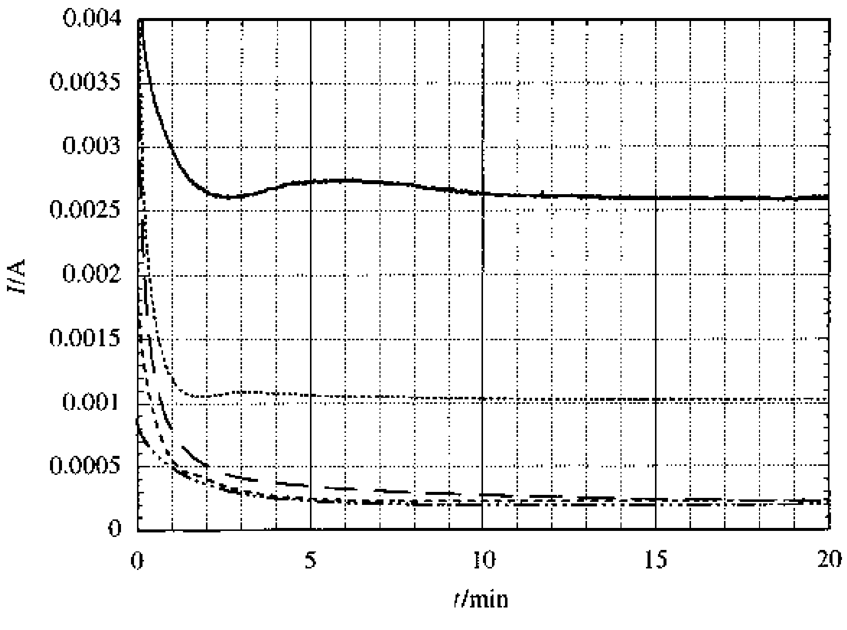

Fig. 10. Chronoamperometry for a platinum rotating disc electrode in 0.1 M NaOH and 0.03 M Na_2S at 90 °C. Electrode area: 0.196 cm^2. Electrode potentials: −0.1 (lower curve), 0, 0.1, 0.2 and 0.3 (upper curve) V vs SCE. Rotation rate: 3000 rpm.

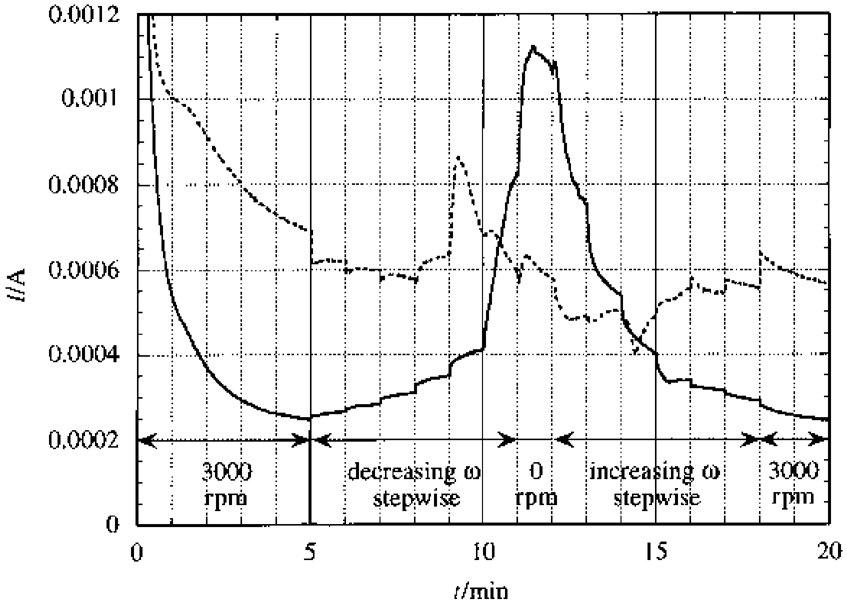

Fig. 11. Chronoamperometry for a platinum rotating disc electrode in 0.1 M NaOH and 0.03 M Na_2S (HS^- solution, solid line) and in 0.1 M NaOH, 0.03 M Na_2S and 0.015 M S^0 (S_nS^{2-} solution, dashed line) at 90 °C. Electrode area: 0.196 cm^2. Electrode potential: 0 V vs SCE. Rotation rate was held constant at 3000 rpm for the first five minutes and then changed stepwise from 3000 to 0 rpm and back in 1 minute intervals, via 1000, 600, 300, 150, 75 and 30 rpm.

times higher than those seen in Fig. 10. Conversely, the currents at 0.2 and 0.3 V were of the same values.

Chronoamperometric experiments, with stepwise variation of rotation rate from 3000 to 0 rpm and then back, were run at all the same five potentials listed in Fig. 10. There was a positive dependence on decreased rotation rate at −0.1, 0 and 0.1 V. The most dramatic response was at 0 V, as shown in Fig. 11. Magnification of the time scale shows that the process is clearly chaotic at the lower rotation rates. As opposed to the results at lower potentials, the current at 0.2 and 0.3 V decreased with decreasing rotation rate. This is probably due to a limitation in the supply of hydrosulfide ions to the electrode surface.

The second curve in Fig. 11 was also recorded at 0 V, but in a polysulfide solution (0.1 M NaOH, 0.03 M Na_2S, 0.015 M S^0). As can be seen from Fig. 11, the responses to the changes in rotation rate are much less pronounced in a polysulfide solution than in a hydrosulfide solution. The currents are also lower than in the corresponding experiment at a 3000 rpm constant rotation rate, except for a peak between nine and ten minutes (75 rpm).

To investigate the effects of hydrosulfide concentration, chronoamperometric experiments were also run in the same manner and in a 0.1 M NaOH, 0.06 M Na_2S electrolyte at 0 V. They were run with and without variation of rotation rate. A constant rotation rate of 3000 rpm gave currents two to three times as high as in the case of when electrolyte was 0.03 M Na_2S. A stepwise decrease of rotation rate gave a clear rise in current. Compared to the 0.03 M Na_2S case in Fig. 11, the relative increase at 0 rpm was smaller, and the sharpest rise occurred at the high rotation rates between 5 and 8 min.

3.3. *Mixed iridium–tantalum oxide coated titanium as anode material*

Noble metal oxide coated titanium is a candidate anode material for an industrial white liquor oxidation process. Cyclic voltammetry was therefore run on a mixed iridium–tantalum oxide coated titanium electrode, using synthetic white liquor at 90 °C, and at three different rotation rates. The results are shown in Fig. 12. The highest current densities are 50 times larger than those in experiments using platinum and dilute solutions. This is at least partly due to the higher HS^- concentration. Consequently, the errors due to iR-drop are more significant and should be kept in mind when analysing the results.

As opposed to the curves in Fig. 7, there are no visible cathodic peaks in Fig. 12. Yet, similarly to Fig. 7, anodic currents show a marked dependence on rotation rate. At the highest potentials, a 3000 rpm rotation rate gives the highest currents. Yet it appears that a low rotation rate is always of benefit in cases when the reaction rate is too slow to be hampered by the slow transport of hydrosulfide ions to the surface. This effect is especially noticeable in the negative-going direction scan. An example of this is at −0.2 V, where the current for the stationary curve is twice as high as that at 300 rpm and four times as high as that at 3000 rpm.

4. Discussion

Results from the experiments using cyclic voltammetry have shown that anodic production of polysulfide ions proceeds with the presence of a layer of elemental sulfur, on the electrode surface. Experiments at 25 °C indicate that it can reach a thickness

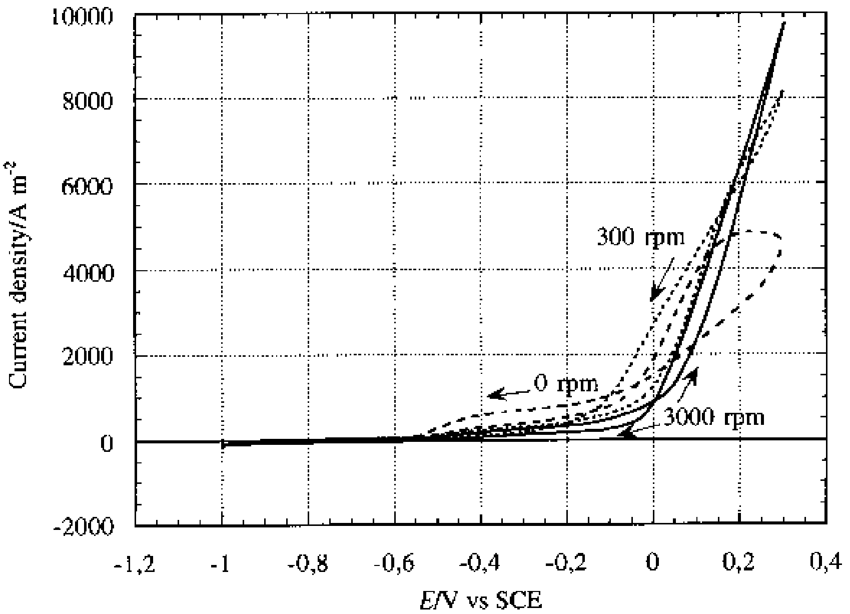

Fig. 12. Cyclic voltammetry for a mixed iridium/tantalum oxide coated titanium rotating disc electrode in 3 M NaOH, 0.7 M Na_2S and 0.25 M Na_2CO_3 at 90 °C. Sweep rate: 100 mV s^{-1}. Rotation rates: 0, 300 and 3000 rpm.

corresponding to up to twenty monolayers before inhibition of electron transfer occurs, and a subsequent reduction in further growth. Little is known about the structure of this layer, but sulfur in bulk conditions is known to have a strong tendency to catenation. This manifests itself in both polysulfide ions and multiatom rings.

Gao *et al.* [32, 33] have studied sulfide oxidation on gold electrodes at room temperature, using *in situ* suface analysis (STM, SERS). In alkaline solution they found indications of the existence of multilayers of S_x species. These included open-chain polymers as well as S_8 and larger rings, all of which exhibit structural disorder. However, these papers convey no information on the growth mechanism of the sulfur layer. An interesting question is whether S^{-II} is anodically oxidized by electron transfer, through the sulfur layer, or if the S^{-II} species itself migrates to the electrode surface, charge transfer taking place there.

A further question is whether sulfur, formed on the electrode surface, is involved as an intermediate in the anodic formation of polysulfide ions through it being continously dissolved by hydrosulfide and/or polysulfide ions. Figure 6(b) shows clearly that polysulfide ions are formed even when the disc current is zero, and at a rate which is close to that occurring at high anodic overpotentials. This fact supports a mechanism which involves formation of elemental sulfur in the first step, followed by the formed sulfur's dissolution by hydrosulfide and/or polysulfide ions. Such a reaction scheme would lead to a limiting current density at high anodic overpotentials, assuming that the sulfur layer grows to a final steady-state thickness.

The chronoamperometric curves in Fig. 10 support the above scheme in the potential region of −0.1 to 0.1 V. In this region currents decrease during the initial transient process, because of the build-up of a sulfur layer, to a steady state value. This current is independent of the electrode potential. In contrast to this behaviour, currents produced at 0.2 and 0.3 V indicate a change in the mechanism, or else an onset of a side reaction. The effect of polysulfide ions in the electrolyte, which increase the reaction rate in the lower potential region but do not affect the currents at 0.2 and 0.3 V, also supports the scheme.

An alkaline polysulfide solution consists of OH^-, HS^- and polysulfide ions of different chain lengths, S_nS^{2-}. A polysulfide ion can be considered to consist of one sulfur atom in oxidation state S^{-II}, denoted as sulfide sulfur, and n atoms in oxidation state S^0, denoted as excess sulfur. The concentrations of these species in the solution can be written as

$$[S^{-II}] = [HS^-] + \Sigma[S_nS^{2-}] \tag{5}$$

$$[S^0] = \Sigma n[S_nS^{2-}] \tag{6}$$

S^{2-} is completely hydrolysed into HS^- and OH^-, even in very alkaline pulping liquors [36].

The mean value of excess sulfur atoms per polysulfide ion, n_{mean}, is reported to vary between 2 and 4.5 in solutions of industrial interest [1]. The concentrations of polysulfide and hydrosulfide ions in a polysulfide solution can be written as

$$[S_nS^{2-}] = [S^0]/n_{\text{mean}} \tag{7}$$

$$[HS^-] = [S^{-II}] - [S^0]/n_{\text{mean}} \tag{8}$$

The results show that between −0.1 and +0.1 V, separate additions of 0.015 M S^0 and 0.03 M Na_2S, to a 0.03 M Na_2S solution, have approximately equal accelerating effects. If n_{mean} is arbitrarily set to 3.5 it follows that 0.0043 M S_nS^{2-} have the same accelerating effect as a seven fold increase in HS^- concentration (0.03 M) in a polysulfide-free solution. These results are rational in view of the fact that polysulfide ions dissolve sulfur considerably faster than hydrosulfide ions do. This is according to Gerischer [37] and Hartler *et al.* [38], who studied the chemical dissolution of elemental sulfur in alkaline sulfide solutions, with and without polysulfide excess sulfur. A.C. impedance measurements by Szynkarzcuk *et al.* [10] on platinum electrodes also indicated faster sulfur layer dissolution in the presence of polysulfide ions. However, the picture is complicated by the fact that in addition to catalysing their own formation, polysulfide ions seem to make the sulfur layer thicker and not thinner, as indicated by the reduction peaks in Figs 7 and 9.

One possible explanation of the behaviour occurring at higher potentials is that side reactions, such as the formation of soluble oxyanions (e.g., sulfate and thiosulfate), occur by oxidation of the sulfur layer in parallel with sulfur dissolution. Experiments on noble metal oxide coated titanium electrodes in synthetic white liquor show a similar behaviour [39]. However, analysis of the electrolysis products showed that the current efficiency for polysulfide ion production was still above 80%. A plausible explanation to the behaviour at high potentials, therefore, seems to be that only an inner layer of sulfur is oxidized to oxyanions. The remaining sulfur is then released into the solution where it reacts to polysulfide ions. The electrode will thus be continuously reactivated, resulting in a higher current, whilst polysulfide ions remain the major product.

Cyclic voltammetry on mixed iridium–tantalum oxide coated titanium, in white liquor, indicate that polysulfide ions catalyse their own formation on this material as well. At 0 and 300 rpm rotation rates there appear to be polysulfide ions left in the diffusion layer, in the negative-going scan, that promote higher currents than in the positive-going direction. Similar behaviour was also observed on graphite electrodes, at this laboratory, which makes it reasonable to assume that the autocatalytic effect of polysulfide ions is obtained with most electrode materials. The absence of a cathodic reduction peak in Fig. 12 is reasonable in view of the above conclusions saying that an increased hydrosulfide concentration promotes the rate of sulfur dissolution. The synthetic white liquor used in the experiment of Fig. 12 had a hydrosulfide concentration that was more than ten times higher than the electrolyte from the experiment shown in Fig. 8.

5. Conclusions

The rate of electrochemical formation of polysulfide ions, on a platinum electrode in alkaline sulfide solutions, increases with temperature and sulfide concentration.

At low anode potentials (−0.1 to +0.1 V vs SCE), the current at steady state conditions is independent of the electrode potential, and is probably determined by the dissolution rate of elemental sulfur formed on the electrode surface. In this potential region the reaction rate is increased by the presence of polysulfide ions, which have an autocatalytic effect. This autocatalysis seems to occur on most electrode materials.

At high anode potentials (above 0.2 V) the reaction mechanism is different. This is evident because the current depends upon the electrode potential, but not on the concentration of polysulfide ions. This change in behaviour is believed to be connected to partial formation of oxyanions.

Sufficiently high current densities are obtained at 90 °C, and at an electrolyte composition corresponding to industrial conditions, to make this electrochemical process industrially interesting.

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