

Electrochemical production of polysulfides and sodium hydroxide from white liquor

Part II: Electrolysis in a laboratory scale flow cell

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Electrochemical production of polysulfide-containing white liquor and pure sodium hydroxide solution was investigated at 90 °C in a laboratory scale flow cell. A mixed iridium–tantalum oxide coated titanium electrode was used as the anode and the two electrolyte compartments were separated by a cation-exchange membrane. The process was demonstrated at current densities up to 5 kA m⁻², resulting in high current efficiencies for both products. The previously reported auto-catalytic effect of polysulfide ions was confirmed, and its technical implications on the use of three-dimensional electrodes were demonstrated and discussed. The current efficiency was found to depend strongly on the degree of conversion of sulfur(–II) to sulfur(0). The anode material showed favourable properties, with respect to activity and selectivity, but suffered from limited durability.

1. Introduction

A process for electrochemical oxidation of white liquor can be integrated into the chemicals recovery cycle of the Kraft pulping mills. The process generates pure sodium hydroxide solution and white liquor containing polysulfide ions. The process concept and background to this work is described in a previous article [1], where the anode process itself was studied using rotating disc and ring-disc electrodes of platinum. In the present work, electrochemical oxidation of white liquor has been studied in a divided flow cell at 90 °C, with a mixed iridium–tantalum oxide coated titanium electrode as the anode. Synthetic white liquor was the anolyte and sodium hydroxide solution was the catholyte.

2. Experimental details

The experimental setup is presented in Fig. 1. The electrolyte solutions were circulated by magnet pumps through polypropylene pipes. The NGW glass electrolyte vessels were covered with PTFE lids equipped with a water cooler. This was to condense vapours and thus prevent excessive evaporation. Heating was done by placing the electrolyte vessels in a thermostated bath.

The galvanostatic experiments were carried out using an Oltronix B32-20R power supply. The amount of charge was measured by a Unisystem U1010B Ah-meter. The potentiostatic experiments were run using a Wenking HP 72 high power potentiostat or a Pine Instruments AFRDE5E bipotentiostat. Data were collected on BBC Goerz Metrawatt X-t and X-Y recorders.

The flow cells were made of plexiglass and the two cell halves were separated by a Nafion[®] 324 cation-exchange membrane. The design of the flow cell is shown in Fig. 2. Three different anode blocks were used, one with a 21 cm² flat electrode, another with a 4.2 cm² flat electrode and the last with a 21 cm² mesh electrode. The flat electrodes were recessed into the cell wall. The anodes were mixed iridium-tantalum oxide coated titanium electrodes, supplied by Permascand AB, Ljungaverk, Sweden. The cathode was made of stainless steel. The mesh electrode was made of four electrode nets welded together to a 3 mm thickness. The width of the anode compartment was 30 mm and the distance from anode to membrane was 6 mm in all three cases. The ratio of electrode area to electrolyte flow rate was so small, that the conversion per single pass was never in excess of 1% of the total concentration of sulfur(–II). The electrode compartments were filled with polypropylene turbulence promoters supplied by ElectroCell AB, Täby, Sweden. The temperature in the anode compartment was monitored using a thermoelement. The anode potential was measured against a 3 M NaOH Hg/HgO reference electrode. The reference electrode was connected to the anode compartment via a capillary. This was introduced through a hole in the electrode so that the tip of the capillary was in the same plane as the electrode surface (or at the front of the electrode in the experiment with the mesh electrode). This arrangement was thought to give a minimal error in the measured potential, due to uncompensated ohmic resistance between the anode and reference capillary.

All chemicals were analytical grade from Merck except for the sulfur which was extra-pure from Riedel-de Haën. The water was purified in a

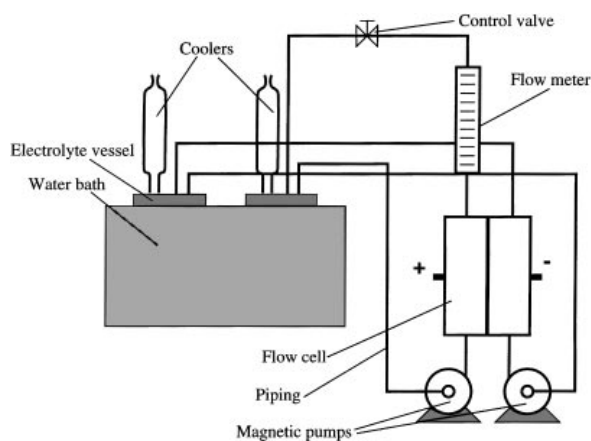


Fig. 1. Schematic experimental setup.

combined Milli-RO 15 and Milli-Q water purification system. Synthetic white liquors were made in the following way. A sodium sulfide stock solution was prepared by dissolving $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ in deoxygenated water. The sulfide concentration was then determined using potentiometric titration and a sulfide-ion selective electrode. This method is described in reference [2]. A known amount of the stock solution and deoxygenated water was then used to dissolve NaOH and Na_2CO_3 in a container. The solution was then cooled to room temperature and diluted to the desired volume in a volumetric flask.

The initial composition of the white liquor, in the electrolysis experiments, was 0.7 M Na_2S , 3M NaOH and 0.25 M Na_2CO_3 . In the experiments involving polarization curves, the sulfide concentration was varied and elemental sulfur was added, simulating partially converted solutions. The initial NaOH concentration in the catholyte was 2 M in all experiments.

Mass transport was characterized by potassium hexacyanoferrate(II/III) solution in the cell with 21 cm^2 electrode area. Both anode and cathode were made of nickel. The electrolyte was $2.5 \times 10^{-3}\text{ M}$ $\text{K}_3\text{Fe}(\text{CN})_6$ and $12.5 \times 10^{-3}\text{ M}$ $\text{K}_4\text{Fe}(\text{CN})_6$ in 1 M KOH, and the experiments were carried out at 23°C . The experimental setup was identical to that shown in Fig. 1 except that both electrolyte streams were pumped from the same electrolyte vessel.

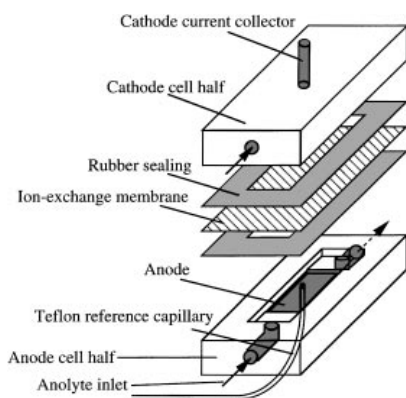


Fig. 2. Schematic view of the electrochemical flow cell.

A spectrophotometric method has been developed to measure the concentrations of sulfur(–II) and sulfur(0) in white liquor. This method was used in the present work and combined with Flow Injection Analysis (FIA), to allow online monitoring of the sulfur species during electrolysis, as described in [5].

3. Results

3.1. Characterisation of mass transport

Slow scan polarization curves were recorded for the reduction of hexacyanoferrate(III) at eight different linear velocities, u , ranging from 0.017 to 0.156 m s^{-1} , in the cell with a 21 cm^2 flat electrode. Well defined current plateaux were obtained from the polarization curves. The limiting current densities, j_L , were used to make a double logarithmic plot of the Sherwood against Reynolds numbers. This plot is shown in Fig. 3 and exhibits two regions of different slopes. These can be explained by the transition from laminar to turbulent flow.

Dimensionless group correlations were calculated for both regions in the form of

$$Sh = a Re^b Sc^{1/3} \quad (1)$$

The Sherwood, Reynolds and Schmidt numbers are respectively defined as

$$Sh = \frac{k_m d_e}{D} \quad (2)$$

$$Re = \frac{u d_e}{\nu} \quad (3)$$

$$Sc = \frac{\nu}{D} \quad (4)$$

k_m is the mass transfer coefficient, defined by the equation

$$j_L = k_m z F C \quad (5)$$

and d_e is the characteristic dimension for the cell, defined as

$$d_e = 2wh/(w + h) \quad (6)$$

ν is the dynamic viscosity, μ/ρ .

d_e was 10^{-2} m for the cell used ($w = 30\text{ mm}$, $h = 6\text{ mm}$). The values of the diffusion coefficient of the hexacyanoferrate(III) ion, $D = 0.764 \times 10^{-9}\text{ m}^2\text{ s}^{-1}$, and the kinematic viscosity, $\nu = 1.019 \times 10^{-6}\text{ m}^2\text{ s}^{-1}$ were taken from [3]. Optimal fits were obtained with $a = 2.37$, $b = 0.41$ for $Re < 600$ and $a = 0.135$, $b = 0.85$ for $Re > 700$.

These results were then used to estimate the Sherwood numbers and limiting current densities in experiments with white liquor, where three different flow rates were used, although all of them giving values of $Re > 700$. Values for the viscosity and density at 90°C were obtained from numerical correlations, and found to be $\rho_{90} = 1145\text{ kg m}^{-3}$ and $\mu = 0.45 \times 10^{-3}\text{ Pa s}$. The diffusion coefficient was calculated using the relationship:

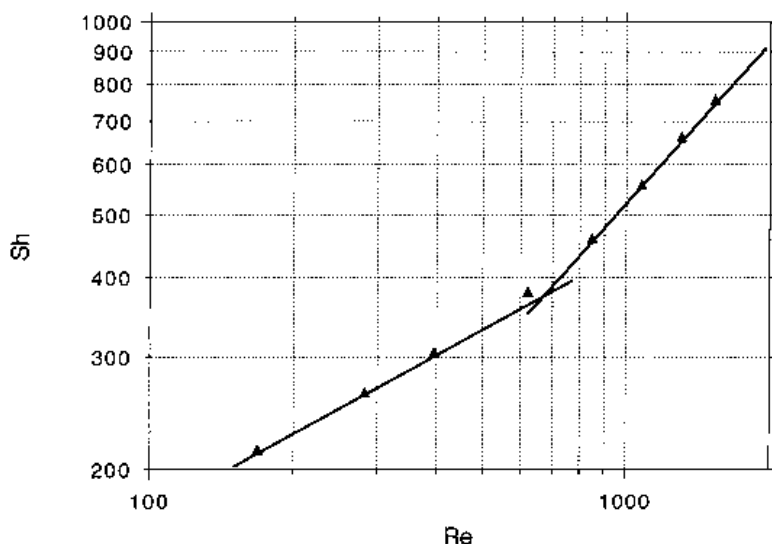
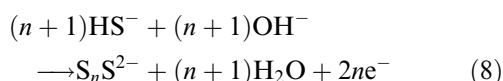


Fig. 3. Double logarithmic plot of the Sherwood number against Reynolds number for the 21 cm² flat electrode flow cell.

$$\frac{D_{T1}\mu_{T1}}{T_1} = \frac{D_{T2}\mu_{T2}}{T_2} \tag{7}$$

and known data at 25 °C. However, no value for the diffusion coefficient of hydrosulfide ion at 25 °C was found within the literature, so this was arbitrarily assigned a value $D_{25} = 0.8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The viscosity at 25 °C, $\mu = 2.0 \times 10^{-3} \text{ Pa s}$, was obtained in the same way as for 90 °C. Using these data the diffusion coefficient was estimated to be $D_{90} = 4.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

It is not wholly straightforward assigning a correct value for z in Equation 5, for the oxidation of hydrosulfide ions. If the anode process is represented as



z should be calculated as $2n/(n + 1)$, and thus depends upon the average chain length of the formed polysulfide ions. The value of z can therefore vary between 1 and 2 as n_{mean} varies from 1 to infinity. n_{mean} is reported to vary from 2 to 4.5 in oxidized white liquors [5], which corresponds to a variation in z from 1.33 to 1.64.

The limiting current densities for three different flow rates were calculated, using the case of unoxidized white liquor ($[\text{HS}^-] = 0.7 \text{ M}$) being oxidized to polysulfide ions. The average chain length was assumed to be 4.5 in the calculations; therefore using $n_{\text{mean}} = 3.5$ which gives $z = 1.56$. The results are summarized in Table 1. The diffusion of different

Table 1. Mass transport calculations for unoxidized white liquor

| $u/\text{m s}^{-1}$ | Re | Sh | $k_n/\text{m s}^{-1}$ | $j_L/\text{A m}^{-2}$ |
|---------------------|------|------|-----------------------|-----------------------|
| 0.159 | 4038 | 705 | 3.05×10^{-4} | 32000 |
| 0.099 | 2516 | 472 | 2.04×10^{-4} | 21400 |
| 0.034 | 868 | 191 | 0.83×10^{-4} | 8700 |

polysulfide ions, in addition to the hydrosulfide ion, need to be considered for oxidized white liquors. Changes in viscosity and density should also be considered.

3.2. Potentiostatic polarization curves

To gain a better understanding of the anode process, potentiostatic polarization curves were recorded, varying electrolyte composition, mass transport conditions and temperature. These experiments were carried out in the cell that had a 4.2 cm² electrode area. The curves were recorded starting with the lowest potential, and at each potential a reading was taken after one minute. The curves in Fig. 4, of initial unoxidized white liquor, were recorded at the same flow rates used in the mass transport calculations above.

The experiments run at the highest flow rate has a curve described by a straight line with a steep slope at very low potentials (Fig. 4). At potentials between -0.4 V and -0.1 V some kind of deactivation is observed and at each potential the current decreases with time. At around -0.1 V a reactivation sets in with markedly increased current densities. Furthermore, at -0.05 V and higher, the currents do not decrease with time, as is the case for the experiment at lower potentials. After this reactivation, the increase in current density with potential is less dramatic above 0 V. Yet there are no signs of current decrease over time, at any fixed potential.

The curves in Fig. 4 display an unusual dependence on flow rate. At 0 V and above, high flow rates give high current density, while the current density at potentials below 0 V shows an opposite dependence. Such an inverse dependence on mass transfer conditions was previously observed [1] using cyclic voltammetry on rotating disc electrodes of both platinum and mixed iridium-tantalum oxide coated titanium. The observation was explained in terms of the polysulfide ions having an autocatalytic effect on the reaction.

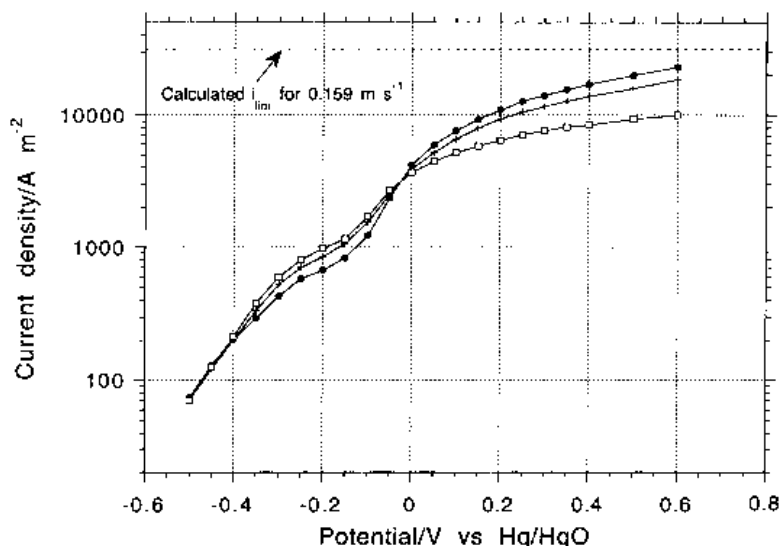


Fig. 4. Polarization curves in unoxidized white liquor at varying flow rates. u : (●) 0.159, (+) 0.099 and (□) 0.034 m s^{-1} . $[\text{S}^{-\text{II}}] = 0.7 \text{ M}$, $[\text{S}^0] = 0 \text{ M}$. Electrode area: 4.2 cm^2 .

The highest current densities for all three flow rates, in Fig. 4, are in the vicinity of the limiting current densities calculated above (Table 1). However, at this high potential of 0.6 V, side reactions may account for a large part of the current and a true limiting current for the main reaction is not observed. Furthermore, mass transport correlations were made for the cell with a 21 cm^2 electrode area, while these curves were recorded with an electrode area of 4.2 cm^2 .

Similar experiments were run using three polysulfide-containing white liquors, simulating 25, 50 and 75% conversion, that is, the total concentration of S^0 and $\text{S}^{-\text{II}}$ was constant at 0.7 M. There was almost no dependence on flow rate up to -0.05 V for the white liquor with 25% conversion, whereas a positive dependence was observed at higher potentials. For the liquors with 50 and 75% conversion, there occurred a positive dependence on flow rate throughout the entire potential range.

Figure 5 shows the polarization curves for all four electrolytes at the highest used flow rate. The polysulfide-containing liquors give significantly higher current densities at low potentials. Reaction rate is apparently reduced by a decreasing concentration of $\text{S}^{-\text{II}}$, at high potentials, although the curve for 25% conversion is somewhat higher than the curve showing unoxidized liquor up to 0.3 V. This latter difference is not very significant and can be explained by slight variations in electrode activity, from day to day. This is because these four curves were recorded on four different occasions, while the curves with varying flow rates were recorded on the same day.

The effect of polysulfide ions in the above experiments have not been isolated from the effect of $\text{S}^{-\text{II}}$ concentration, since they were run using either a varying concentration of $\text{S}^{-\text{II}}$ in the solution, or with a varying supply of $\text{S}^{-\text{II}}$ through mass transport. To remedy this deficiency, experiments were run at a

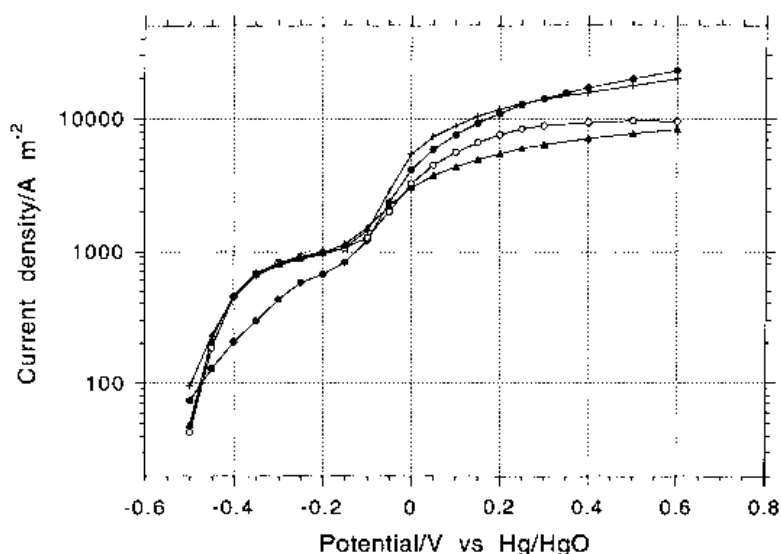


Fig. 5. Polarization curves in white liquors of varying composition. $u = 0.159 \text{ m s}^{-1}$. Electrode area: 4.2 cm^2 . $[\text{S}^{-\text{II}}] = 0.7 \text{ M}$ (●); $[\text{S}^{-\text{II}}] = 0.525 \text{ M}$, $[\text{S}^0] = 0.175 \text{ M}$ (+); $[\text{S}^{-\text{II}}] = 0.35 \text{ M}$, $[\text{S}^0] = 0.35 \text{ M}$ (O); $[\text{S}^{-\text{II}}] = 0.175 \text{ M}$, $[\text{S}^0] = 0.525 \text{ M}$ (▲).

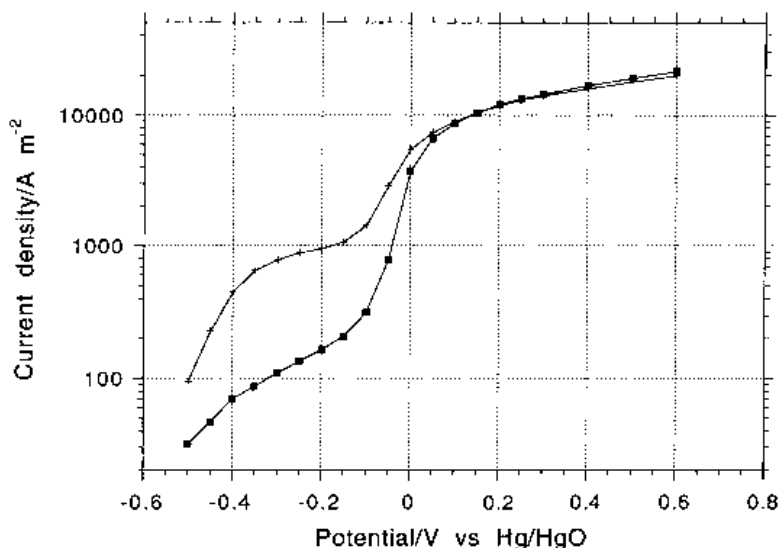


Fig. 6. Polarization curves in white liquor with and without elemental sulfur. $u = 0.159 \text{ m s}^{-1}$. Electrode area: 4.2 cm^2 . $[\text{S}^{-\text{II}}] = 0.525 \text{ M}$ (■) and $[\text{S}^{-\text{II}}] = 0.525 \text{ M}$, $[\text{S}^0] = 0.175 \text{ M}$ (+).

fixed concentration of $\text{S}^{-\text{II}}$. A polarization curve was first recorded in a solution with only $\text{S}^{-\text{II}}$. Elemental sulfur was then added to the solution and was allowed to dissolve before a new curve was recorded. A pair of such curves are shown in Fig. 6. The two curves demonstrate clearly the autocatalytic effect of polysulfide ions at low potentials, while they converge above 0V. This indicates there was no effect of polysulfide ions in this region.

Polarization curves at 80 and 90 °C, in Fig. 7, show the effect of temperature. The anolyte is a polysulfide-containing white liquor corresponding to 25% conversion. The difference between the graphs at the two different temperatures is clear but not dramatic. It remains rather constant throughout the entire potential range where the sharp increase in current density between -0.1 and 0 V is seen at 80 °C as well.

3.3. Galvanostatic electrolysis

Galvanostatic experiments were run at 90 °C in the cell with 21 cm^2 anode area. Anode potential and anolyte composition are shown, in Figs 8 and 9, as functions of charge passed in an experiment with 3 kA m^{-2} current density. 75 Ah corresponds to 100% conversion of $\text{S}^{-\text{II}}$ to S^0 at 100% current efficiency. The potential stays at around 0V during more than half of the experiment; but between 65 and 80% conversion (50 to 60 Ah) there is a sharp increase in potential. This increase in potential can be explained in terms of changes occurring in the electrolyte composition, which will be discussed below. The cell voltage was around 3.1 V in the beginning of the experiment. During the experiment it increased, following the change in anode potential, to a final value

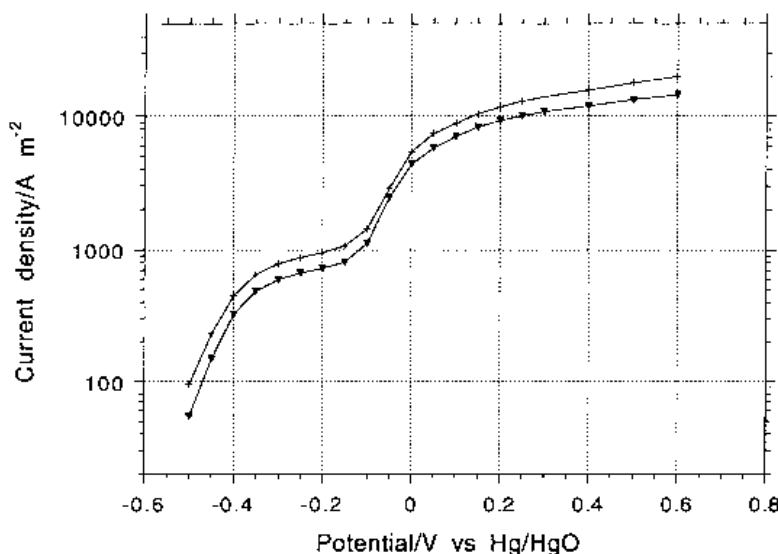


Fig. 7. Polarization curves in white liquor at 80 °C (▼) and 90 °C (+). $[\text{S}^{-\text{II}}] = 0.525 \text{ M}$, $[\text{S}^0] = 0.175 \text{ M}$. $u = 0.159 \text{ m s}^{-1}$. Electrode area: 4.2 cm^2 .

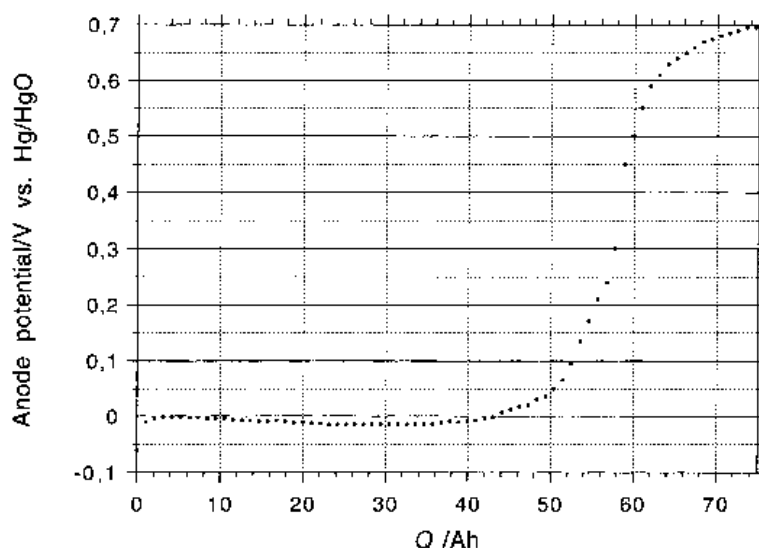


Fig. 8. Variation of anode potential with amount of charge passed in a galvanostatic experiment at 3000 A m^{-2} , $u = 0.159 \text{ m s}^{-1}$. Electrode area: 21 cm^2 .

of 3.7 V. It should be possible to decrease the cell voltage considerably with an optimized cell design. This could be greatly helped by the electrode gap being made much smaller.

In Fig. 9, and in the graphs following, the amounts of chemical are used instead of concentrations, since the volume of the electrolytes change during the experiment. The volume changes partly because of transport of sodium ions and accompanying water through the membrane to the cathode compartment, and partly because evaporation could not be completely eliminated. It has been assumed in the calculations that the volumes change linearly over time. It can be seen that during the first half of the experiment, the amounts of $\text{S}^{-\text{II}}$ and S^0 vary in fair agreement to the straight lines which correspond to 100% current efficiency for the main reaction. Yet, during the later part of the experiment, the current efficiency decreases and even goes to a negative value indicating

the onset of side reactions. This change is confirmed by considering the increase in anode potential from Fig. 8. The side reactions must include formation of sulfur in higher oxidation states (e.g., thiosulfate and sulfate) since the total amount of $\text{S}^{-\text{II}}$ and S^0 decreases after the increase in anode potential. In this work, however, a reliable analysis method for these species was not available. The development of such a method remains a future important goal. Ion chromatography as described by Douek *et al.* [6], is believed to be the most promising method.

Samples taken from the catholyte during the experiment showed that the NaOH concentration increased continuously from an initial value of 2.00 M to a final value of 3.13 M. This corresponds to a current efficiency of 90% throughout the experiment. Since hydrogen evolution is the only possible cathode reaction, the current efficiency is only limited by migration of hydroxide ions through the membrane to

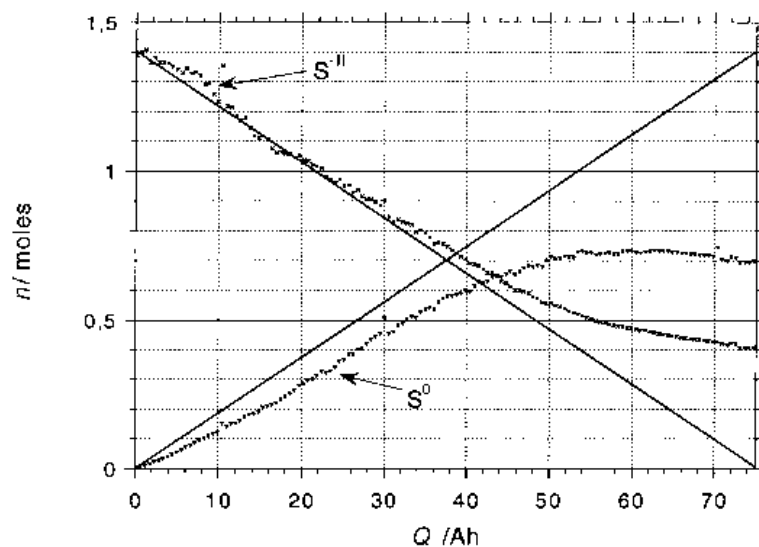


Fig. 9. Results of continuous analysis of the anolyte in a galvanostatic experiment at 3000 A m^{-2} . Initial anolyte volume: 2 dm^3 . Solid lines: theoretical curves for 100% current efficiency. Sulfide sulfur, $\text{S}^{-\text{II}}$. Polysulfide excess sulfur, S^0 .

the anode compartment. The weighing of the electrolytes, before and after the experiment, showed a loss of less than 40 g during the experiment, that is, less than 1% of the total electrolyte weight (Table 2). The loss is basically attributed to evaporation. When this loss is taken into account, together with the transport of hydroxide ions through the membrane, it can be calculated that each sodium ion passing through the membrane carries, in average, 3.6 water molecules with it.

Results from a galvanostatic experiment at a higher current density of 5 kA m^{-2} , are shown in Figs 10 and 11. During the beginning of the experiment, the anode potential lies at a level slightly higher than in the experiment of 3 kA m^{-2} . Here too, the increase in anode potential coincides fairly well with the decline in current efficiency, but only at this higher current density it does occur at an earlier stage of the electrolysis, and rise to a higher level. During the first third of the experiment, current efficiency appears to be high, although the precision of the analysis method does not allow a detailed quantitative comparison to the experiment of 3 kA m^{-2} .

One way to achieve higher current densities and/or lower overpotentials is to use three-dimensional electrodes. Figures 12 and 13 show results from an experiment with such an electrode design at 3 kA m^{-2} . The results in Fig. 13 indicate an excellent current efficiency, up to two thirds of the experiment, and again the decline in current efficiency is accompanied by a sharp rise in anode potential. It is interesting to note that the anode potential decreases by 0.25 V during the first 30 Ah. It should also be noted that even after 50 Ah, where the side reactions take over completely, the anode potential never reaches 0.1 V.

3.4. Potentiostatic electrolysis

A problem with galvanostatic experiments is that both electrolyte composition and potential vary so much

Table 2. Weight of electrolytes before and after galvanostatic experiment at 3000 A m^{-2}

| | Anolyte/g | Catholyte/g |
|---------------------|-----------|-------------|
| Before electrolysis | 2354 | 2152 |
| After electrolysis | 2119 | 2351 |

that their effects on current efficiency can not be isolated. Therefore an experiment with potentiostatic electrolysis, at a flat electrode, was carried out at +0.05 V. This was to see if, regardless of electrolyte composition, current efficiency would remain constant throughout the experiment. The results of the experiment are shown in Fig. 14. As can be seen from this Figure, current varies and reaches a maximum value of 3.25 kA m^{-2} between 10 and 20 Ah (or around 20% conversion). The current then gradually falls, probably because of the decrease in reactant concentration. The results from analyses show that good current efficiency was achieved. This is seen by S^0 describing a fairly straight line, up to around 40 Ah, after which the rate of the side reactions increases.

4. Discussion

Behaviour of the mixed iridium-tantalum oxide coated titanium electrode in white liquor, is in many ways similar to that observed on platinum in dilute solutions [1]. The polarization curves show that the process can be similarly divided into a low and a high potential region. However, under the present conditions, transition takes place at a considerably lower potential. In the low potential region reaction rate appears to be limited by the dissolution of elemental sulfur from the surface. Likewise, the current shows a transient behaviour, when potential was stepped to a higher value, indicating a build-up of a thicker sulfur layer. If the current is limited by the dissolution of elemental sulfur, the polarization curves should have

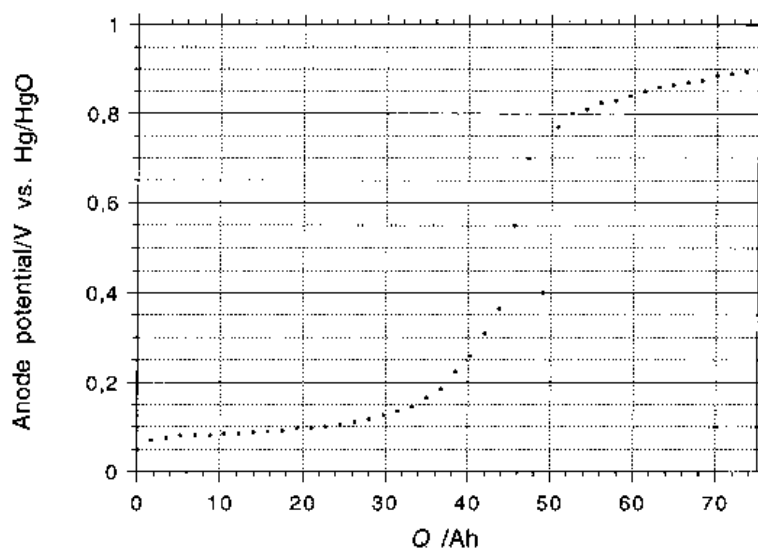


Fig. 10. Variation of anode potential with amount of charge passed in a galvanostatic experiment at 5000 A m^{-2} , $u = 0.159 \text{ m s}^{-1}$. Electrode area: 21 cm^2 .

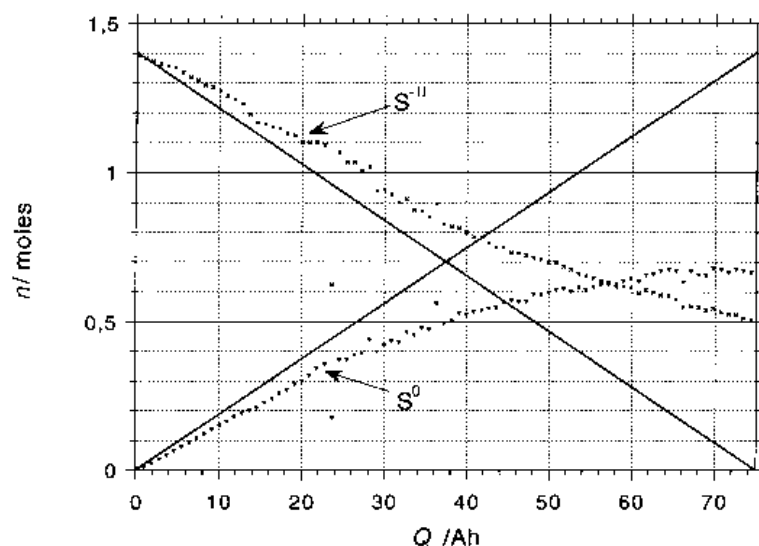


Fig. 11. Results of continuous analysis of the anolyte in a galvanostatic experiment at 5000 A m^{-2} . Initial anolyte volume: 2 dm^3 . Solid lines: theoretical curves for 100% current efficiency. Sulfide sulfur, S^{II} . Polysulfide excess sulfur, S^0 .

a region of total potential independence. Yet this is never observed. This can at least partly be because each point was recorded after only one minute and thus a true steady state value was never really reached.

Polysulfide ions have an autocatalytic effect, as is demonstrated both by addition of elemental sulfur and by variation in the mass transport conditions. If the average polysulfide ion chain length, $n_{\text{mean}}+1$, is assigned a typical value of 4.5, it can be calculated (see [1] for details) that curve (b) in Fig. 6 was recorded in a solution containing $0.050 \text{ M S}_n\text{S}^{2-}$ and 0.475 M HS^- compared to 0.525 M HS^- in curve (a). This comparatively small concentration of polysulfide ions is thus responsible for more than a five-fold increase in current density.

At potentials above -0.1 V , a reactivation is observed and the autocatalytic effect of polysulfide ions is lost. It was suggested in [1] that this change in

behaviour could be because the sulfur atoms close to the electrode are oxidized to form oxyanions, whilst the other atoms are released. The electrode is thereby reactivated without the action of polysulfide ions. This hypothesis is supported by the fact that fairly high current efficiencies were obtained during the first part of the galvanostatic flat electrode experiments, although the electrode was well into the high potential region. Furthermore, an almost 100% current efficiency, in the experiment involving the mesh electrode, might then be because the potential was in the low potential region, where polysulfide ions are formed according to the chemical dissolution reaction scheme.

The results show that current efficiency is determined not only by electrode potential but also by electrolyte composition. When conversion is too high, formation of oxyanions can become the dominating reaction, even at potentials around 0 V (Figs 12–14).

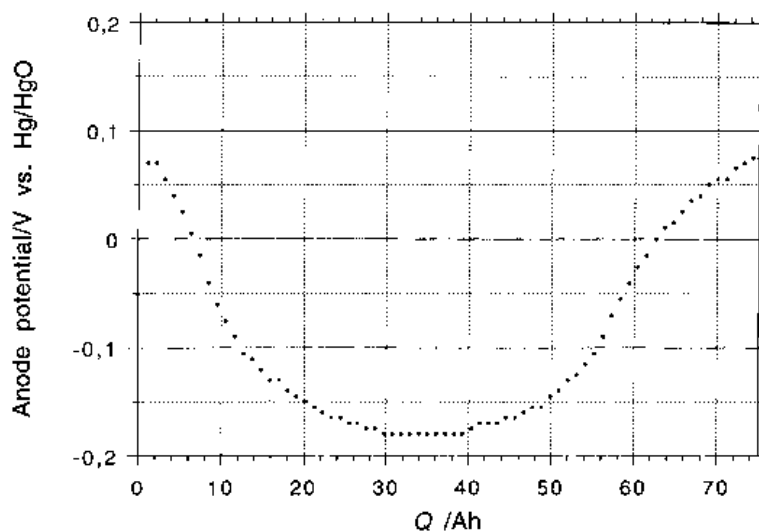


Fig. 12. Variation of anode potential with amount of charge passed in a galvanostatic experiment with mesh electrode. Current density: 3000 A m^{-2} . $u = 0.159 \text{ m s}^{-1}$. Electrode area: 21 cm^2 .

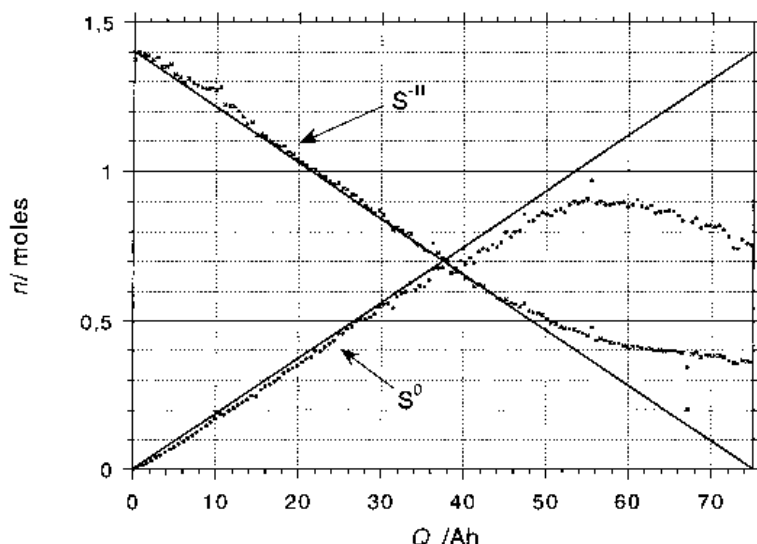
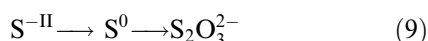


Fig. 13. Results of continuous analysis of the anolyte in a galvanostatic experiment at 3000 A m^{-2} with mesh electrode. Initial anolyte volume: 2 dm^3 . Solid lines: theoretical curves for 100% current efficiency. Sulfide sulfur, $\text{S}^{-\text{II}}$. Polysulfide excess sulfur, S^0 .

The reactions at the anode might be modelled as a scheme of consecutive reactions as in Equation 9. Here thiosulfate is assumed to be the dominating side reaction:



If the reactions are of the second order or higher, the concentration dependence is very significant. This may account for the rather sharp changes in selectivity that can be seen in the analysis plots (Figs 9, 11, 13 and 14) when a critical concentration is reached.

The decrease in anode potential, during the first 30 Ah of the experiment using the mesh electrode (Fig. 12), can be explained by the autocatalytic effect of polysulfide ions, as illustrated by the polarization curves in Figs 5 and 6, together with the theory of secondary current distribution in three-dimensional electrodes (e.g., see [7]). The Wagner number, as de-

finied in Equation 10 and where L is a characteristic length, can be used to evaluate the secondary current distribution in a three-dimensional electrode:

$$Wa = \frac{\partial \eta \kappa}{\partial i L} \quad (10)$$

For unoxidized white liquor $d\eta/di$, at and below 0 V will be low (Fig. 5). This means a low Wagner number and an uneven current distribution. The current will thus be concentrated to the front of the electrode, resulting in a high local current density and high electrode potential. As electrolysis proceeds, and the concentration of excess sulfur (S^0) increases, $d\eta/di$ increases in the potential region of interest. This gives a higher Wagner number and a more even current distribution through the depth of the electrode. A lower local current density in the front of the electrode will thus result, and a lower electrode

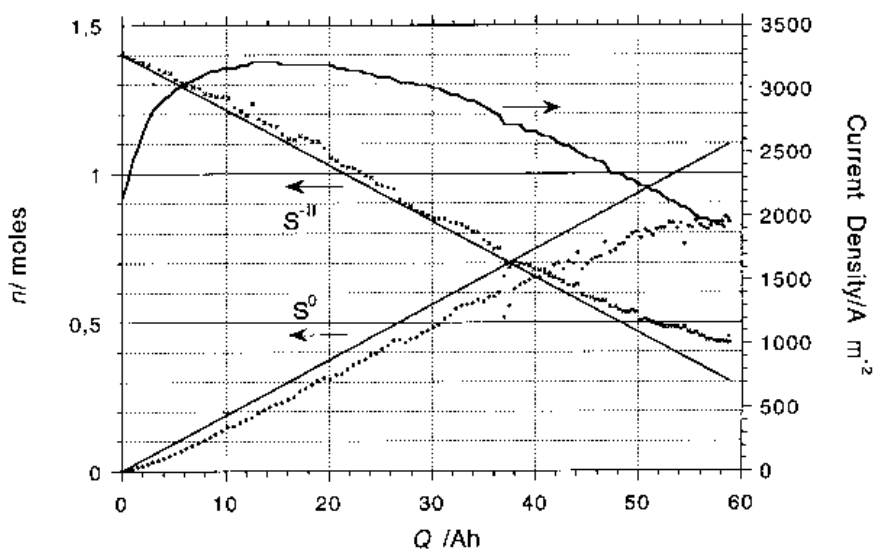


Fig. 14. Variation of anolyte composition and current density with amount of charge passed in a potentiostatic electrolysis experiment. Anode potential: 0.05 V vs Hg/HgO. $u = 0.159 \text{ m s}^{-1}$. Initial anolyte volume: 2 dm^3 . Electrode area: 21 cm^2 . Solid lines: theoretical curves for 100% current efficiency. Sulfide sulfur, $\text{S}^{-\text{II}}$. Polysulfide excess sulfur, S^0 .

potential will be observed. It can therefore be concluded that due to the specific properties of this process, a three-dimensional electrode can be a good choice both in terms of overpotential and current efficiency.

The experiments in this work were restricted to only one type of anode material. The results are promising with respect to current density and efficiency but limited life time seems to be a problem. The flat electrodes experienced a loss of activity and visible signs of corrosion after relatively short times. Corrosion was more pronounced at points that had been in contact with the turbulence promoters, suggesting that it is affected by hydrodynamics. Excessively high potentials might be a key factor in corrosion since the mesh electrode, that was held at relatively low potentials, seemed unaffected by the experiments.

The search for an optimal electrode material is an important goal for future research. Since the process appears to be suitable for three-dimensional electrodes, durability is perhaps more important than excellent electrocatalytic activity. Another important factor, which may prove prohibitive for widespread industrial application, is the cost of electrode material. Of the electrode materials tested in white liquor to date, the mixed iridium–tantalum oxide coated titanium electrode has shown to have the best electrocatalytic activity, superior to both platinum and graphite. Packed bed graphite electrodes could still be interesting because of the low cost. Yet this is still dependent on a sufficient lifetime. Metal sulfide electrodes, such as CoS, MoS and CuS have been tested as cathodes for the reduction of polysulfide ions in aluminium/sulfur batteries and photoelectrochemical cells [8, 9]. They might prove suitable as anodes for electrochemical white liquor oxidation.

5. Conclusions

The electrochemical production of polysulfide ions and sodium hydroxide was demonstrated, in a membrane cell, at industrially relevant current densities and high current efficiencies for both products. Furthermore, the production was run successfully at more than 50% conversion.

Polysulfide ions show an autocatalytic effect on the anode process, especially at potentials below 0 V vs Hg/HgO. Because of this effect, the process is particularly suited for three-dimensional electrodes. Electrolysis with a three-dimensional electrode gives a higher current efficiency, lower overpotential and allows a higher degree of conversion, before side reactions dominate.

The current efficiency depends strongly on the degree of conversion of sulfur(–II) to sulfur(0). At higher degrees of conversion, current efficiency can deteriorate even at relatively low potentials and current densities.

The mixed iridium–tantalum oxide coated titanium electrode shows favourable properties, with respect to activity and selectivity, but suffers from limited durability. Finding an optimal electrode material is a major goal for future research.

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