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Short Communication

Graphite as anode material for the electrochemical production of polysulfide ions in white liquor

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1. Introduction

The electrochemical production of polysulfide-containing white liquor and pure sodium hydroxide solution in a membrane cell has been studied [1–3]. The process is intended for integration in the cooking-chemicals recovery system of a kraft pulping mill, providing on-site generation of two valuable products; polysulfide ions increase the pulp yield and sulfide-free sodium hydroxide solution is used in the alkaline bleaching stages. The electrode and consequent cell reactions are as follows: anode

$$(n+1)\,\mathrm{HS}^- + (n+1)\,\mathrm{OH}^- \rightarrow \mathrm{S}_n\mathrm{S}^{2-} + (n+1)\,\mathrm{H_2O} + 2n\,\mathrm{e}^- \tag{1}$$

cathode

$$2\,\mathrm{H_2O} + 2\,\mathrm{e}^- \rightarrow 2\,\mathrm{OH}^- + \mathrm{H_2} \tag{2}$$

cell reaction

$$(n+1)\,\mathrm{HS}^- + (n-1)\,\mathrm{H_2O} \rightarrow \mathrm{S}_n\mathrm{S}^{2-} + (n-1)\,\mathrm{OH}^- + n\,\mathrm{H_2} \tag{3}$$

If the solution already contains polysulfide ions, these are also involved as reactants. It was found that the electrolysis can be run at industrially relevant current densities and high current efficiencies for both products using mixed iridium–tantalum oxide coated titanium [2] and porous nickel [3] as anode materials. There is, however, some concern regarding the long-term activity of these materials under the present conditions, that is, 3 M NaOH, 0.7 M (Na_2S + S^0) and 0.25 M Na_2CO_3 at 90 °C. Furthermore, noble metal oxide coated titanium electrodes are relatively expensive. It is therefore of interest to explore the use of other electrode materials in order to find a material with an even better combination of lasting electrochemical performance and low cost.

Successful use of graphite [4, 5] and activated glassy carbon [6], as the anode in electrochemical processes for the cleaning of hydrogen sulfide from natural and process gases, has been reported. Furthermore, carbon catalysts are used in commercial thermochemical processes for generating polysulfide ions in white liquor with air as the oxidizing agent. Therefore, graphite/carbon might well be useful as the anode for electrochemical generation of polysulfide ions in white liquor. However, experimental conditions in [4–6] are different from the present application, and described only in limited detail. In the present work, packed beds of graphite grains were chosen for a preliminary assessment of their possible use as anode material, using the same experimental methodology as in our previous papers.

2. Experimental details

The flow cell experimental set-up is described in [2]. Graphite grains with a diameter of 1–2 mm were kindly supplied by ElectroCell AB, Täby, Sweden. The packed bed had a thickness of 6.5 mm, a projected area of 21 cm^2 and a porosity of around 50%. A flat nickel electrode at the rear of the bed was used as current collector. Its active contribution to the current density was considered insignificant at the potentials used. This assumption was based on an estimation of the effective conductivity of the electrolyte phase of the bed and results from kinetic investigations on nickel rotating disc electrodes [3]. The reference capillary was introduced from the back, through a hole in the current collector, so

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[†] deceased.

that its tip was positioned in the same plane as the front of the bed, that is, towards the membrane. The potential was measured against a Hg/HgO (3 M NaOH) reference electrode. The anode and cathode chambers were separated by a Nafion® 324 cation-exchange membrane. The cathode was made of stainless steel.

Details of the electrolyte preparation have been described previously [1, 2]. The initial anolyte composition was 0.595 M Na_2S, 0.105 M S^0, 3 M NaOH and 0.25 M Na_2CO_3, which simulates a partially oxidized white liquor with 15% conversion of S^{II-} to S^0. A 2 M NaOH solution was used as the starting catholyte. The experiments were run at 90 °C, although all concentrations are those relevant at room temperature. The anolyte flow rate was measured with a rotameter, which gave a velocity of the electrolyte in the packed bed of around 0.2 m s^{-1}, taking the porosity into account.

Galvanostatic experiments were run using an Oltronix B32-20R power supply. Slow scan polarization curves were recorded using a Wenking HP 72 high power potentiostat and a Wenking VSG 83 voltage scan generator. Data were collected using BBC Goerz Metrawatt *x–t* and *x–y* recorders, and the amount of charge was measured by a Unisystem U1010B Ah-meter.

Spectrophotometric in-line monitoring of sulfide sulfur (S^{II-}) and polysulfide excess sulfur (S^0), was done using a Zeiss MSC 320 spectrometer equipped with an attenuated total reflectance (ATR) probe for u.v. measurements. This analysis method is described in [7, 8]. The ATR probe was placed directly into the anolyte vessel, and calibration was made using the starting anolyte as reference sample.

3. Results and discussion

Galvanostatic electrolysis experiments were run in batch recycle mode at 3 kA m^{-2}. A polysulfide-containing starting anolyte was used because it better resembles conditions in a continuous large scale process and because it is known that the presence of polysulfide ions catalyses the reaction on previously investigated electrode materials. 50.85 Ah were passed during this experiment, which corresponded to a conversion to 83% S^0 at 100% current efficiency.

Figure 1 shows anolyte composition and anode potential as functions of charge passed. Amounts of chemical are used instead of concentrations, since the volume of the anolyte decreases slightly during the experiment. This is partly due to migration of sodium ions and associated water molecules through the membrane and into the cathode chamber, and partly due to evaporation that could not be completely eliminated. The solid lines are theoretical curves for 100% current efficiency. In another experiment, two potentiostatic polarization curves were recorded, one in the starting anolyte and a second after passing 18.75 Ah galvanostatically at 3 kA m^{-2}. These curves are shown in Figure 2.

Figure 1 clearly shows that polysulfide ions are formed at a relatively high current efficiency during the first half of the experiment. After approximately 30 Ah, the current efficiency falls and even becomes negative, which indicates the occurrence of side reactions. The curve for sulfide sulfur, S^{II-}, falls at a rate that agrees fairly well with the theoretical curve. Yet, the

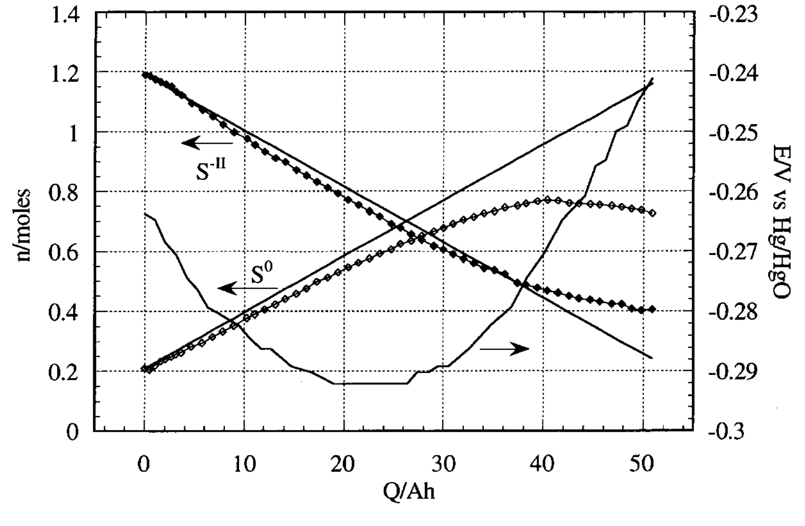

Fig. 1. Anolyte composition and anode potential as functions of charge passed in a galvanostatic electrolysis experiment at 3 kA m^{-2}. Initial anolyte volume: 2 dm^3. Initial anolyte composition: 0.595 M Na_2S, 0.105 M S^0, 3 M NaOH and 0.25 M Na_2CO_3. T = 90 °C. Solid lines: theoretical curves for 100% current efficiency. Sulfide sulfur, S^{II-}. Polysulfide excess sulfur, S^0.

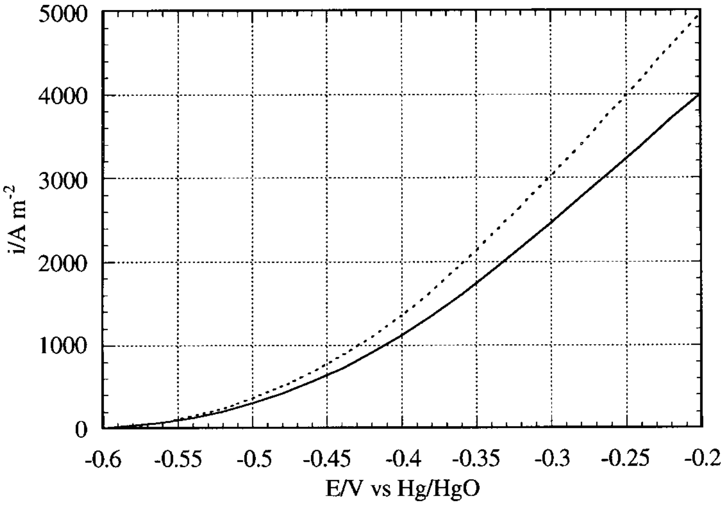

Fig. 2. Slow scan potentiodynamic polarization curves. Scan rate: 1 mV s^{-1}. Solid line: initial anolyte (0.595 M Na_2S, 0.105 M S^0, 3 M NaOH and 0.25 M Na_2CO_3). Dashed line: after passing of 18.75 Ah.

slightly negative deviation, relative to the theoretical curve, is surprising, since it suggests that sulfide sulfur is consumed by a non-electrochemical process in parallel to its electrochemical oxidation. However, the relative deviation is never in excess of 5%, which is within experimental error at this level of sophistication. In summary, the general behaviour agrees well with observations when using mixed iridium–tantalum oxide and nickel [2, 3].

This fact is also true for the potential–time profile in Figure 1. The measured values should be compared with an equilibrium potential close to −0.6 V. The anode potential decreases at the beginning of the experiment, and reaches a minimum at 20–25 Ah, after which it again increases until electrolysis was completed. With the above mentioned materials, the decrease in anode potential was explained in terms of the autocatalytic effect of polysulfide ions, the concentration of which should be at least twice as high, at the minimum in potential, as at the start of electrolysis. It can thus be concluded that this beneficial effect also exists with graphite. Furthermore, the subsequent increase in anode potential coincides with the decline in current efficiency.

Figure 2 shows the two polarization curves that were recorded during a galvanostatic experiment, identical to the one described above, although without continuous analysis of S^{II-} and S^0 concentrations. Judging from Figure 1, the concentration of polysulfide excess sulfur should be around 0.25 M, for the curve recorded after 18.75 Ah. The curves were recorded in a cyclic potentiodynamic sweep of 1 mV s^{-1}. There was virtually no hysteresis between the negative- and positive-going scans. This indicates that the potential scan has no irreversible effect on the electrode surface. The curve recorded after 18.75 Ah exhibits significantly higher current densities, which supports the earlier conclusion that polysulfide ions catalyse the electrode process. A current density of 5 kA m^{-2} is obtainable at 400 mV overpotential ($E = -0.2$ V).

The measured potentials in the galvanostatic experiment are lower than for three-dimensional iridium–tantalum oxide, but higher than for porous nickel; the minima in potential for these materials in equivalent experiments at 3 kA m^{-2} were around −0.2 and −0.4 V, respectively [2, 3]. The potential–charge curves for all three materials are displayed together in Figure 3, for comparison. The negative shift in the x-direction of the starting point, for the iridium–tantalum oxide curve, is because that experiment started with an unoxidized white liquor. It is, unfortunately, difficult to make a fair comparison of the intrinsic electrochemical performance of the different materials from experiments with three-dimensional electrodes, since the anode potential is a complex function of both electrode kinetics and electrode design; the three electrodes differed considerably in porosity and specific surface area. The relatively small variation in potential for the porous nickel electrode can probably be attributed to its extremely high specific surface area. Likewise, the relatively strong variation for the IrO_2/Ta_2O_5 electrode is probably because it has a lower specific surface area, but also because of its kinetic behaviour at different electrolyte compositions and potentials, as discussed in [2].

It would be desirable to run experiments with planar graphite electrodes in order to obtain more detailed knowledge of the anode process, without having to cope

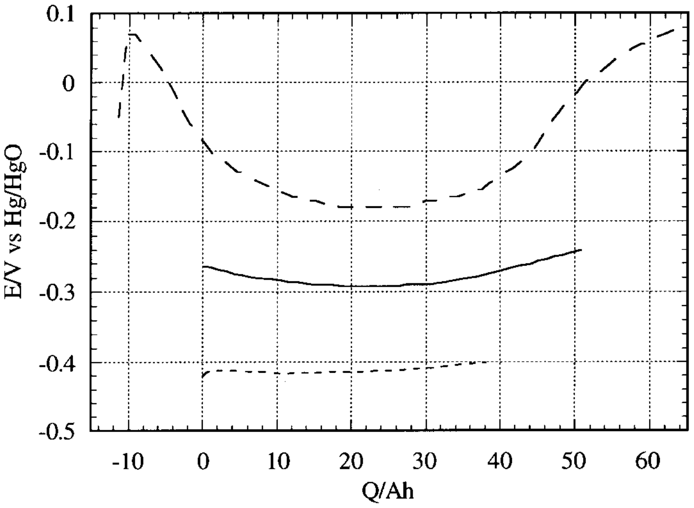

Fig. 3. Anode potential against charge passed in galvanostatic electrolysis experiments at 3 kA m^{-2} with different electrode materials. Graphite packed bed (——) (from Fig.1). Porous nickel (- - - -) (from [3]). 3D iridium–tantalum oxide coated titanium (– – – –) (from [2]). $Q = 0$ Ah corresponds to a starting anolyte simulating 15% conversion.

with the complexities of three-dimensional electrodes. However, preliminary experiments with a rotating disc electrode of pyrolytic graphite indicates that it might be difficult to find planar graphite electrodes that are equivalent to the graphite grains in terms of their electrochemical properties.

The long-term performance of graphite could not be reliably assessed from the results presented in this paper, since no experiment lasted for more than eight hours. However, it should be noted that there were no observations that indicated problems with deactivation or corrosion. Indeed, the absence of hysteresis in the slow scan polarization curves is encouraging. Furthermore, the visual appearance of the graphite grains was completely unaffected by electrolysis.

4. Conclusions

A packed bed of graphite grains was successfully tested as the anode for electrochemical production of polysulfide ions in white liquor. The electrode potential and current efficiency fall in the same range as results obtained when using mixed iridium–tantalum oxide coated titanium 3D mesh and porous nickel. Furthermore, the observed selectivity–charge behaviour exhibited the same general features as with those materials. Polysulfide ions exhibit an autocatalytic effect with graphite. No signs of physical deterioration or loss of activity were observed on the time scale of the experiments, although experiments of much longer duration would be needed to truly assess the durability of graphite. In view of these results, and its low cost, the packed bed graphite anode is an attractive alternative in the further development of a viable full-scale industrial process.

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