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Morphology of sodium polysulphides formed electrolytically on graphite fibres in molten sulphur

L. SUSKI, J. KOLACZ

Polish Academy of Sciences, Institute of Physical Chemistry, Molten Salts Laboratory, 30-059 Kraków, al. Mickiewicza 30, Poland

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A cell has been constructed which enables the observation by microscopy of the electrochemical formation of Na_2S_x on graphite fibres in a thin layer of liquid sulphur. The polysulphide phase initially forms only on the graphite surface although later other small droplets of this phase are deposited in the bulk of liquid sulphur. In contrast to the mechanisms in the literature the formation of these droplets by an electrochemical route is suggested. It is probably due to electronic conduction by dissolved sodium in the liquid sulphur.

1. Introduction

The formation of liquid sodium polysulphides by the reaction

$$2Na^+ + xS + 2e \rightarrow Na_2S_x \qquad (1)$$

takes place at the cathode of sodium–sulphur batteries. The kinetics and mechanism of this reaction have been extensively investigated. However, many fundamental problems are still to be resolved.

The process cannot be directly compared to other classical electrode reactions. The sulphur–sulphide half-cell in the Na–S battery consists of graphite electrode conducting electrons and a solid electrolyte transferring sodium ions. Liquid sulphur has almost perfect insulating properties and electrons must be transferred to the site of Reaction 1 via graphite or the carbon electrode conductor. The liquid sodium polysulphides of general formula Na_2S_x ($3 \leqslant x \leqslant 5$), formed by Reaction 1, are insoluble in the liquid sulphur phase. Hence the model shown in Fig. 1 is generally accepted for this process.

At the solid electrolyte/liquid sulphur interface the current flows at those places where graphite directly touches the membrane. On cathodic polarization of the graphite electrode a liquid phase of sodium polysulphides starts to be deposited at these places. This phase shows high ionic conductivity. Its formation extends the area where Na^+ ions may be transferred and hence the reaction sites available for further electron transfer.

The practical problem of the construction of sodium–sulphur batteries has focused electrochemical research firstly on processes in liquid polysulphides [1]. In such cells the liquid sulphur phase appears as a product of the anodic decomposition of Na_2S_x. Only a few papers have described the initial steps in the cathodic process of Na_2S_x formation in the pure sulphur liquid phase [2]. The results of optical microscopy investigations may be summarized as follows:

(a) The formation of the liquid Na_2S_x phase takes place at the area of contact of the three phases: solid electrolyte–graphite–liquid sulphur, according to the diagram in Fig. 1.

(b) Droplets of polysulphide formed at the contact area of the three phases may be mechanically dispersed in the liquid sulphur. This purely mechanical process of polysulphide dispersion finishes by covering all the solid electrolyte/sulphur interface with a uniform liquid Na_2S_x layer.

These visual investigations have been carried out using graphite porous felt. In these conditions the possibility of identifying processes at the triple phase contact area was limited. The aim of the present paper is to carry out similar visual observations under conditions where there is a

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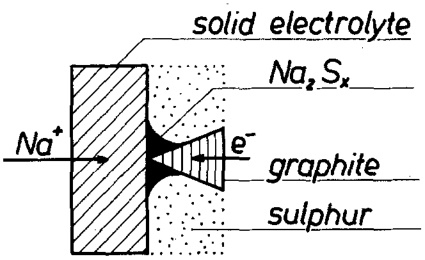

Fig. 1. Schematic morphology of liquid Na_2S_x cathodic formation at the graphite surface in liquid sulphur.

regular and simple geometry of the triple phase contact area.

2. Cell design and experimental methods

Visual microscopic observations were carried out in a cell simulating the Na–S battery. A simplified cross-section of the cell is represented in Fig. 2.

Sodium glass was used as the membrane separating the electrode compartments. This membrane had the shape of a test tube (1 in Fig. 2), the bottom of which had been blown to make it as thin as possible and to decrease its electrical resistance. The tube contained the eutectic mixture of molten sodium salts ($NaNO_3$ + $NaNO_2$), Pt electrode, thermocouple Pt + PtRh, as well as the quartz light conducting rod (5). This rod carried a stream of light from a halogen lamp (6), to the reaction space. The glass tube was inserted in the aluminium body and immersed in the liquid sulphur (9). The aluminium walls were insulated from liquid sulphur by a mica sheet. Some graphite fibres had been inserted into the liquid sulphur. These fibres touched the bottom of the glass tube. Their ends were pressed to the aluminium body of the cell by an aluminium cover (11). In this cover a window of synthetic leucosapphire (12), was inserted. This window enabled observation of the process taking place on the graphite fibres through the stereoscopic microscope St 31 (PZO Warsaw). The microscope was focused on the centre of the window where graphite fibres were in contact with the glass and where the layer of liquid sulphur was the thinnest – few tenths of a mm. It is known that liquid sulphur is dark and nontransparent at 580 K, the lowest temperature for operation of the Na–S battery. Hence only the use of a very thin layer of liquid sulphur in the reaction area enabled the passage of sufficient light through the dark red liquid sulphur.

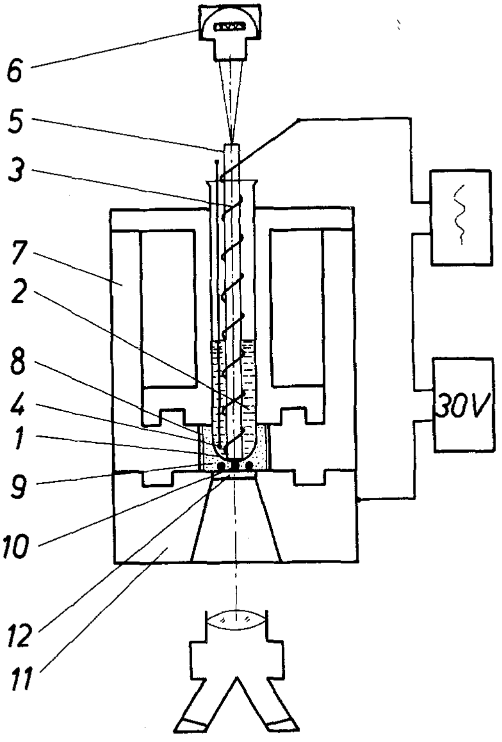

Fig. 2. Cross-section of the experimental cell.

A 30 V direct current source was connected between the body of the cell (and hence the graphite fibres) and a platinum electrode immersed in the molten salt inside the glass tube. The whole sulphur-containing compartment was tightly closed.

After heating the cell to a temperature of 580 ± 0.5 K the electrolysis was started using graphite fibres as a cathode where the sodium polysulphide formation according to Reaction 1 took place. After obtaining appropriate pictures of the dark droplets of the liquid polysulphide phase in the red sulphur the current direction was inverted and the process of the anodic decomposition of Na_2S_x started.

During the experiments photographs of the microscopic observations were taken.

3. Result and discussion

The observations carried out in the first phase of the cathodic electrolysis on graphite fibres

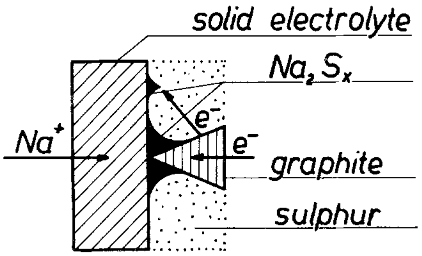

Fig. 3. Schematic morphology of liquid Na_2S_x cathodic formation simultaneously at the graphite surface and in the bulk of liquid sulphur.

essentially support the opinion of other authors. At the beginning of electrolysis the resistance of the system was high and under 30 V only a low current of approximately 10^{-6} A passed through the cell. This current was probably determined by the resistance of the glass membrane. The nucleation of the first droplets of the liquid polysulphides took place exclusively on the surface of graphite fibres at sites where there was the best contact between the fibres and the glass membrane. With the growth of the polysulphide droplets the ionic conductance area and the current value increased.

The first interesting observation concerns the appearance of Na_2S_x droplets some distance from the cathodic graphite fibres. This is schematically represented in Fig. 3.

The series of photographs in Fig. 4 represents the particular steps in the growth of these droplets.

The authors of earlier microscopic investigations used graphite felt as electrodes and considered this part of the polysulphide phase to be mechanically detached from the large droplets formed on the cathode surface [2]. This was a logical explanation but the present observations carried out under different conditions of fibre microcathode geometry make such a mechanism rather improbable. In the very thin layer of liquid

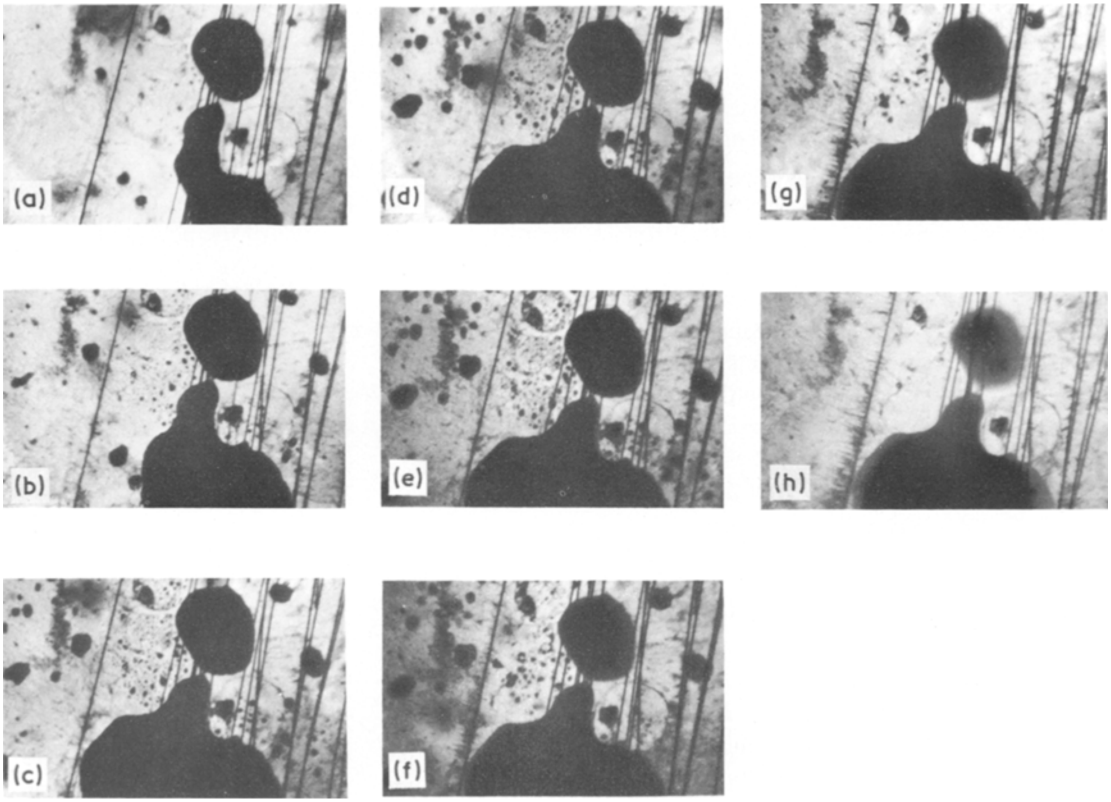

Fig. 4. Microscopy photographs of the cathodic growth (a–d) and anodic decomposition (e–h) of the Na_2S_x liquid phase during electrolysis in liquid sulphur with a cathode of graphite fibres. Formation of small Na_2S_x droplets in the bulk of the sulphur phase and their decomposition are visible.

sulphur neither movements which could make possible the dispersion of droplets nor transitory steps in this phenomenon have been observed. These droplets grow without moving from their initial positions, evidently without direct contact with the graphite microelectrodes.

To identify the mechanism of this effect, the observation of anodic decomposition of the Na_2S_x phase is of great interest. As may be seen on photographs e–h in Fig. 4 the 'electrodeless' formed droplets decompose and disappear during the initial stages of anodic polarization when the main polysulphide droplets still exist. The last observation rules out the decomposition of the 'electrodeless' formed droplets via dissolution of the polysulphides in sulphur and a concentration gradient of dissolved species. This gradient, and hence the diffusion of polysulphides through the solution cannot take place as long as the polysulphide phase exists around the graphite electrode. Our observations have also been recorded on film and then it may easily be seen that the anodic removal of 'dispersed' droplets occurs in the presence of the polysulphide phase at the graphite fibre electrode.

Hence both the cathodic formation and the anodic decomposition of the 'dispersed' droplets cannot occur in any but a direct way and must be of an electrolytic nature. These processes are probably occurring at the sulphur/glass interface.

It should be emphasized, however, that visual observations are not sufficient to provide evidence of the mechanism of electron conduction to places where the small 'dispersed' droplets are formed electrolytically without contact with the graphite electrode. According to the principal laws of electrochemistry the transport of electrons through the liquid sulphur is essential to make such a process possible. This transport is impossible in pure sulphur having an electrical conductivity as low as $10^{-14}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at this temperature. It is known from the literature that in liquid sulphur saturated with products of the reaction with sodium this conductivity increases by seven orders of magnitude [3]. The contribution of this product to the conductivity need not be ionic. There is a lack of information concerning the entities formed by sodium in very dilute solution in liquid sulphur. Its solubility is very low but is quantitatively unknown. If sodium forms atoms in the electrode reaction:

$$Na^+ + e \rightarrow Na \qquad (2)$$

and exists in this solution as the same entity, it could have the role of electron donor and contribute to the electronic conductance of the n-type semiconductor. The formation of such a semiconductor could explain at least qualitatively the effect of the Na_2S_x formation in the bulk of the liquid sulphur.

If this hypothesis is correct the addition of semiconductors to the sulphur should improve conditions for the formation of droplets in the bulk of liquid. Selenium constitutes such a semiconductor which is miscible with liquid sulphur at this temperature. The S–Se solutions show intrinsic semiconductor properties [4].

The results of observations carried out with sulphur containing 5 at% of selenium support our hypothesis concerning the mechanism of 'dispersed' Na_2S_x droplet formation. In this case the number of such droplets is higher and their growth is faster than in the pure sulphur.

The contribution of sodium dissolved in the liquid sulphur to the total conductivity of the system, as well as the electrolytic formation of polysulphides in the bulk of the liquid sulphur phase should be taken into account when formulating mathematical models of the polysulphides–sulphur–carbon half-cell in Na–S batteries.

Acknowledgement

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