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Electrochemical Behavior of Graphite and Ni-Cr Electrodes in Sodium Polysulfide in the Absence and Presence of Hydrogen Sulfide

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Figure 4 shows the variation in conductivity as a function of reciprocal temperature. Two distinct regions were observed. The activation energy was calculated from these plots. The activation energy decreases with increase in Na⁺ concentration from 0.37 to 0.2 eV at low temperature and 1.32 to 0.91 eV at higher temperature regions.

Dielectric parameters (ε and tan δ) were measured from 10⁻¹⁰⁻¹⁶ Hz at 25°, 100°, and 200°C. A decrease in dielectric constant was observed with increase in frequency (Fig. 5 and 6). Dependence of dielectric loss on temperature and frequency is shown in Fig. 7 and 8. By the addition of Na⁺, loss value increased from 0.16 to 0.8.

Conclusions

1. Cyclodehydration of poly(amide-acid) is influenced by the presence of Na⁺ ions. An increase in Na⁺ ion concentration resulted in a decrease in cyclodehydration reaction.

2. The conductivity measurement showed sodium ion participation in conduction.

3. A decrease in resistivity and activation energy is observed with increase of sodium ion concentration.

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REFERENCES


2. A. E. S. Lloyd and J. R. Chin, ibid., p. 889.


at high (>600°C) temperature. Bartlett et al. (5) have proposed the use of molten NaHS in this application. The sulfur literature (6, 7) shows that in systems where sulfur and sulfide co-exist, species exist in form $S_x$ or $S_{2-}^x$, where $x$ varies from 2 to 10 or even higher, depending on temperature and the medium; thus, formation of polysulfide is inevitable in any process for sulfur production from hydrogen sulfide. Since sodium polysulfides have relatively low melting points (below 400°C), and the following reaction may be possible

$$NaS_x + H_2S \rightarrow NaHS_x + NaHS$$  \[1\]

which may result in high effective solubility of $H_2S$ in the melt. Hence, sodium polysulfide melt may serve as a more effective electrolyte than NaHS. If this melt has the correct properties, its use in an electrolyzer with a structure similar to that of the molten carbonate fuel cell should result in a simple process for the recovery of both elemental sulfur and gaseous hydrogen from hydrogen sulfide. Until the present time, there is no data on the effective solubility of hydrogen sulfide in this melt and on the corresponding kinetics of the hydrogen evolution. This investigation was conducted to determine the suitability of sodium polysulfide melt as electrolyte for the decomposition of $H_2S$. For this purpose, the electrochemical behavior of graphite and Ni-Cr electrodes in this melt in the presence and absence of $H_2S$ was investigated using voltammetric, chronopotentiometric, and chronopotentiometric techniques.

**Experimental**

Sodium tetrasulfide (Alfa Ventron) was used in the experiments without further purification. The counter-electrode was a graphite rod; the working electrode was either a graphite rod or a Ni-Cr alloy (90% Ni, 10% Cr) plate. When the graphite rod was used as the working electrode, only the flat bottom surface of the electrode was exposed to the electrolyte, the rest of the electrode being sealed with a high-temperature cement. The Ni-Cr electrode was spot welded with pure nickel wire for electrical contact, all except the reaction zone being sealed with the same cement.

Figure 1 shows a schematic view of the experimental Pyrex glass cell. The reference graphite electrode was in a compartment separated by a glass frit, as shown in Fig. 1b. This reference electrode compartment was partially filled with pure sulfur before being introduced into the cell, which resulted in the entry of some melt from the main cell through the fritted glass. A stable potential of the sodium tetrasulfide at the graphite and at the Ni-Cr electrodes, respectively, at 320°C in a nitrogen atmosphere. When the ohmic resistance between the working electrode and reference electrode was corrected, the potential at the peak current was almost independent of the scan rate, and was about −0.31V at the graphite electrode and about −0.35V at the Ni-Cr electrode.

The voltammetric experiments were repeated with mixtures of 10% $H_2S$ and 90% $H_2$ and 10% $H_2S$ and 90% $N_2$ bubbling through the melt. Experiments were carried out after the gas mixture had been bubbled through the melt for about 2h. The voltammograms obtained in this experiment were identical to those with pure $N_2$ bubbling through the melt. The voltammograms obtained here were similar to those at relatively high scan rates (10-12), where the peak current may be reasonably attributed to mass transport limitations. However, in the present work, a distinct peak current which varied linearly with the square root of the scan rate was still observed even at the scan rate of 0.5 mV/s on the graphite electrode. This peak current occurring at a low scan rate is more likely due to the formation of a blocking layer than due to diffusion of reactants since the current interruption after the peak current revealed a potential plateau at about −0.285V, indicating the presence of two phases at the electrode-electrolyte interface. Supporting evidence for blocking was the smaller current observed in the second potential sweep and the shift of the potential in the negative direction. The equilibrium potential of $S_{2-}^{2+}/S_{2-}^{2+}$ is −0.295V and that of $S_{2-}^{2+}/S_{2-}^{2+}$ is

![Fig. 1A. Schematic of the experimental cell, B reference electrode](image1)

![Fig. 2. A typical cyclic voltammogram at the graphite electrode with $N_2$ bubbling; the electrode area 0.28 cm², temperature 320°C, scan rate 2 mV/s.](image2)

![Fig. 3. A typical cyclic voltammogram at the Ni-Cr electrode with $N_2$ bubbling; the electrode area 0.32 cm², the scan rate 5 mV/s, temperature 320°C.](image3)
tion product, the plateau current being apparently limited of the plateau increased and became a peak as the scan current continued to increase after the plateau. The height the one in Fig. 2 appeared on the voltammogram, and the may consist of Na\textsubscript{2}S\textsubscript{4} and Na\textsubscript{2}S\textsubscript{2}.

The influence of H\textsubscript{2}S on the chronoamperometric results is shown in Fig. 6. The transient time became shorter when the Ni-Cr electrode was reached at the Ni-Cr electrode without about 25s, whereas the current continuously decreased even after 300s at the graphite electrode. A plot of the current vs. potential at a fixed time at the Ni-Cr electrode was linear, and its slope decreased gradually with time as shown in Fig. 5.

The decrease in current with time shown in the chronoamperometric curves may result from chemical reactions which generate zero-valent sulfur in the form of a higher polysulfide, for example

\[
\text{Na}_2\text{S}_x + \text{H}_2\text{S} \rightarrow \text{Na}_2\text{S}_{x+1} + \text{H}_2 \quad [2]
\]

The free energy change for the above reaction is less than 20 kJ/mol (11, 13), and it becomes smaller as the polysulfide chain length decreases.

**Chronoamperometry.**—Figure 4 shows typical chronoamperometric curves at the graphite and Ni-Cr electrodes in a nitrogen atmosphere. The steady state was reached at the Ni-Cr electrode within about 25s, whereas the current continuously decreased even after 300s at the graphite electrode. A plot of the current vs. potential at a fixed time at the Ni-Cr electrode was linear, and its slope decreased gradually with time as shown in Fig. 5.

The decrease in current with time shown in the chronoamperometric curves may result from two factors, namely, increasing resistance of the electrode surface and consumption of the reactant. As shown in Fig. 5, there is a linear relation between current and potential or overpotential, i.e., \( i = k(\eta) \), where \( k(\eta) \) is only a function of time, and \( \eta \) is the overpotential; the quantity \( k(\eta) \) can be considered to be the conductivity at time \( t \), and its reciprocal repre-
Fig. 7. Polarization curves at the Ni-Cr electrode the electrode area 0.32 cm², temperature 320°C. (a, left) At the initial time (t = 0.5s); (b, right) at steady state.

Fig. 8. Relationship between resistance and time at the Ni-Cr electrode, electrode area 0.32 cm², temperature 320°C.

Fig. 9. The relationship between resistance and the integral of the current at the present time minus the current at the steady state, the Ni-Cr electrode, the electrode area 0.32 cm², temperature 320°C.

Fig. 10. Cathodic chronopotentiometric curves at graphite electrode, temperature 300°C, I_app = 5 mA, electrode area 0.071 cm²; curve 1, N₂ bubbling; curve 2, after 0.5h of H₂S bubbling; curve 3, after 1h or longer of H₂S bubbling.

Chronopotentiometry.—The current at steady state represents the reaction rate of a chemical reaction between the reaction product and the bulk electrolyte, or of the mass transport rate from the surface to the bulk or vice versa. A higher current at a steady state corresponds to a higher exchange rate between the product of the electrode reaction and the melt. The chronopotentiometric technique can identify reactions at the electrodes and trans-
When the experiment was carried out after H$_2$S bubbling containing H$_2$S was used. The second plateau occurs at the potential with time occurred when pure nitrogen gas or a mixture of H$_2$S and nitrogen gases was bubbled through the melt. The first transition time increases when a gas mixture of H$_2$S and nitrogen gases was bubbled through the melt. The first transition time increases when a gas containing H$_2$S was used. The second plateau occurs at the same potential, and is independent of the gas composition. When the experiment was carried out after H$_2$S bubbling for 1h or longer, the potential oscillated after the second plateau occurred. The following processes may take place during the cathodic polarization at a constant current. Within the first plateau, higher polysulfide species are reduced to a lower polysulfide species. Gradual accumulation of the resulting species near the electrode surface will finally form a continuous film, resulting in a sharp rise in the potential. However, the species in this phase is not a solid film and is reducible at more negative potentials. As the potential reaches the values where reduction occurs, another plateau appears. The product formed in the second plateau may form a continuous film, causing another sharp rise in potential. The presence of H$_2$S delayed the formation of these continuous films near the electrode surface.

Figure 11 shows potential decay curves after the currents were interrupted. As expected, two potential plateaus appear on this curve, at about $-0.28$V and at about $-0.4$V, respectively. The short plateau at $-0.4$V shows that the film is very thin, which may indicate that the electrolyte can react with the reaction product and remove it from the surface, so that the film never becomes very thick. The equilibrium potential of the redox couple Na$_2$S$_2$/Na$_2$S is $-0.35$V (12). Activation and concentration overpotentials may cause the potential to shift about $50$ mV in the cathodic direction. Therefore, the two phases may be Na$_2$S$_2$ at $-0.28$V and Na$_2$S at $-0.4$V, respectively. The latter is probably in a solid state because here the potential increased greater.

The identical shapes of the curves in Fig. 10 indicates that the reaction mechanism did not change when H$_2$S gas was bubbled through the melt; however, the change in transition time suggests that mass transport has been enhanced. This may be due to the removal of the product of reactions of sodium polysulfide near the surface through chemical reactions, such as reaction [1] and the following

$$\text{Na}_2\text{S}_2 + \text{H}_2\text{S} \rightleftharpoons \text{NaH}_2\text{S}_2 + \text{NaH}_2\text{S}$$

[4]

When Na$_2$S is formed, removal of Na$_2$S$_2$ may involve the following reactions

$$\text{Na}_2\text{S} + \text{H}_2\text{S} \rightleftharpoons \text{NaH}_2\text{S}_2$$

[5]

$$\text{Na}_2\text{S} + \text{H}_2\text{S} \rightleftharpoons \text{NaH}_2\text{S}_2 + \text{H}_2$$

[6]

The potential oscillation after the second potential plateau may then result from continuous removal of Na$_2$S$_2$ from the surface. Figure 11 shows that the plateau at $-0.4$V becomes shorter, and even disappears when the containing gas H$_2$S was bubbled through the melt.

**Conclusions**

The electrochemical behavior of sodium tetrasulfide melt at graphite and the Ni-Cr electrodes in the presence of hydrogen sulfide is complicated, and has not been fully elucidated. However, the following conclusions were derived within the limit of the experiments performed in this work: two continuous phases on the electrodes, apparently Na$_2$S$_2$ and Na$_2$S, formed at $-0.28$ and $-0.4$V vs. Na$_2$S$_2$/Na$_2$S during the cathodic polarization. However, the blocking effect by these layers on the Ni-Cr electrode was much less significant than on graphite. The presence of H$_2$S did not influence the reactions occurring at the electrodes, but significantly reduced the formation rate of continuous phases (either Na$_2$S$_2$ or Na$_2$S) during cathodic polarization. The effect of H$_2$S on the formation of these films may be due to chemical processes such as reaction [1] and [2] occurring near the electrodes. A small amount of hydrogen gas was

![Graphical representation](image-url)
formed at these potentials, possibly by a chemical reaction between polysulfides and hydrogen sulfide.

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REFERENCES

The Use of Sodium Ion Conducting Glasses in Na/S(IV) Molten Chloroaaluminate Electrochemical Cells

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Rechargeable molten salt cells of the type Na$_3$Al$_2$O$_3$/SCl$_2$ in AlCl$_3$-NaCl, have previously been studied in our laboratory (1-4). The cells operate typically at 180-250°C, and, when fully charged so that the sulfur is in the $S^{4+}$ oxidation state, have an open-circuit voltage of about 4.3V. Many cells, with capacities in the range 1-20 A-h have been built and tested, and development of the system is in progress.

A number of sodium ion conducting glasses have recently been made and tested by Bloom and co-workers (5, 6). These glasses have been used, for example, in conjunction with narrow $\alpha$-alumina tubes as separators in contact with molten sodium, polysulfides, and AlCl$_3$-NaCl mixtures (7, 8).

The present note reports on studies directed toward the possibility of using these sodium ion conducting glasses as separators in small Na/S(IV) molten chloroaaluminate cells.

Experimental

AlCl$_3$ (Fluka, puriss.) was further purified and NaCl (Mallinckrodt, reagent grade) was dried using standard procedures (9). Sodium metal (Fisher, certified) was filtered through Pyrex wool before use. All transfers and weighing of reagents were carried out in a nitrogen-filled dry box. Cells were sealed, but, as an added precaution, weighing of reagents were carried out in a nitrogen-filled dry box. Cells were sealed, but, as an added precaution, weighing of reagents were carried out in a nitrogen-filled dry box. Cells were sealed, but, as an added precaution, weighing of reagents were carried out in a nitrogen-filled dry box.

"T-glass" (6) was used as the sodium ion conducting glass in this study. It has a high linear expansion coefficient ($15 \times 10^{-4}$ K$^{-1}$) as compared to $3.2 \times 10^{-6}$ K$^{-1}$ for Pyrex glass), an important consideration in using it for cell fabrication. Two types of cells were used. In cell (a), a circular disk of T-glass (ca. 3.0 mm diam, 1.0 mm thick) was connected to a short tube of soda glass (3.0 mm id) via a graded seal made from glass mixtures of intermediate coefficients of expansion. The soda glass was in turn attached to a Pyrex tube via a second graded seal. This assembly was used as the inner compartment in a small Pyrex cell of concentric design similar to previous designs which used tubes of $\beta$-alumina as the inner compartment (1).

In cells of type (b), a T-glass membrane was used to seal one end of a short length of $\alpha$-alumina tubing (1.6 mm id, 3.0 mm od), which then served as the inner compartment of a concentric cell with an outer compartment of Pyrex. Swagelok fittings were used both to seal the open end of the $\alpha$-alumina tube and to couple this tube to the Pyrex outer compartment.

Tungsten wires served as current collectors in both types of cell. The inner compartment generally held the premelted mixture of sulfur, AlCl$_3$, and NaCl, with sulfur being the limiting reagent.

Results

Prior to the construction of the cells, weight loss tests were performed on the four sodium ion conducting glasses listed in Table I to determine their stability in a melt of AlCl$_3$-NaCl (63:37 mole percent [m/o]). Small pieces (ca. 100 mg) of the glasses were sealed in Pyrex tubes containing the AlCl$_3$-NaCl mixture, and the tubes were then heated to 205-210°C. After 14 days, the glasses all showed weight losses of at most 0.7%, which was considered to be

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