THE ELECTROCHEMICAL BEHAVIOR OF SULFIDE IONS IN MOLTEN CRYOLITE

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ABSTRACT

The electrochemical behavior of sulfide ions in molten cryolite (Na$_3$AlF$_6$) has been studied by cyclic voltammetry using graphite electrodes at 1323 K. The oxidation of sulfide ions is found to proceed via a quasi-reversible mechanism, i.e., one in which the current is controlled by both diffusion and charge transfer kinetics,

\[ \text{S}^2^- \xrightarrow{k_g, \theta} \text{S} + 2e^- \]

The transfer coefficient $\theta$ and the standard rate constant $k_g$ are estimated to be 0.5 and 0.0042 cm/sec, respectively. The apparent diffusion coefficient for sulfide ions in cryolite at 1323 K is about $3.93 \times 10^{-5}$ cm$^2$/sec.

INTRODUCTION

Since the work of Delarue (1,2) on the anodic oxidation of sulfide ions in molten salts, many investigations have been published on the subject. However, as indicated by the reviews (3-5) written on the electrochemical behavior of sulfide ions in molten salts, the mechanism of the reaction is still controversial and cannot be interpreted in an unambiguous manner.

The electrochemical behavior of sulfide ions in molten salts is of considerable interest from both fundamental and applied viewpoints. The oxidation of sulfide ions offers challenging fundamental research since the chemistry and electrochemistry of sulfur-sulfide in molten systems are quite complex. From the applied viewpoint, knowledge of the electrochemical reaction of sulfide is important for (i) battery technology such as high-temperature secondary batteries (6) and (ii) metallurgical molten-salt processes such as metal electrowinning from sulfides (5).

Most of the previous such studies reported in the literature were carried out on sulfides in chloride melts at a temperature range of
700-850 K. Recently, in connection with research on the production of aluminum via the electrolysis of \( \text{Al}_2\text{S}_3 \), the present authors investigated the anodic oxidation of sulfide in \( \text{MgCl}_2-\text{NaCl-KCl} \) eutectic (7), \( \text{AlCl}_3-\text{MgCl}_2-\text{NaCl-KCl} \) melts (8), and \( \text{LiF-NaF} \) eutectic (9) at a higher temperature (1023 K). The electrochemical behavior of sulfide in molten cryolite (\( \text{Na}_3\text{AlF}_6 \)) at 1323 K was also studied using the technique of cyclic voltammetry. The results obtained from that study are presented in this paper.

**EXPERIMENTAL**

The cell in the present work consisted of three electrodes inserted into a pyrolytic boron nitride crucible (5.2 cm dia., 7.2 cm high, Union Carbide) containing a blended mixture of molten cryolite and \( \text{Al}_2\text{S}_3 \). The boron nitride crucible was dipped into alumina granules held in a stainless steel crucible. The steel crucible was placed inside a furnace tube. The flanged top of the furnace tube was sealed to another flange consisting of inlet ports that provided access to the melt. The furnace tube was heated by a three-zone Mellen furnace (Model C-2-121) with a Mellen temperature controller (Model 919).

A three-electrode system was used for all measurements. The working electrode was a graphite rod (0.63 cm dia., Union Carbide, grade ECV) insulated with hot-pressed boron nitride (Carborundum) so that only a defined surface area was exposed to the molten salt. Another graphite rod served as the counter electrode. A Pt wire was used as a quasi-reference electrode.

The molten salt was prepared from an accurately weighed and blended mixture of cryolite and \( \text{Al}_2\text{S}_3 \) reagent (Cerac Pure, 99.9% pure) inside a helium atmosphere glovebox. The mixture was charged into the boron nitride crucible and brought out of the glovebox, and the cell was quickly assembled under argon. An argon atmosphere was maintained above the cell in all experiments. For cyclic voltammetric measurements, standard voltammetric instrumentation was employed.

**RESULTS AND DISCUSSION**

For background information, voltammetry of pure cryolite without sulfide added was carried out. A typical voltammogram of the melt at 1323 K is shown in Fig. 1. The voltammetric curves for cryolite resemble those reported in the literature for \( \text{Na}_3\text{AlF}_6 \) (10, 11) and \( \text{NaF} \) (12). The steeply rising cathodic current observed at about -0.5 V vs. Pt reference electrode (all potentials given vs. Pt reference electrode) is attributed to aluminum deposition. An anodic peak was observed at approximately +2.5V. This anodic peak represents the so-called critical current, i.e., the maximum current that is attained before the normal anode reaction is superseded by the anode effect, which is attributable to dewetting of the electrode by fluorocarbon compounds.
As shown in Fig. 2, the background current of molten cryolite is quite small in the potential range +0.6 to -0.2V. Within this potential range, voltammograms of the cryolite melt containing Al2S3 show a pair of peaks: the anodic oxidation of sulfide ions and, on the reverse scan, the cathodic reduction of the oxidation products (Fig. 3).

The anodic oxidation of sulfide in cryolite was studied at two Al2S3 concentrations, 1.3 x 10^{-5} and 3.1 x 10^{-5} mol/cm^3. Voltammograms for 1.3 x 10^{-5} mol/cm^3 sulfide in cryolite melt at sweep rates of 10-500 mV/sec are shown in Fig. 3. The properties of the voltammetric curves obtained at both sulfide concentrations can be summarized as follows:

(i) Peak potential for the oxidation of sulfide, E^a⁰, shifts anodically with increasing sweep rate, v.

(ii) Plots of the peak current, i_p, vs. the square root of sweep rate, v^{1/2}, are straight lines (Fig. 4). The slope of these lines is proportional to the concentration of Al2S3.

(iii) The separation between the anodic peak potential and the cathodic peak potential, |E^a⁰ - E^c⁰|, increases as v increases (Table I).

| Potential Separation Data* for the Oxidation of Sulfide in Cryolite at 1323 K |
|---------------------------------------------|---------------------------------------------|
| 1.3 x 10^{-5} mol/cm^3 Al2S3 | 3.1 x 10^{-5} mol/cm^3 Al2S3 |
| v(mV/sec) | [E^a_p - E^c_p] (mV) | [E^a_p - E^c_p] (mV) |
| 10 | 125 | 125 |
| 20 | 120 | 125 |
| 50 | 185 | 180 |
| 100 | 285 | 290 |
| 200 | 360 | 345 |
| 500 | 500 | 490 |

*Corrected for ohmic drop.

The above properties are in agreement with the criteria for a quasi-reversible charge-transfer mechanism (13), i.e., one in which the current is controlled by both diffusion and charge transfer kinetics. For this type of reaction mechanism, if the sweep rate is slow enough, the reaction approaches reversible behavior. At slow sweep rates, at 1323 K, the anodic-to-cathodic peak separation and the peak-to-half-peak separation of a quasi-reversible reaction approach 253/n and
126.5/n mV, respectively, where n is the number of electrons involved in the electrochemical reaction. The voltammograms indicate that, at sweep rates of 10 and 20 mV/sec, the reactions obtained for sulfide ions are reversible, and the experimental values for the potential separations suggest two as the number of electrons involved for the anodic oxidation of sulfide ions. Using the Randles-Sevcik equation for reversible reactions (13) and the experimental values for i_p at 10 and 20 mV/sec, an average value of 3.93 x 10^{-5} cm^2/sec was obtained for the diffusion coefficient of sulfide in molten cryolite at 1323 K.

Thus, it is hypothesized that the oxidation of sulfide ions in cryolite involves the following reaction:

\[
S_2^2- \rightarrow S + 2e^- (1)
\]

where k_S is the standard heterogeneous rate constant and \( \beta \) is the transfer coefficient.

The shape of the voltammogram for a quasi-reversible oxidation reaction depends on \( \beta \) and \( k_S \). For large values of \( \beta \), the anodic peak is much sharper and the peak current is larger than those of the corresponding cathodic peak. The opposite is true for small values of \( \beta \). For \( \beta = 0.5 \), the anodic-to-cathodic peak current ratio is equal to unity. The experimental values for the ratio of anodic-to-cathodic peak currents obtained at different sweep rates and the two different sulfide concentrations in this study are approximately one, thus suggesting that \( \beta = 0.5 \).

The standard heterogeneous rate constant \( k_S \) can be derived from a working curve, developed by Nicholson (14), showing variation of the peak separation \( |E_p^a - E_p^c| \) with the kinetic parameter \( \psi \), which is defined as

\[
\psi = \frac{k_S}{(nFv \sqrt{RTD})^{1/2}}
\]

where \( F \) is the Faraday, \( D \) is the diffusion coefficient, \( R \) is the universal gas constant, and \( T \) is the temperature. It was found that only the values of peak separation at 100 and 200 mV/sec in Table I could be used to estimate \( k_S \). From these peak separation values and Nicholson's working curve, \( k_S \) was calculated to be about \( 4.2 \times 10^{-3} \) cm/sec.
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Fig. 1 Voltammogram of Molten Cryolite. $T = 1323$ K, Electrode Area = 0.32 cm$^2$, $v = 100$ mV/sec.

Fig. 2 Background Current of Molten Cryolite in the Potential Range +0.6 to -0.2V. $T = 1323$ K, Electrode Area = 0.32 cm$^2$, $v = 100$ mV/sec.
Fig. 3 Voltammograms of the Oxidation of Sulfide Ions in Molten Cryolite at Different Sweep Rates. $T = 1323 \, K$, Electrode Area = 0.32 cm$^2$, Concentration = $1.3 \times 10^{-5}$ mol/cm$^3$

Fig. 4 Plots of $i_p$ vs. $v^{1/2}$ for the Anodic Oxidation of Sulfide Ions in Cryolite. $T = 1323 \, K$, Electrode Area = 0.32 cm$^2$

$\Delta$: $1.3 \times 10^{-5}$ mol/cm$^3$, $\circ$: $3.1 \times 10^{-5}$ mol/cm$^3$