SPECTROELECTROCHEMICAL AND OTHER STUDIES OF SULFUR AND ITS HALIDES IN CHLOROALUMINATE MELTS: APPLICATION TO A NEW RECHARGEABLE HIGH VOLTAGE LOW TEMPERATURE CELL

G. Mamantov, V. E. Norvell, L. Klatt, K. Tanemoto, R. Marassi, Y. Ogata, M. Matsunaga, J. P. Wiaux, and C. B. Mamantov

Department of Chemistry, The University of Tennessee
Knoxville, Tennessee 37916
and the
Analytical Chemistry Division, Oak Ridge National Laboratory,* Oak Ridge, TN 37830

ABSTRACT

The electrooxidation of sulfur in molten AlCl$_3$-NaCl has been investigated by means of UV-visible and electron spin resonance spectroelectrochemistry and ring-disk voltammetry. An electrode reaction sequence for the oxidation of S$_2$ to S(IV) is presented. The use of tetravalent sulfur as a positive electrode material for a rechargeable molten salt cell is briefly discussed.

INTRODUCTION

It has been previously shown (1) that sulfur dissolved in acidic (AlCl$_3$-rich) chloroaluminate melts (AlCl$_3$-NaCl mixtures) can be electrochemically oxidized in three steps to yield tetravalent sulfur. Bulk coulometry (1) and preliminary spectroelectrochemical results (2) indicated that the first oxidation step yields at least two species. Coulometry (1) indicated that the products of the second and third oxidation steps are S(I) and S(IV), respectively.

Based on published electrochemical and spectrophotometric studies, a reaction scheme was proposed for oxidation of sulfur in acidic chloroaluminate melts which involved S$_2^+$, S$_{16}^{2+}$, S$_8^{2+}$, S$_2^{2+}$, and S(IV) at various stages in the oxidation (1). Previous studies of sulfur cations in oleum and superacid solvents (3-5) and in chloroaluminate melts (6,7) have indicated the existence of several species which were not observed electrochemically. This work has involved ESR spectroelectrochemistry (8), additional UV-visible absorption spectroelectrochemistry (8), and ring-disc voltammetry (9) which have provided a better understanding of the pathways involved in the electrochemical oxidation of sulfur in chloroaluminate melts. The

*Operated by Union Carbide Corporation for the Department of Energy.

By acceptance of this article, the publisher or recipient acknowledges the U. S. Government's right to retain a non-exclusive, royalty-free license in and to any copyright covering the article.
experimental details and description of the instrumentation used for the spectroelectrochemical studies are available (2,8).

The feasibility of using tetravalent sulfur as a positive electrode material in rechargeable molten chloroaluminate cells has been demonstrated previously (10-17). Laboratory cells of the type

\[
\text{Na/Na}^+ \text{ ion conductor/SCl}_3^+ \text{ in molten AlCl}_3\text{-NaCl}
\]

have an open circuit voltage of 4.2V and high energy densities; they operate at temperatures in the range of 180-250°C. A brief description of such cells is included in this paper.

RESULTS AND DISCUSSION

Ring-Disc Voltammetry.— Voltammograms obtained at a rotating glassy carbon ring-disc electrode in the AlCl₃-NaCl (53-47 mole % = 53/47) melt at 200°C are shown in Fig. 1. The voltammogram obtained at the disc electrode is in good agreement with prior results obtained by other electrochemical methods at stationary electrodes in more acidic melts (63/37) at higher temperatures (1). Such an agreement is reasonable since for chloroaluminate melts an increase in temperature results in a smaller pCl (18). The potential of the ring electrode was kept at a value at which the positive oxidation states of sulfur should be reduced to elemental sulfur. The voltammogram obtained at the ring electrode indicates that the reduction of products is observed as expected.

ESR Studies.— ESR measurements of sulfur oxidized either chemically or electrochemically in chloroaluminate melts indicate the presence of at least three radicals (19). ESR spectroelectrochemical experiments involving oxidation of sulfur at an optically transparent electrode (OTE) at 132-225°C also produced three signals with g-values of 2.0277 (A), 2.0155 (B) and ~2.013 (C). The potential dependence of these three radicals at 132°C, shown in Fig. 2, indicates that signal A reaches its maximum intensity at a less positive potential than does signal C. This suggests that radical A contains sulfur in a lower formal oxidation state than radical C.

This relationship is supported by studies of sulfur radicals with the same g-values which were produced in other solvents (3-5). Hyperfine splitting analysis has determined that radical C is S₅⁺ (5). The nature of radical A is uncertain as no hyperfine splitting data are available, however, experimental evidence has shown that this radical is formed under less oxidizing conditions than required for S₅⁺ (3,4). The earlier belief that this lower oxidation state radical was S₇⁺ (3) has lately been questioned (4), and the matter remains unresolved.

The signal for the third radical observed in the melt, B, is weak in intensity compared to A and C (at 132°C), and it appears to
have a different lineshape. The nature of this radical remains to be
determined, and it will not be considered further here.

UV-Visible Spectroelectrochemical Studies.— UV-visible spectro-
electrochemical measurements on sulfur cations produced in the first
oxidation step at 150–250° yield absorption bands with maxima at 600,
730 and 960nm, and a shoulder around 450nm (Fig.3). An additional
shoulder, not shown in the Figure, is observed in the 330–350 nm
region. The 600nm band has previously been assigned to $S_8^{2+}$, and the
450, 730 and 960 nm bands have been attributed to $S_{16}^{2+}$ (2,6,7). The
absorption in the 330–350 nm region has not been assigned to any spec-
cific species in the melt, however, a similar spectral feature ob-
served by Gillespie and coworkers in liquid $SO_2$ was attributed to a
$S_{19}^{2+}$ cation (4).

The observed potential dependence of the 600,730 and 960 nm bands,
as illustrated in Fig. 4, is consistent with the relative formal oxi-
dation states of the species assigned to them. A comparison of Figs.
2 and 4 suggests a chemical relationship between the radical A and
$S_{16}^{2+}$, and likewise between C and $S_8^{2+}$. Such equilibria have been
proposed earlier in other solvents (3), however, because of subsequent
studies (4), these simple equilibria may no longer be valid.

Further information on the nature of the equilibria in the melt
was obtained by studying the effect of sulfur concentration on the
absorption bands. These studies indicate that the lower oxidation
state products are favored at higher sulfur concentrations. This re-
sult is consistent with bulk coulometry measurements(1). Analysis of
absorbance vs. time curves for the visible absorption bands indicates
that $S_{16}^{2+}$ and radical A are formed initially. These products are
involved in chemical reactions and equilibria, however, as the elec-
trode potential becomes more positive, they are eventually oxidized
further to form $S_8^{2+}$ and $S_5^{2+}$.

It is clear that an unequivocal reaction sequence for this sulfur
oxidation in the melt cannot be formulated due to uncertainties in
some of the species involved, particularly radical A. A reaction
sequence which supports the experimental data may, however, be sug-
gested if we assume that radical A is $S_8^{2+}$. This hypothesis is
supported by voltammetric data which indicate that a simple one elec-
tron transfer is the first step in the oxidation of $S_8$ in the melt (1).
A reaction sequence based on this hypothesis is shown below:

$$S_8 = S_8^{2+} + e \quad [1]$$
$$2S_8^{2+} \rightleftharpoons S_{16}^{2+} \quad [2]$$
$$S_8^{2+} = S_8^{2+} + e \quad [3]$$
$$S_8^{2+} + S_8 \rightleftharpoons S_{16}^{2+} \quad [4]$$
$$S_{16}^{2+} + S_8^{2+} \rightleftharpoons S_5^{2+} + S_{19}^{2+} \quad [5]$$
The second sulfur oxidation step results in the formation of S(II), probably as S$_2$Cl$^+$ (1). Fig. 5 illustrates spectra obtained when S(II) is produced at a platinum OTE. The spectrum at 1.85V applied to the OTE is in good agreement with the spectrum obtained when S$_2$Cl$_2$ is dissolved in the melt; it is also consistent with the "calculated" spectrum given by Fehrmann et al. (6). Nernst plots were constructed for several reactions proposed for this oxidation step, using the spectroelectrochemical data to calculate the ratio [O]/[R]. The resulting plots suggest that the following reactions are most probable:

$$ S_8^{2+} + S_8 \leftrightarrow 8S_5^+ \quad [6] $$

$$ S_8^{2+} = 4S_2^{2+} + 6e \quad [7] $$

$$ 2S_5^+ = 5S_2^{2+} + 8e \quad [8] $$

It is possible that these reactions proceed through an S$_4^{2+}$ intermediate, however, the spectroelectrochemical data do not conclusively provide such evidence. S$_4^{2+}$ is known to exist in other solvents (3), and Fehrmann et al. (6) have previously postulated its existence in chloroaluminate melts.

The third oxidation step yields S(IV) which has no absorption maxima in the spectral range studied (6). As S$_2^{2+}$ is oxidized to S(IV), the spectroelectrochemical data indicate the presence of at least two absorbing species. Therefore, this oxidation step may also proceed through an intermediate species, probably involving sulfur in the +2 oxidation state. The overall oxidation step may be described by the following reaction:

$$ S_2^{2+} = 2S(IV) + 6e \quad [9] $$

Application to a Rechargeable Cell.- As mentioned earlier, tetravalent sulfur is being utilized in a new low temperature molten salt rechargeable cell (16,17)

$$ \text{Na/}\beta\text{-alumina/SCl}_3^+ \text{ in molten AlCl}_3-\text{NaCl}. $$

The discharge process involves the reduction of S(IV) to elemental sulfur, which can be reduced further to sulfide.

Typical galvanostatic charge-discharge curves for a cell used to study the discharge of sulfur (IV) to sulfur and the potential of each electrode vs. an aluminum reference electrode are shown in Fig. 6. Most cells had AlCl$_3$/NaCl molar ratios of ~70/30 before discharge and ~50/50 at the end of discharge. High energy density values, large percent utilization of the active positive electrode material and good energy efficiency have been demonstrated. The performance of cells prepared in the discharged and charged states was found to be the
One cell was operated continuously for more than 10 months; 476 deep charge-discharge cycles were attained.

ACKNOWLEDGEMENTS

We would like to acknowledge the collaboration of R. Livingston, H. Zeldes, and M. Conradi, Chemistry Division, Oak Ridge National Laboratory, in obtaining preliminary electron spin resonance spectra of sulfur radicals in chloroaluminate melts. We would also like to thank Professor J. Q. Chambers for the use of his ESR spectrometer. This work has been supported by the Department of Energy, Contract EY-76-S05-5053, University of California Subcontract 4502810 and the NSF Grant CHE 77-21370. Support by the U. S. Department of Energy, Basic Energy Sciences is also acknowledged. VEN acknowledges receipt of an Oak Ridge Associated Universities Fellowship.

REFERENCES

1. R. Marassi, G. Mamantov, M. Matsunaga, S. E. Springer, and J. P. Wiaux, J. Electrochem. Soc., 126, 231 (1979).
2. G. Mamantov, V. E. Norvell, and L. N. Klatt, J. Electrochem. Soc., 127, 1768 (1980).
3. R. J. Gillespie and J. Passmore, in "Advances in Inorganic Chemistry and Radiochemistry," Vol. 17, H. J. Emelius and A. G. Sharpe, Editors, pp. 49-89, Academic Press, New York (1975).
4. R. C. Burns, R. J. Gillespie, and J. F. Sawyer, Inorg. Chem., 19, 1423 (1980).
5. H. S. Low and R. A. Beaudet, J. Amer. Chem. Soc., 98, 3849 (1976).
6. R. Fehrmann, N. J. Bjerrum, and F. W. Poulsen, Inorg. Chem., 17, 1195 (1978).
7. N. J. Bjerrum, in "Characterization of Solutes in Non–Aqueous Solvents," G. Mamantov, Editor, pp. 251–271, Plenum Press, New York (1978).
8. V. E. Norvell, K. Tanemoto, G. Mamantov and L. N. Klatt, J. Electrochem. Soc., in press.
9. G. Mamantov and C. B. Mamantov, unpublished work.
10. G. Mamantov, R. Marassi and J. Q. Chambers, "High Energy Cathodes for Fused Salt Batteries," Technical Report ECOM–0060–F, April 1974.
11. G. Mamantov, R. Marassi, and J. Q. Chambers, Abstract 8, p. 24, The Electrochemical Society Extended Abstracts, New York, N. Y., October 13–17, 1974.
12. G. Mamantov, R. Marassi, and J. Q. Chambers, U.S. Pat. 3,966,491 (1976).
13. G. Mamantov, R. Marassi, J. P. Wiaux, S. E. Springer, and E. J. Frazer, Abstract 89, p. 243, The Electrochemical Society Extended Abstracts, Atlanta, Georgia, October 9–14, 1977.
14. G. Mamantov and R. Marassi, U.S. Pat. 4,063,005 (1977).
15. G. Mamantov, R. Marassi, J. P. Wiaux, S. E. Springer and E. J. Frazer, in "Proceedings of the Symposium on Load Leveling," N. P. Yao and J. R. Selman, Editors, pp. 379–383, The Electrochemical
16. G. Mamantov, R. Marassi, M. Matsunaga, Y. Ogata, J. P. Wiaux and E. J. Frazer, J. Electrochem. Soc., 127, 2319 (1980).

17. G. Mamantov, R. Marassi, Y. Ogata, M. Matsunaga and J. P. Wiaux, in "Proceedings of 15th Intersociety Energy Conversion Engineering Conference," Volume 1, 809107, Seattle, Wash., August 18-22, 1980, American Institute of Aeronautics and Astronautics.

18. G. Torsi and G. Mamantov, Inorg. Chem., 11, 1439 (1972).

19. R. Livingston, G. Mamantov, J. P. Wiaux, H. Zeldes, M. Conradi, and R. Marassi, unpublished work.
Fig. 1. Current-voltage curve at glassy carbon RRDE in 0.8x10^{-2} M sulfur in 53/47 AlCl3/NaCl melt at 200 °C.

Fig. 2. Potential dependence plot for radicals A, B, and C. Sulfur concentration (as monomer): 8.20x10^{-3} molal.
Fig. 3. Absorption spectra of the products of the first sulfur oxidation step for two temperatures. Applied potentials: 1.30V (---), 1.50V (-------), 1.60V (--------), 1.70V (-----). Sulfur concentration: 1.50 X 10^{-2} molal.

Fig. 4. Potential dependence plot for the absorption bands shown in Fig. 3 at 150°C. o, 600 nm; ●, 730 nm; △, 960 nm.
calculation for the process.

8.6% Percent utilization for

from heating at 850°C. Decharge time

and no electrodes (a) reference to

curves and percentage of (a) (a)

Figure 6. An instantaneous change-decharge

concentration: 1.35 x 10^{-2} mol/L.

1.824 (a) (-) 1.859 (a) 1.775

Figure 5. Absorption spectra of the products of the second

phase.

2.0 3.0 4.0