The Determination of Electronic Transport Properties in Molten Sodium Sulfate at 1173 K

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ABSTRACT

The electronic conductivity of molten Na_2SO_4 has been investigated by the steady state polarization method of Wagner and Hebb. It is noted that the electronic conductivity in the melt occurs mainly due to the electrons. The transient relaxation method was employed to determine the diffusion coefficient of electrons and its average value was 3.15×10^{-3} (cm^2/sec) at 1173 K. Corresponding to a drift mobility of 0.031 $cm^2/V\text{-}S$.

1. INTRODUCTION

Metals and alloys for gas turbines and aircraft engines, especially those operating in a marine atmosphere or on low grade fuels, may experience an accelerated oxidation rate in the temperature range of 1033–1273 K. This form of attack is known as hot corrosion, which is mainly attributed to the condensation of molten Na_2SO_4 salt. The hot corrosion process has been described mainly by chemical models i.e., the acidic-basic fluxing models /1–3/ and the dissolution-reprecipitation models /4/. Recently, the idea that the hot corrosion mechanism involves electrochemical reactions has been studied by several authors /5,6/,

However, little is known about the transport properties in molten Na_2SO_4. Hence, this study is concerned with obtaining such information to aid in the elucidation of the mechanisms of the process.

The d.c. polarization technique advanced by Wagner and Hebb /7,8/ was applied to study the partial electronic conductivities of molten Na_2SO_4 at 1173 K. From the polarization measurements the product of the drift mobility u_i (cm^2/sec) and the concentration c_i ($particle/cm^3$) of the species i may be determined by the relation with conductivity, σ_i:

$$\sigma_i = q\ c_i\ u_i \qquad (1)$$

where q is the elementary charge.

Measurements of voltage relaxation were carried out to obtain the diffusion coefficient of the predominant electronic species in the melt. From the above relationship the concentration of the corresponding species can be calculated.

2. THEORETICAL BACKGROUND

The idea that an appropriate choice of electrodes enables the suppression of either ionic or electronic transport in a galvanic cell provides the basis for the polaization technique. This technique has been extensively employed to investigate electronic conductivity in ionic solids /9–14/ and has also been applied to a few molten systems /15–17/.

Wagner /7/ has derived the appropriate relation for the polarization conditions from transport theory. This relation states that, under steady state conditions, the total current due to passage of electronic species through the polarization cell is given by

$$I_{elect} = I_\theta + I_\oplus \qquad (2)$$

$$= \frac{RTA}{LF}\left\{ \sigma^o_\theta\left[1 - \exp\left(-\frac{EF}{RT}\right)\right] + \sigma^o_\oplus\left[\exp\left(\frac{EF}{RT}\right) - 1\right]\right\}$$

where I_θ, $I_\oplus$: electron and electron hole currents, respectively

$\sigma_\theta{}^\circ$,$\sigma_\oplus{}^\circ$: electron and electron hole conductivity, respectively
E : actual applied voltage
F : Faraday constant
R : gas constant
T : temperature (K)
L/A : cell constant.

In the derivation of Eq. (2) it is assumed /16,17/ that

(i) excess electrons and holes follow the laws of ideal dilute solutions,
(ii) their mobilities are independent of concentrations,
(iii) the change in the concentration of atomic defects arising from thermal disorder with variation in the metal to nonmetal ratio is small,
(iv) convection in the melt is negligible.

The division of Eq (2) by [1-exp(-EF/RT)] and rearrangement gives

$$I_{elect} \left\{ \frac{LF}{RTA} \, \frac{1}{\left[1 - \exp\left(-\frac{EF}{RT}\right) \right]} \right\} = \sigma_\theta^o + \sigma_\oplus^o \exp\left(\frac{EF}{RT}\right) \tag{3}$$

and a plot of the left hand side of Eq. 3 versus exp (EF/RT) gives $\sigma_\theta{}^\circ$ as the intercept and $\sigma_\oplus{}^\circ$ as the slope.

In the present work, D.C. current flowing through the polarization cell is measured at various applied voltages which are kept below the decomposition potentials of the sample to ensure that the measured current is only the electronic current.

If the electron conductivity of a pure Na_2SO_4 melt is somewhat more predominant than the electron hole conductivity at a given Na_2SO activity i.e., $\sigma_\theta{}^\circ \gg \sigma_\oplus{}^\circ$, then Eq. 2 provides:

$$I_{elect} \cong I_\theta = \frac{RTA}{LF} \sigma_\theta^o \left[1 - \exp\left(-\frac{EF}{RT}\right) \right] \tag{4}$$

Rearranging the above equation gives:

$$I_\theta \times \frac{LF}{RTA} = \sigma_\theta^o \left[1 - \exp\left(-\frac{EF}{RT}\right) \right] \tag{5}$$

A plot of lefthand side versus [l-exp(-EF/RT)] thus yields a straight line with a slope $\sigma_\theta{}^o$ and an intercept zero. Similarly, plotting ln [I_θ x (LF/RTA)] versus ln [l-exp(-EF/RT)] gives a straight line of a slope unity and an intercept ln $\sigma_\theta{}^o$ if Eq. 4 is true for all values of E applied. In this case, $\sigma_\theta{}^o$ can be determined from the plot of the Eq. 5 or a plot ln [I_θ x (LF/RTA)] versus ln [l-exp(-EF/RT)].

Voltage Relaxation Method

The steady state polarization method of Wagner and Hebb provides only the product of the concentration and

$$\sigma_i = \frac{c_i D_i q^2}{kT} \tag{6}$$

$$D_i = u_i \frac{kT}{q} \tag{7}$$

either the drift mobility or the diffusion coefficient of species i according to the following equations /18/:

where D_i is the diffusion coefficient of species i, k is Boltzman constant and T is the absolute temperature.

The voltage relaxation method was employed to separate the contributions of the concentration and the mobility to the electronic conductivity of a Na_2SO_4 melt. In this technique the same cell as used for d.c. polarization measurement was polarized until a steady state current was reached. Assuming that the diffusion coefficients are not dependent on the concentration and that concentrations are sufficiently low to anticipate ideal behavior, linear concentration profiles may be established for the predominantly conducting electronic species. Thus, the polarization cell is biased at steady state and at time zero. If the electrons are the major charge carriers and the applied potential is removed, a relaxation of the cell voltage can be observed as a function of time, which is given by /19/:

$$E(t) = -\frac{kT}{q} \ln \frac{C_\theta(t)}{C_\theta^o} \tag{8}$$

where E(t): measured potential difference across the cell as function of time

$C_\theta(t)$: time dependent electron concentration at the melt/inert electrode interface

$C_\theta{}^o$: electron concentration at the melt/reference electrode interface.

Fick's second law may be applied for this case where there is a concentration gradient across the electrolyte of length L:

$$\frac{\partial C_\theta}{\partial t} = D_\theta \frac{\partial^2 C_\theta}{\partial x^2} \tag{9}$$

An initial linear change in concentration and the constant concentration at both electrodes at all times were the boundary conditions for Eq. (9). The solution of Fick's second law is derived from the literature /20,21/ to give:

$$\frac{C_\theta(t) - C_\theta^o}{C_\theta - C_\theta^o} = \frac{2}{L}\sqrt{D\,t} \left\{ \frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty} (-1)^n \,\mathrm{ierfc}\, \frac{nL}{\sqrt{D\,t}} \right\} \tag{10}$$

If $Dt << L^2$ then Eq. (10) becomes:

$$\frac{C_\theta(t) - C_\theta^o}{C_\theta - C_\theta^o} = \frac{2}{L}\sqrt{D\,t}\,\left(\frac{1}{\sqrt{\pi}} + 1\right) \tag{11}$$

The substitution of Eq. (11) in Eq. (8) provides:

$$E\,(t) = -\frac{k\,T}{q} \ln\left[1 + \frac{2}{L}\left(\frac{C_\theta - C_\theta^o}{C_\theta^o}\right)\sqrt{\frac{D\,t}{\pi}}\right] \cong \mathrm{const} + \frac{2\,k\,T}{qL}\sqrt{\frac{D\,t}{\pi}} \tag{12}$$

Thus, the slope of a plot of E(t) versus square root time will yield the value of the diffusion coefficient and hence the drift mobility of electrons.

3. EXPERIMENTAL PROGRAM

Mass flow controllers (MKS Model 1259 B) coupled with 4 channel readout (MKS Type 247 C) were utilized to fix the activity of sodium oxide in the melt by using gas mixtures. A schematic experimental arrangement is shown in Fig. 1. Commercial SO_2 + O_2 gas mixtures from Liquid Carbonic co. were utilized to fix the acidity of the melt at 1173 K. A constant voltage was supplied to the polarization cell via the EG & G Model 273 potentiostat and the current was measured as a function of time by using an IBM PC computer. A Solid State electrometer, Keithley Model 610C, was utilized to check the actual potential on the polarization cell. The reference electrode was a silver wire immersed into a 10 m/o Ag_2SO_4/Na_2SO_4 melt contained in the Na ion conducting membrane, a mullite tube (0.7 cm O.D) /21/. Platinum wires were employed to lead two gold electrodes into the potentiostat. Pure gold crucibles were used for these experiments. The distance between the two gold electrodes was fixed at 0.7 cm, the height of the molten salt was 1.3 cm, and the blocking electrode was placed 0.4 cm from the bottom of the crucible. An alumina shield was involved, so that the electronic species could travel only the edge of one electrode to that of the other via the molten salts. An anhydrous ultrapure sodium sulfate from Alfa Products was used without further treatment. An A.C. impedance technique was utilized to determine the cell constant with the same cell geometry by measuring the conductivity of an 0.1 N KCl solution instead of the molten salts /22/.

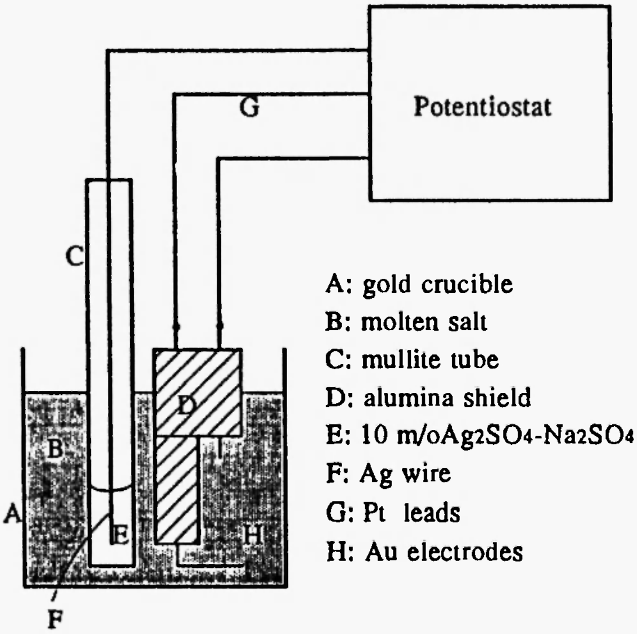

Fig. 1. Schematic cell arrangement for d.c. polarization experiment.

4. RESULTS AND DISCUSSION

The Wagner-Hebb type polarization technique was used to determine the partial electronic conductivity of a pure Na_2SO_4 melt as a function of Na_2O activity at 1173

K. The theoretical basis for this experimental technique has been given by Wagner and Hebb. The appropriate equations from transport theory in which the ionic currents are suppressed were given by Eq. (2) and Eq. (3). As shown in Eq. (2), the total current that is observed between such electrodes under steady state condition changes with the applied potential as the sum of two electronic contributions. Fig. 2 shows that the electronic contributions increases logarithmically as a function of potential. This indicates that the measured current is mostly due to the electrons, i.e., the second term of the righthand side of Eq. (2) is negligible. An example of the graphical interpretation of Eq. (3) for a pure Na_2SO_4 melt at an Na_2O activity of 10^{-11} is shown in Fig. 3. The MINITAB program at the Pennsylvania State University was utilized for regression analysis to obtain a slope and an intercept of the plot. The results give an electron conductivity of 1.617×10^{-3} (ohm–cm)$^{-1}$ and an electron hole conductivity of 1.407×10^{-5} (ohm–cm)$^{-1}$ in a pure Na_2SO_4 melt when the Na_2O activity equals 10^{-11}.

Thus, the partial conductivities of electrons and electron holes were obtained as a function of Na_2O activity in the melt and are depicted in Fig. 4. It can be seen that electron conduction in pure Na_2SO_4 is considerably larger than that of electron holes over the entire Na_2O activity range. Furthermore, it is noted that both electron and electron hold conductivities remain relatively constant regardless of the changes in Na_2O activities. Thus, the partial electronic conductivities of a pure Na_2SO_4 melt are not dependent on the acidity and/or basicity of the melt.

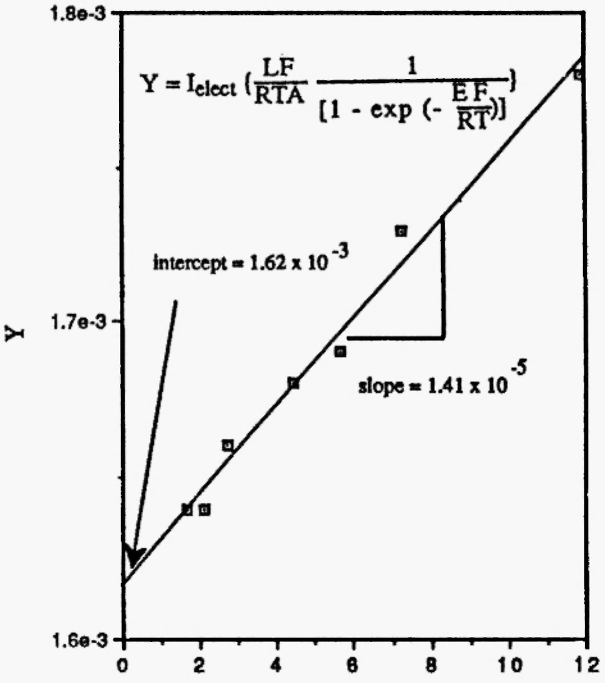

Fig. 2. Current vs. potential in a pure Na_2SO_4 melt at a log a_{Na_2O} equals to −11 at 1173 K.

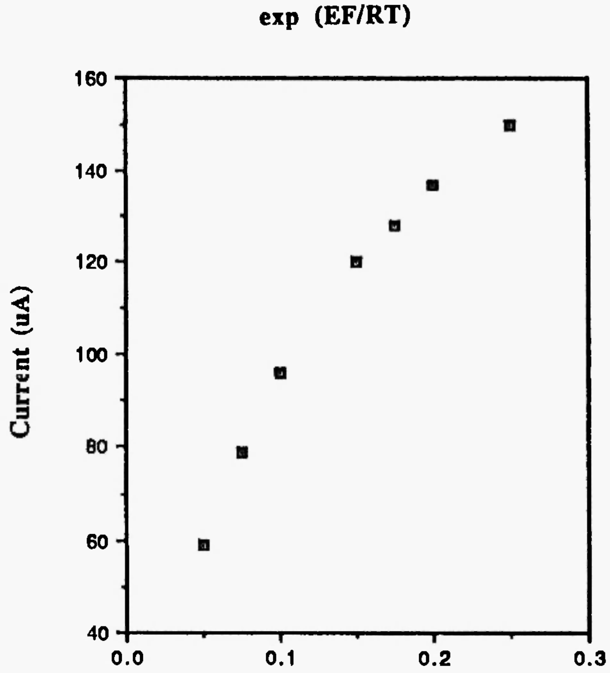

Fig. 3. Y versus exp (EF/RT) in a pure Na_2SO_4 melt at a log a_{Na_2O} equals to −11 at 1173 K.

From the results shown in Fig. 4, it is assumed that the electron hole conductivity in a Na_2SO_4 melt is negligible as compared to the electron conductivity. The validity of the assumption was examined by Eq. (5) which is plotted as shown in Fig. 5. The slope of the plot was taken as the electron conductivity of the melt and the differences in results from Fig. 3 and Fig. 5 are not significant. Thus, the assumption that the electron conductivity is predominant was applicable for a pure sodium sulfate melt at the given experimental atmosphere.

The voltage relaxation method suggested by Weiss

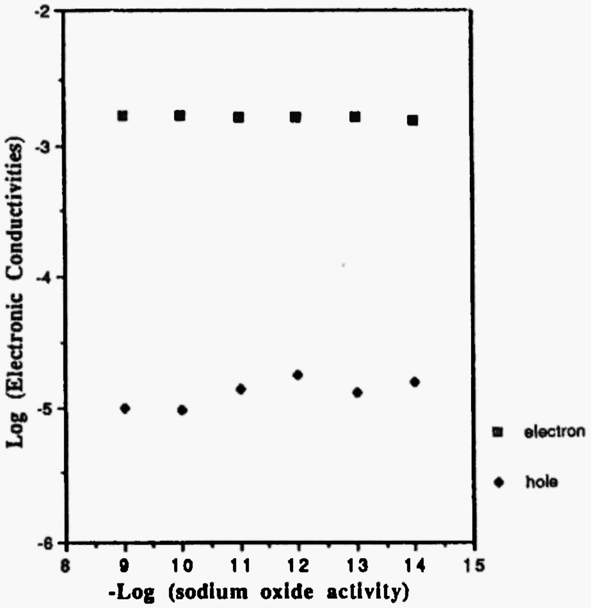

Fig. 4. Electronic conductivities in a pure Na_2SO_4 melt as a function of Na_2O activity at 1173 K. to −11 at 1173 K.

was applied to determine the diffusion coefficient of the electrons in a Na_2SO_4 melt at 1173 K. One typical example of the potential change as a function of square root time is shown in Fig. 6 when the Na_2O activity is 10^{-11}. The square root law of the voltage-time relationship as described in Eq. (10) was applied since a linear decay of the potential was observed as a function of square root time.

Raleigh /23/ mentioned that the possible serious interference due to the charging of the electrical double layer electrolyte/inert electrode interface must be considered when using the voltage relaxation method. At high double layer capacitance and low bulk concentrations of the electronic species, the observed decay of the cell potential might be governed by the relaxation of the double layer charge. The possible error due to the double layer charge was estimated with the assumption that drainage of the double layer charge was predominant rather than the diffusion of the electronic species in the electrolyte when the cell potential was removed. An electron conductivity of 1.68×10^{-3} $(\text{ohm-cm})^{-1}$, the distance between the electrodes, L, of 0.7 cm and the double layer capacitance, $C_{d.l.}$, of 120 uF/cm^2 /24/ at 1173 K were used to evaluate the cell voltage and time relationship according to equation /23/:

$$-\frac{dE}{dt} = \frac{RT\sigma_\theta^o}{FLC_{d.l.}}\left\{1-\exp\left(-\frac{EF}{RT}\right)\right\}$$

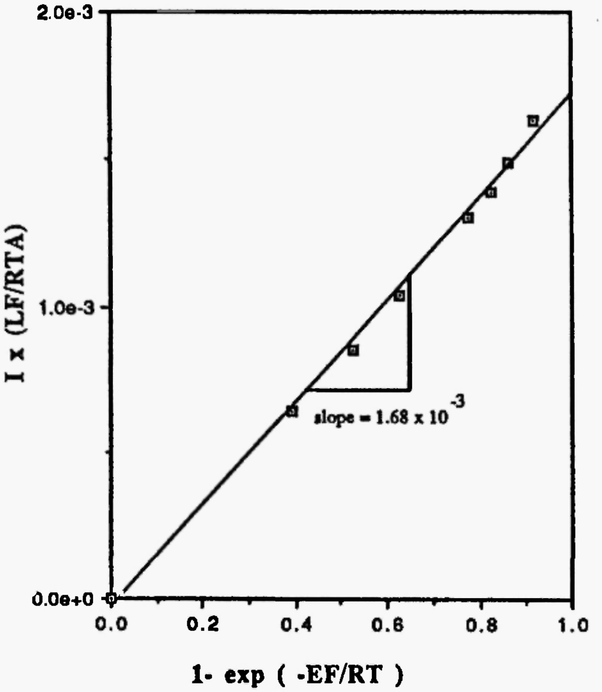

Fig. 5. I x (LF/RTA) vs. 1-exp(-EF/RT) in a pure Na_2SO_4 melt as a function of Na_2O activity at 1173 K.

The corresponding voltage relaxation due only to the double layer charge was estimated. The calculated shows that within the applied voltage range of 0.05–0.25 volt, the potential relaxation due to the double layer charge is much faster than the experimentally observed potential decay. For example, the cell potential reaches 1×10^{-4} volt in less than 1 second from the applied potential. This indicates that the double layer effect on the voltage relaxation cell involved in this study is hardly detectable.

The diffusion coefficient of electrons, which are the major minor defects in a Na_2SO_4 melt, was determined from the slope of straight lines in Fig. 6 and its average value is 3.15 (±0.17) × 10^{-3} cm^2/sec according to Eq. (10). The corresponding drift mobility of electrons is 0.031 (±0.002) $cm^2/volt$ sec. The concentration of electrons in the melt is calculated as 3.29×10^{17} $particles/cm^3$. The mobility of electrons in molten KCl have been reported to be 0.03 cm^2/volt sec at 1093 K /25/ and in molten NaCl it was 0.034 cm^2/volt sec at 1166 K /26/.

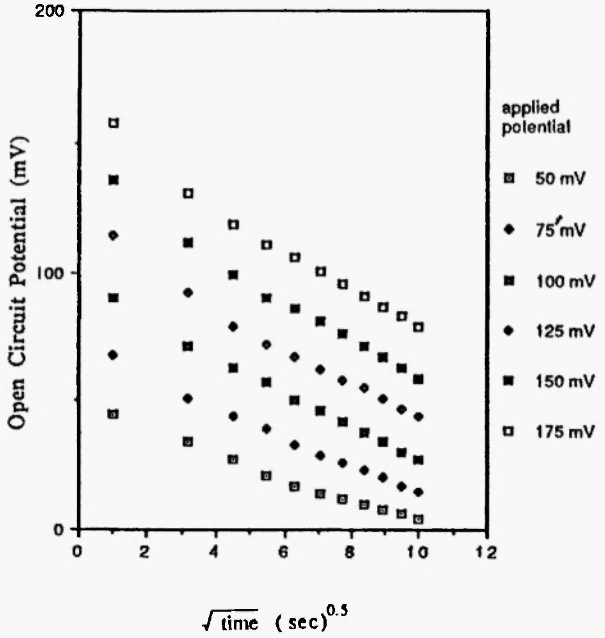

Fig. 6. Potential decay as a function of square root time in a pure Na_2SO_4 melt as a function of Na_2O activity at 1173 K.

ACKNOWLEDGEMENTS

The authors are pleased to acknowledge the office of Naval Research for the financial support of their project on contract No. N0014-86-K-0133. Discussion with our monitor Dr. A.J. Sedricks of ONR were most helpful.

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