In order to aid in further understanding hot corrosion processes, investigations of the electrical behavior of molten Na₂SO₄ have been undertaken. Wagner-Hebb type polarization experiments and total electrical conductivity measurements by an A.C. impedance technique were carried out on melts of Na₂SO₄, both pure and those containing 10⁻³ m/o, 1.8x10⁻¹ m/o, and supersaturated (10 m/o) NiO, as a function of Na₂O activity at 1173 K. Additionally, the relative contributions of cation versus anion transport in the molten sodium sulfate was investigated by employing a potentiostatic polarization technique.
It was observed that the total electrical conductivity of pure Na$_2$SO$_4$ was of the order of $2.57 \times 10^{-1}$ (ohm-cm)$^{-1}$ and varied only slightly with changes in the activity of Na$_2$O. From the Wagner-Hebb type D.C. polarization experiments on pure Na$_2$SO$_4$, the electron conductivity was shown to be much greater than the electron hole conductivity over the entire range of Na$_2$O activities. The partial conductivity of electrons in Na$_2$SO$_4$ was about three orders of magnitude less than the total electrical conductivity. Thus, transport number of electrons, $t_e$, is of the order of $10^{-4}$ in a pure Na$_2$SO$_4$ melt at 1173 K. From the potentiostatic polarization technique, the cation transport number of a pure sodium sulfate melt was about 0.86 at 1173 K.

The introduction of NiO into Na$_2$SO$_4$ melts at 1173 K did not produce massive changes in the total electrical conductivities of these melts as compared to those of a pure Na$_2$SO$_4$ melt. However, the addition of NiO in the melt decreases the electronic conductivities as well as the transport numbers of electronic species, regardless of the concentrations of NiO in the melt at 1173 K.
ABSTRACT

In order to aid in further understanding hot corrosion processes, investigations of the electrical behavior of molten Na$_2$SO$_4$ have been undertaken. Wagner-Hebb type polarization experiments and total electrical conductivity measurements by an A.C. impedance technique were carried out on melts of Na$_2$SO$_4$, both pure and those containing $10^{-3}$ m/o, $1.8 \times 10^{-1}$ m/o, and supersaturated (10 m/o) NiO, as a function of Na$_2$O activity at 1173 K. Additionally, the relative contributions of cation versus anion transport in the molten sodium sulfate was investigated by employing a potentiostatic polarization technique.

It was observed that the total electrical conductivity of pure Na$_2$SO$_4$ was of the order of $2.57 \times 10^{-4}$ (ohm cm)$^{-1}$ and varied only slightly with changes in the activity of Na$_2$O. From the Wagner-Hebb type D.C. polarization experiments on pure Na$_2$SO$_4$, the electron conductivity was shown to be much greater than the electron hole conductivity over the entire range of Na$_2$O activities. The partial conductivity of electrons in Na$_2$SO$_4$ was about three orders of magnitude less than the total electrical conductivity. Thus, transport number of electrons, $t_e$, is of the order of $10^{-4}$ in a pure Na$_2$SO$_4$ melt at 1173 K. From the potentiostatic polarization technique, the cation transport number of a pure sodium sulfate melt was about 0.86 at 1173 K.

The introduction of NiO into Na$_2$SO$_4$ melts at 1173 K did not produce massive changes in the total electrical conductivities of these melts as compared to those of a pure Na$_2$SO$_4$ melt. However, the addition of NiO in the melt decreases the electronic conductivities as well as the transport numbers of electronic species, regardless of the concentrations of NiO in the melt at 1173 K.
I. INTRODUCTION

Hot corrosion is generally defined in broad terms as an accelerated or catastrophic oxidation of alloys and other materials. This form of attack is particularly severe in the temperature range of 1033 - 1273 K and it has affected both aircraft engines and industrial gas turbines. There is a general agreement that condensed alkali metal salts, notably Na2SO4, are a prerequisite to hot corrosion. The source of this salt may be (a) the direct ingestion of sea salt in a marine environment, (b) the formation of Na2SO4 during combustion of fuels containing both sodium and sulfur, (c) the formation of Na2SO4, during combustion, from sodium - contaminated, airborne dust and sulfur in the fuel [1].

The exact mechanisms of hot corrosion are still uncertain, but from many studies on the hot corrosion mechanisms of metals and alloys, the various mechanisms that have been proposed can be broadly classified into two categories: (a) acidic - basic fluxing models [2-4] and (b) dissolution - reprecipitation electrochemical model [5]. The overall mechanisms of hot corrosion involve the dissolution of normally protective oxide layers and the formation of porous, nonadherent, and hence unprotective scales when alloy surfaces are covered by a thin film of liquid sodium sulfate. It appears that the initial formation of metal oxides is necessary for the initial reaction and the transport of oxygen through the molten salt phase is required to form such metal oxides.

Little is known about the electronic transport properties in molten Na2SO4. This study is, therefore, concerned with obtaining such information to aid in the elucidation of the mechanism of the process. A potentiostatic polarization technique was employed to estimate the ionic transport numbers of a pure sodium sulfate melt at 1173 K. The electronic conductivities by Wagner-Hebb type polarization studies [6,7] as well as total electrical conductivity measurements by an A.C. impedance technique were carried out on molten Na2SO4 as a function of Na2O activities at 1173 K since the proposed models...
which describe the degradation behavior of alloys are strongly dependent on SO$_2$, O$_2$, and/or SO$_3$ gas pressure, i.e., the Na$_2$O activity in the Na$_2$SO$_4$ deposit. The transport numbers of electronic species in Na$_2$SO$_4$ melt were evaluated by dividing the values of electronic conductivities by those of total electrical conductivities. Additionally, such studies were conducted in molten Na$_2$SO$_4$ containing NiO to elucidate the effect of NiO on the transport mechanism in the Na$_2$SO$_4$ melt at 1173 K.

II. THEORETICAL BACKGROUND

(i) Total Conductivity Measurement

A.C. impedance measurements were conducted to obtain polarization free total electrical conductivity of molten sodium sulfate and the melts containing NiO. In D.C. techniques, a space charge of either ions or electrons form in the vicinity of the electrodes, which leads to a non-uniform field across the specimen. However, in A.C. impedance techniques, the use of small amplitude sinusoidal potentials does not disturb the electrode properties and at higher frequencies polarization at the specimen electrode may be eliminated. Thus, an A.C. impedance technique was utilized to measure the resistance of a pure Na$_2$SO$_4$ melt and melts containing NiO since the melts showed some polarization effects at the electrodes in our preliminary D.C. experiments.

Impedance can be thought of as the resistance of a circuit to an alternating waveform; as opposed to a pure resistance it has not only magnitude but also direction - phase angle. One of the advantages of A.C. impedance techniques over conventional D.C. electrical conductivity efforts is the ability to separate the real and imaginary components of impedance. An impedance, $Z$, can be completely defined by specifying the magnitude, $|Z|$, and the angle, $\phi$, or alternatively by specifying the magnitude of its real, $Z'$, and imaginary, $Z''$, components [8].
There are a number of graphical interpretations available for impedance data analysis over a wide frequency range [9]. A plot of $Z'$ versus $wZ''$ was employed to evaluate the resistance of the molten salts. A plot of $Z'$ versus $wZ''$ shows a straight line with a slope of $-R_pC$ and an intercept of $R_\Omega + R_p$ according to the following equation:

$$Z' = R_\Omega + R_p - R_p C w Z''$$  \hspace{1cm} (2.1)

where $Z'$ is the real part of the impedance  
$Z''$ is the imaginary part of the impedance  
$R_\Omega$ is the resistance of the electrolyte  
$R_p$ is the polarization resistance  
$C$ is the capacitance  
$w$ is angular frequency ($= 2\pi f$)

The real and imaginary part of the impedance can be expressed by the following relationship [10].

$$Z' = R_\Omega + \frac{R_p}{1 + w^2C^2R_p^2}$$  \hspace{1cm} (2.2)

$$Z'' = \frac{wCR_p^2}{1 + w^2C^2R_p^2}$$  \hspace{1cm} (2.3)

Thus, as frequency increases the straight line of a plot of $Z'$ versus $wZ''$ levels off and the projection of this point onto the $Z'$ axis affords the sum of the resistances of the electrolyte and the circuit leads according to the equation (2.2).
(ii) Electronic Conductivity Measurement

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 polarization technique. This technique has been extensively employed to investigate electronic conductivity in ionic solids [11-16] and has also been applied to a few molten systems [17-19].

Wagner [6] 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

\[
I_{\text{elec}} = I_0 + I_\oplus
\]

\[
= \frac{RTA}{LF} \left\{ \sigma_0^* \left[ 1 - \exp \left( -\frac{EF}{RT} \right) \right] + \sigma_\oplus^* \left[ \exp \left( \frac{EF}{RT} \right) - 1 \right] \right\} \tag{2.4}
\]

where \( I_0, I_\oplus \): electron and electron hole currents, respectively

\( \sigma_0^*, \sigma_\oplus^* \): electron and electron hole conductivity, respectively

\( E \): applied voltage

\( F \): Faraday constant

\( R \): gas constant

\( T \): temperature (K)

\( L/A \): cell constant.

In the derivation of equation (2.4) it is assumed [18,19] 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 equation (2.4) by \([1-exp(-EF/RT)]\) and rearrangement gives

\[
I_{\text{elect}} \left\{ \frac{LF}{RTA} \left[ \frac{1}{1-exp\left(-\frac{EF}{RT}\right)} \right] \right\} = \sigma^0 + \sigma^\Phi \exp\left(\frac{EF}{RT}\right) \tag{2.5}
\]

and a plot of the left hand side of equation (2.5) versus \(exp\ (EF/RT)\) gives \(\sigma^0\) as the intercept and \(\sigma^\Phi\) as the slope. These values, combined with total electrical conductivity results, permit the evaluation of the transport numbers of each electronic carrier in the molten salts.

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.

(iii) Evaluation of Ionic Transport Numbers

The potentiostatic polarization cell technique was employed to determine ionic transport numbers for molten sodium sulfate at 1173 K. In a recent application of this technique reasonable agreement was obtained with transport numbers from Tubandt and tracer diffusion techniques [20]. This technique is based on a two electrode cell. A constant D.C. potential is applied by a potentiostat and the current is monitored as a
function of time. The electrode is chosen to be reversible with respect to the cation present in the electrolyte.

Under the influence of a D.C. field cations migrate to the negative electrode and anions to the positive electrode. As the concentration of anions increases near the positive electrode, local charge neutrality requires that a cation accompany each anion. This process establishes a salt concentration gradient across the electrolyte. As the cell polarizes the amount of current carried by the anion decreases but the amount carried by the cation remains constant. When the back potential created by the concentration gradient exactly opposes the applied potential the anions no longer carry current and the cell is completely polarized with respect to the anion. Thus, the ratio of final current, due to the cation only, to the initial current, due to the cation and anion, yields the cation transport numbers of molten Na$_2$SO$_4$.

III. EXPERIMENTAL PROGRAM

(i) Gas Control

Variations on our previous measurements [21] was performed. In particular instead of using the SO$_2$/O$_2$ obtained by flowing helium over a ZnO/ZnSO$_4$ mixture mass flow control meters (MKS Model 1259B) coupled with 4 channel readout (MKS Type 247C) was utilized for better control of SO$_2$/O$_2$ ratios.

(ii) A.C. Impedance Measurements

A.C. impedance measurements were performed to obtain polarization free total electrical conductivity. As shown in Figure 1, the three electrode system was utilized for the A.C. impedance measurements. The reference electrode was a silver wire immersed into a 10 m/o Ag$_2$SO$_4$/Na$_2$SO$_4$ melt contained in the Na ion conducting membrane, mullite
tube (0.7 cm O.D.) [22]. Pure gold wires serve as the working electrode and counter electrode. Platinum wires welded to those electrodes were employed as leads to connect to the EG & G Model 273 potentiostat coupled with Model 5208 Lock-In amplifier. The schematic arrangements for the A.C. impedance measurements are depicted in Figure 2.

The total electrical conductivity of a pure Na2SO4 melt and the melts containing various oxides was determined by measuring the resistance of the melts from the relation:

\[ R = \left( \frac{1}{\sigma} \right) \text{Cell Constant} \quad (3.1) \]

where \( R \) is the resistance measured in ohms, \( \sigma \) is the conductivity of the melt expressed in \((\text{ohm-cm})^{-1}\) and the cell constant is given in terms of \( \text{cm}^{-1} \).

The cell constant, which is a characteristic of the conductivity cell, depends on the length between the electrodes and the surface area of the electrode exposed to the melt. The cell constant is usually predetermined by measuring the resistance across an ionic solution of known specific conductivity. Since the specific conductivity values of KCl solution are well established [23], an 0.1 N KCl solution was employed to determine the cell constant for the proposed work. The cell constant measurements were conducted at about 250°C utilizing identical cell arrangements with the gold crucible to contain an 0.1 N potassium chloride solution instead of the melt.

(iii) Wagner - Hebb Type Polarization Experiments

Wagner-Hebb type polarization technique was used to determine the partial electronic conductivities of a pure Na2SO4 melt and melts containing NiO as a function of Na2O activity at 1173 K.
A constant voltage was supplied to the polarization cell via a Keithley 260 Nanovolt Source as shown in Figure 3. A Keithley Digital Multimeter, Model 177 was used as an ammeter. A Solid State Electrometer, Model 610C was utilized to check the actual voltage on the polarization cell.

Figure 4 shows the details of the polarization cell arrangements. Platinum wires were employed to lead gold electrodes into the power source and multimeter. Pure gold crucibles were used for these experiments. 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.

(iv) Potentiostatic Polarization Experiment

Most molten salts are ionic conductors. Thus, it seems logical to assume that molten sodium sulfate is an ionic conductor. The relative contributions of the different carrier species (cation vs. anion) was investigated by this technique.

A constant D.C. potential was applied via a Keithley 260 Nanovolt Source and the current was monitored by using a Keithley Digital Multimeter Model 177.

A symmetric cell configuration was employed and the electrode was chosen to match the cation in the molten sodium sulfate. The reversible electrode consists of a mullite tube conductive to sodium ions, containing a silver electrode immersed into a melt of Ag$_2$SO$_4$-90 m/o Na$_2$SO$_4$. Mullite is a two-phase ceramic consisting of mullite grains (3Al$_2$O$_3$ - 2SiO$_2$) enveloped by silica. At high temperatures dissolved alkali metal compounds in the silica film allow transport of alkali metal cations under an electrochemical driving force with essentially no electronic conduction [24,25].
IV. RESULTS and DISCUSSION

(i) Pure Na$_2$SO$_4$

The measured total electrical conductivities of a pure Na$_2$SO$_4$ at 1173 K are depicted in Figure 5 as a function of the activity of Na$_2$O in the melt. The total electrical conductivities remain rather constant regardless of the changes in Na$_2$O activities. The total electrical conductivity of a pure Na$_2$SO$_4$ melt was averaged as 0.257 (ohm-cm)$^{-1}$ which is about one order of magnitude smaller than the literature values [26-29]. This discrepancy is most probably caused by the facts that the previous investigators had: (1) a relatively impure Na$_2$SO$_4$, (2) a reaction between their quartz capillary and molten sodium sulfate, and (3) a reaction with their Pt electrodes. It was observed that there was significant deterioration of the quartz crucibles used to contain the Na$_2$SO$_4$ melts in our preliminary work and that there was a reaction of Na$_2$SO$_4$ melts with Pt electrodes initially utilized.

From the Wagner-Hebb type polarization measurements on pure Na$_2$SO$_4$ melt at 1173 K the partial conductivities of electrons and electron holes were obtained and are depicted in Figure 6. It can be seen that electron conduction in pure Na$_2$SO$_4$ is considerably larger than that of electron holes over the entire Na$_2$O activity range. Furthermore, it is noted that both electron and electron hole conductivities remain relatively constant regardless of the changes in Na$_2$O activities. Thus, the total electrical conductivity as well as partial electronic conductivities of a pure Na$_2$SO$_4$ melt are not dependent on the acidity and/or basicity of the melt.

From the measured values of total electrical conductivities and electronic conductivities, the transport numbers of electronic species may be computed. These numbers are plotted in Figure 7 for a pure Na$_2$SO$_4$ melt. The transport numbers of electrons are of the order of $10^{-4}$ while those of electron holes are of the order of $10^{-6}$. 
This indicates that the electronic conduction in a pure Na$_2$SO$_4$ melt arises primarily via electron transport over the whole Na$_2$O activity range. The transport numbers of electronic species in molten salts have not been measured extensively but the few that have been measured are somewhat larger than those determined in this study, e.g., $t_e = 3 \times 10^{-3}$ in the molten eutectic of LiCl-KCl at 450°C [30].

(ii) Na$_2$SO$_4$ Melt Containing NiO

Ni based alloys have been used as construction materials for numerous applications at high temperatures. The simultaneous oxidation and hot corrosion of these alloys in SO$_2$ and O$_2$ gas mixture environments cause serious degradation of these materials. High temperature corrosion of Ni based alloys with gaseous SO$_2$ and O$_2$ have been well documented [31-38]. It is proposed that such serious degradation is due to the fluxing of protective oxide scales by the molten salts.

The present work was performed to assist in understanding the effect of NiO on the behavior of the electronic species in the melt in equilibrium with gaseous SO$_2$ and O$_2$. This work included measuring the total electrical conductivity by an A.C. impedance technique and conducting Wagner-Hebb type polarization experiments in the Na$_2$SO$_4$ melt containing NiO as a function of Na$_2$O activity at 1173 K.

The measured total conductivity of a pure Na$_2$SO$_4$ and the melts containing 10$^{-3}$ m/o, 1.8 x 10$^{-1}$ m/o, and supersaturated (10 m/o) NiO are shown in Figure 8 as a function of Na$_2$O activity at 1173 K. The total electrical conductivities remain rather constant regardless of the change in Na$_2$O activities and change in the amount of NiO in the melt. These results are somewhat contradictory to the proposed hot corrosion models [2-5] which describe the degradation behavior of the alloys as strongly dependent on the Na$_2$O activity in the molten sodium sulfate. Thus, efforts to check our previous results utilizing
certified SO2/O2 gas mixtures will be made on a pure Na2SO4 melt and the melts containing NiO. It is noted that the introduction of NiO into a Na2SO4 melt does not show massive changes in total electrical conductivities as compared to those of a pure Na2SO4 melt. These results indicate that the mobilities of the ions resulting from the dissolution of NiO are not significantly different from the ions present in the Na2SO4 melt. Thus, a phase stability diagram, constructed from the thermodynamic data, will be utilized to relate the responsible solute species to the electrical behavior of the molten salts. The choice of log PO2 and log PSO3 as coordinates for a phase stability plot has an advantage of explaining the possible species of metal oxides in the Na2SO4 melt as a function of the acidity of the melt.

The electronic conductivities observed for the melts containing NiO are shown in Figures 9 to 11. Basically, these results show that electron conductivities remain higher than the electron hole conductivities at all concentrations of NiO and throughout the entire range of Na2O activities. Thus, the changes in acidity and/or basicity of the melt due to the introduction of NiO does not produce significant differences in partial electronic conductivities. However, the addition of NiO in molten Na2SO4 slightly decreases the electronic conductivities over the whole Na2O activity range compared to those of a pure Na2SO4 melt. In addition, the results show an increase in electron conductivities in the low Na2O activity region, especially for the melt containing supersaturated (10 m/o) NiO as shown in Figure 11. This behavior may relate to the dissolution products of NiO in the low Na2O activity region.

Combining total electrical conductivities and partial electronic conductivities it is possible to calculate the transport numbers of electronic species in the melt with the additions of NiO. These results are plotted in Figures 12 to 14, for the melts containing 10^{-3} m/o, 1.8x10^{-1} m/o, and supersaturated (10 m/o) NiO, respectively. It can be seen that the transport numbers of electrons remain consistently higher than those of electron holes in accord with the partial and total electrical conductivities. These results imply that
the electrons are the major species contributing to the electronic conduction in such melts. It is noted that there is a significant increase in the transport numbers of electrons in the low Na2O activity region in the melt containing supersaturated (10 m/o) NiO as shown in Figure 14. This resulted from the greater increase in electron conductivities than the increase in total electrical conductivities in this region.

(ii) Ionic Transport in Molten Salts

It is generally observed [39-41] that Na\textsuperscript{+} ion conductivity prevails in solid Na\textsubscript{2}SO\textsubscript{4} (235-883 C) and that the partial electronic conductivity is negligible. Thus the electrode for the potentiostatic polarization cell was chosen to be reversible with respect to the cation (Na\textsuperscript{+}) present in the molten sodium sulfate. If the cation reversible electrode works properly, then complete cell polarization is expected when the anion diffusion, created by a salt gradient, exactly opposes the migration of this ion under the influence of the applied potential.

Thus, cations in the melt are the only charge carriers and this was evidenced as a plateau in the current versus time curve as shown in Figure 15. The similar trends were observed at other sodium oxide activities in the melt and the cationic transport numbers of molten sodium sulfate were evaluated by dividing the final current, due to the cation only, by the initial current, due to the cation and anion.

The cationic transport numbers are displayed as a function of Na2O activity in the melt in Figure 16. This result shows the cationic transport numbers are decreased as the sodium oxide activity of the melt are decreased. In another words, the contribution of the possible anion species such as SO\textsubscript{4}\textsuperscript{2-}, S\textsubscript{2}O\textsubscript{7}\textsuperscript{2-} and O\textsuperscript{2-} increases as the acidity of the melt increases.
(iii) Final Remarks

The efforts on this proposal and by others [42] have shown that a number of possible steps in the hot corrosion process are not rate controlling. The diffusion in the gas phase boundary layer, chemical reaction at the gas phase/Na$_2$SO$_4$ interface, diffusion in the boundary layer at the Na$_2$SO$_4$/gas phase and diffusion in the bulk Na$_2$SO$_4$ are not major kinetic controlling steps. Thus, the chemical reaction at the liquid Na$_2$SO$_4$/alloy interface could be a possible rate controlling step. To clarify which of the processes near the liquid Na$_2$SO$_4$/alloy interface is rate controlling for the hot corrosion process, both conductivity and direct hot corrosion tests on Na$_2$SO$_4$ doped with CaSO$_4$ and Na$_3$VO$_4$ are under consideration.

V. SUMMARY AND CONCLUSION

The main thrust of this experimental program was to obtain some of the transport properties in the aggressive molten salt Na$_2$SO$_4$. The total electrical conductivity measurements by an A.C. impedance technique and Wagner-Hebb type polarization experiments provided the total electrical conductivity, electron conductivity, and electron hole conductivity of a pure Na$_2$SO$_4$ melt at 1173 K. From these measurements the transport numbers of electrons, $t_e$, and electron holes, $t_\Phi$, were calculated as follows:

$$t_e = 3.71 \times 10^{-4} ; \quad t_\Phi = 6.95 \times 10^{-6}$$

Such experimental investigations show that the pure Na$_2$SO$_4$ melt had a somewhat low total electrical conductivity and the electronic conduction, which is somewhat lower than that of other molten salts, occurs primarily via the transport of electrons.
The effect of NiO on the electronic conduction as well as total electrical conductivity of the melt was examined by the same methods as applied to a pure Na$_2$SO$_4$ melt. The average values of the total electrical conductivities as well as partial electronic conductivities and their transport numbers are arranged in Tables 1 and 2, respectively. It is apparent from these tables that the addition of NiO does not change the total electrical conductivity significantly but decreases the electronic conductivities and the transport numbers of electronic species when compared to those of pure Na$_2$SO$_4$ melt, although there was a slight increase in partial electronic conductivities in a melt containing supersaturated (10 m/o) NiO, probably due to the dissolution product of NiO in the melt.

The cationic transport numbers of pure Na$_2$SO$_4$ melt was obtained by utilizing the potentiostatic polarization technique. The result indicates that the contribution of the anion species to the ionic current was not negligible especially in the acidic region of the melt.
Table 1. Average values of total electrical conductivities and partial electronic conductivities in a pure Na$_2$SO$_4$ melt and the melt containing NiO at 1173 K.

<table>
<thead>
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<th>Log $\sigma$</th>
<th>Log $\sigma^0$</th>
<th>Log $\sigma^0$</th>
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<tr>
<td>pure Na$_2$SO$_4$</td>
<td>-0.59</td>
<td>-4.03</td>
<td>-5.76</td>
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<td>Na$_2$SO$_4$ with 10$^{-3}$ m/o NiO</td>
<td>-0.64</td>
<td>-5.27</td>
<td>-6.34</td>
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<td>Na$_2$SO$_4$ with 1.8x10$^{-1}$ m/o NiO</td>
<td>-0.57</td>
<td>-5.82</td>
<td>-6.70</td>
</tr>
<tr>
<td>Na$_2$SO$_4$ with 10 m/o NiO</td>
<td>-0.76</td>
<td>-4.32</td>
<td>-5.94</td>
</tr>
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Table 2. Average values of transport numbers of electronic species in a pure Na$_2$SO$_4$ melt and the melt containing NiO at 1173 K.

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<tr>
<td>pure Na$_2$SO$_4$</td>
<td>3.7 x 10$^{-4}$</td>
<td>7.0 x 10$^{-6}$</td>
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<tr>
<td>Na$_2$SO$_4$ with 10$^{-3}$ m/o NiO</td>
<td>2.6 x 10$^{-5}$</td>
<td>2.3 x 10$^{-6}$</td>
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<tr>
<td>Na$_2$SO$_4$ with 1.8x10$^{-1}$ m/o NiO</td>
<td>6.1 x 10$^{-6}$</td>
<td>8.2 x 10$^{-7}$</td>
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<tr>
<td>Na$_2$SO$_4$ with 10 m/o NiO</td>
<td>4.0 x 10$^{-4}$</td>
<td>8.4 x 10$^{-5}$</td>
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Figure 1. Schematic A.C. impedance cell arrangement

Figure 2. Schematic diagram of A.C. impedance experiment
Figure 3. Schematic circuit diagram for Wagner-Hebb type polarization experiment

Figure 4. Wagner-Hebb type polarization cell arrangement
Figure 5. Log (total conductivity) versus Na$_2$O activity in a pure Na$_2$SO$_4$ melt at 1173 K
Figure 6. Electronic conductivities in a pure Na$_2$SO$_4$ melt as a function of Na$_2$O activity at 1173 K.
Figure 7. Transport numbers of electronic species in a pure Na$_2$SO$_4$ melt as a function of Na$_2$O activity at 1173 K.
Figure 8. Log (total conductivity) versus Na$_2$O activity in a Na$_2$SO$_4$ melt containing 10$^{-3}$ m/o, 1.8 $\times$ 10$^{-1}$ m/o, and supersaturated (10 m/o) NiO at 1173 K
Figure 9. Electronic conductivities in a Na$_2$SO$_4$ melt with the addition of $10^{-3}$ m/o NiO as a function of Na$_2$O activity at 1173 K.
Figure 10. Electronic conductivities in a Na$_2$SO$_4$ melt with the addition of 1.8 x 10$^{-1}$ m/o NiO as a function of Na$_2$O activity at 1173 K.
Figure 11. Electronic conductivities in a Na\textsubscript{2}SO\textsubscript{4} melt with supersaturated (10 m/o) NiO as a function of Na\textsubscript{2}O activity at 1173 K
Figure 12. Transport numbers of electronic species in molten Na$_2$SO$_4$ containing 10$^{-3}$ m/o NiO at 1173 K.
Figure 13. Transport numbers of electronic species in molten Na₂SO₄ containing $1.8 \times 10^{-1}$ m/o NiO at 1173 K.
Figure 14. Transport numbers of electronic species in molten Na$_2$SO$_4$ containing supersaturated (10 m/o) NiO at 1173 K
Figure 15. Current versus time plot for the melt at -log (Na$_2$O activity) equals to 14 at 1173 K.
Figure 16. Cationic transport numbers of the Na$_2$SO$_4$ melt as a function of Na$_2$O activity at 1173 K.
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