ELECTRONIC CONDUCTION IN MOLTEN HALIDES

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Abstract

Methods to measure electronic conductivity in molten halides are reviewed. These include increase of total conductivity with addition of metal, polarization techniques, chronopotentiometry, and motion of colored subhalides in a potential gradient. The applicability of the Nernst-Einstein equation and the role of convection are considered. Results are presented for several halide melts. Applications of these results are elucidated, including self-discharge rate of molten salt batteries, measurement of alloy thermodynamics using molten salt electrolytes, and kinetics of tarnishing reactions with formation of liquid films.

Methods to Measure Electronic Conductivity

Molten halides are predominantly ionic conductors, but they also generally possess a smaller but measurable electronic conductivity. Methods used to measure electron and electron hole conductivities are reviewed here and some applications are considered.

In the case of alkali and alkaline earth halides it is usually possible to add excess metal to the molten salts and at the same time to measure the increase in the total electrical conductivity. This increase in conductivity is accepted to be electronic and in some cases becomes greater than the ionic conductivity. Results have been reviewed and tabulated by both Bredig(1) and Corbett(2) so that this technique will not be discussed further here.

When the electronic component of conductivity is much smaller than the ionic conductivity, other methods are necessary and these will be discussed in this article. The so-called polarization technique(3,4) has been extensively employed to measure a small component of electronic conductivity in ionic solids(5-18) and has also been used to...
study electron and electron hole conductivity in molten LiCl-KCl eutectic.\(^{(19)}\) Recent results also have been obtained for NaCl.\(^{(20)}\)

In this method, steady-state currents are measured on cells of the type

\[
Ta(s) \mid NaCl(\ell) \mid NaCl(\ell) + PbCl_2 (1 \text{ mole } \%) \mid Pb(\ell)
\]

(1)

for different applied voltages. The applied voltage is always below the decomposition potential so that only electronic conduction is present.

With this arrangement it has been shown\(^{(4-5)}\) that the steady-state current is given by the expression

\[
i = \frac{RT}{FG} \left( \sigma_e^{ref.} \left[ \exp \left( \frac{EF}{RT} \right) - 1 \right] + \sigma_h^{ref.} \left[ 1 - \exp \left( -\frac{EF}{RT} \right) \right] \right)
\]

(1)

where \(G\) is the cell constant, \(E\) is the applied potential, \(\sigma_e^{ref.}\) is the electron conductivity of the salt equilibrated with the reference electrode, and \(\sigma_h^{ref.}\) is the electron hole conductivity of the salt equilibrated with the reference electrode.

Generally under reducing conditions or high applied potential the electron hole current is negligible so that equation (1) reduces to

\[
i = \frac{RT}{FG} \sigma_e^{ref.} \left[ \exp \left( \frac{EF}{RT} \right) - 1 \right]
\]

(2)

The value of \(\sigma_e^{ref.}\) is obtained from current-potential curves using equation (2). Values of \(\sigma_e\) are calculated at other activities of Na in the melt by the equation

\[
\sigma_e = \sigma_e^{ref.} \left( \frac{a_{Na}}{a_{Na}^{ref.}} \right)
\]

(3)

The activity of Na in the reference compartment, \(a_{Na}^{ref.}\), is measured directly with an auxiliary electrode as shown below or may be calculated by considering the equilibria of the reaction.

\[
Pb + NaCl = PbCl_2 (NaCl) + Na (Pb)
\]

(4)
where \( a_{Na}^{ref.} = \exp \left( -\frac{\Delta G^0}{2RT} \right) \frac{1}{a_{PbCl_2}} \) (5)

\( \Delta G^0 \) being the free energy change for reaction (4) with reactants and products in their standard state and \( a_{PbCl_2} \) the activity of PbCl\(_2\) in the reference compartment. The assumptions underlying equations 1 to 5 imply a cell of constant cross section, a constant mobility of electrons and electron holes, small deviations from ideal metal to nonmetal ratio, free electron concentrations dilute enough so that classical statistics can be applied, and absence of convection in the melt.

Figure 1 shows an experimental arrangement recently used to study molten NaCl. An alumina tube of constant cross section and packed with alumina powder to eliminate convection, is filled with NaCl. An inert tantalum electrode is made negative with respect to the lead pool. A Na-Bi alloy (mole fraction Na = .10) of known Na activity inside of a Vycor tube measures the Na activity of the reference compartment. The Vycor acts as a solid electrolyte conductive to Na\(^+\) ions. The salt in the reference compartment is contained in a large Vycor container. The entire experiment is housed in a larger quartz container which is filled with purified argon. The cell constant is obtained by measuring the AC resistance of the cell.

The current-potential curves obtained with this set-up are shown in Figure 2. From this curve the value of \( \sigma_{ref.} \) may be obtained. Using equation 3, values of \( \sigma_{Na} \) are obtained at other activities and these results are shown in Figure 3. The values of \( \sigma_{Na} \) shown on this figure are obtained from another method which is explained later. Figure 4 shows the results of Bredig and Bronstein\(^{(21)}\) for high activities of Na. At the composition of saturation for Na in NaCl at 830\(^{0}\) where \( a_{Na} = 1 \), the two sets of results can be compared. The square shows results from the polarization method and as can be seen the two methods agree very well.

Figures 5 and 6 show similar results for LiCl-KCl eutectic. These results were obtained using an alumina tube as shown in Figure 1. Previous results\(^{(19)}\) obtained using a Vycor tube are to be supplanted with the results shown here. It is now believed that quartz or Vycor cannot be used in this system, due most probably to an exchange...
which takes place with the salt giving currents which are too large.

Polarization measurements have also been used to measure electron hole conductivity in LiCl-KCl eutectic. The cell used was

\[
\text{C} \mid \text{LiCl-KCl(eut.)} \mid \text{C-Cl}_2
\]

with a Cl\(_2\) reference electrode and a glassy carbon inert electrode. The steady-state current is given by the expression

\[
i = \frac{RT}{FG} \sigma_{\text{ref}}^h [1 - \exp \left( - \frac{EF}{RT} \right)]
\]

where \(E < 1.5\) volts. After \(\sigma_{\text{ref}}^h\) is obtained the electron hole conductivities at other partial pressures of Cl\(_2\) obtained from

\[
\sigma_h = \sigma_{\text{ref}}^h \frac{p_h^{\text{Cl}_2}}{p_{\text{Cl}_2}^{\text{Cl}_2}}
\]

Results are shown in Figure 6. The chlorine partial pressure and lithium activity of the melt are inter-related by the equation

\[
a_{\text{Li}} p_{\text{Cl}_2}^{\text{Li}} = a_{\text{LiCl}} \exp \left( \frac{\Delta G_f^{\text{LiCl}}}{RT} \right)
\]

where \(\Delta G_f^{\text{LiCl}}\) is the free energy of formation of LiCl.

Another method to measure a small component of electronic conduction is a moving boundary technique used by Herzog and Klemm to study PbCl\(_2\). A visible boundary is formed at the interface between PbCl\(_2\) saturated with Pb and unsaturated PbCl\(_2\). By measuring the velocity of this boundary in a potential gradient one can obtain the mobility of trapped electrons in PbCl\(_2\). Thus

\[
u_{\text{sub.}} = \frac{\sigma_{\text{ion}}}{|I|} \left( \frac{dx^*}{dt} \right)
\]
where $u_{\text{sub}}$ is the mobility of the subhalide, $i$ is the current density, and $(dx^*/dt)$ is the velocity of the boundary. The electronic conductivity may be calculated from the expression

$$\sigma_e = n_{\text{sub}} u_{\text{sub}} F$$

where $n_{\text{sub}}$ is the solubility of Pb in PbCl$_2$ in equivalents/cc. Results from these experiments showed a mobility of the subhalides ranging from $4.2 \times 10^{-4}$ to $12.3 \times 10^{-4}$ cm$^2$/v sec at $580^\circ$C and from $8.7 \times 10^{-4}$ to $28.6 \times 10^{-4}$ cm$^2$/v sec at $630^\circ$C. These correspond to electronic conductivities of $3.12 \times 10^{-4}$ to $9.13 \times 10^{-5}$ ohm$^{-1}$cm$^{-1}$ at $580^\circ$C and $2.63 \times 10^{-4}$ to $1.32 \times 10^{-3}$ ohm$^{-1}$cm$^{-1}$ at $630^\circ$C.

Chronopotentiometry has been used to measure the concentration and diffusion coefficient of subhalides or excess metal dissolved in molten halides. When a subhalide moves in a concentration gradient, it can transport electrons through the salt; therefore, the above-mentioned diffusion coefficients prove useful in applications where transport of electrons is important. Appropriate equations will be considered in the applications section. Table 1 lists some results.

| Subhalide | $T(\degree \text{C})$ | $D_{\text{sub}}$ (cm$^2$/sec) | $n_{\text{sub}}$ (moles/cc) |
|-----------|----------------------|-----------------------------|-----------------------------|
| AgCl      | 520                  | $2 \times 10^{-5}$          | $4.09 \times 10^{-6}$       |
| PbCl$_2$  | 518                  | $1.8 \times 10^{-5}$        | $1.0 \times 10^{-6}$        |
| ZnCl$_2$  | 500                  | $7.6 \times 10^{-6}$        | $3.19 \times 10^{-6}$       |
| MgCl$_2$  | 750                  | $5.3 \times 10^{-6}$        | $3.77 \times 10^{-6}$       |

Since the diffusion coefficients of subhalides are the same order of magnitude as other ions in molten salts, trapped electrons and not free or quasi-free electrons are the mobile species. Consequently the Nernst-Einstein equation

$$D_i = \alpha_i \frac{RT}{n_i} \frac{1}{(z_i F)^2}$$

(11)
cannot be used to obtain electronic conductivities from the diffusion coefficients. Nevertheless, since many electrochemical cells involve only a concentration gradient and not a potential gradient, appropriate equations can be derived in terms of diffusion coefficients.

Since, in general, the mobilities of electrons in molten salts are orders of magnitude lower than in metals, measured values only have significance in the absence of convection.(4) It is a situation very similar to the measurement of diffusion coefficients in liquids.

Chronopotentiometry also has been used to measure the diffusion coefficients of Cl₂ dissolved in molten salts.(26,27) The dissolved Cl₂ can transport electron holes through the salt in the same way that subhalides transfer electrons. Table 2 shows some results obtained by Van Norman and Ryabukhin.

| T(°C) | Dₜ (cm²/sec) | nCl₂ (moles/cc) |
|-------|--------------|-----------------|
| AgCl  | 3.7 x 10⁻⁴   | 2.31 x 10⁻⁷     |
| PbCl₂ | 3.5 x 10⁻⁴   | 0.78 x 10⁻⁷     |
| LiCl-KCl | 1.6 x 10⁻⁴ | 1.54 x 10⁻⁷     |
| NaCl  | 2 x 10⁻³     | 2.3 x 10⁻⁷      |

In the case of NaCl, since the diffusion coefficient is two orders of magnitude greater than that of diffusion of ions, the Nernst-Einstein equation was used to calculate the electron hole conductivity and the results are shown in Figure 3.

Applications

Some examples will be considered here in order to show a few of the applications of measured values of electronic conductivity and diffusion coefficients of subhalides and halogen gases in molten salts.

The following cell has been considered for use as a molten salt battery.(28)

Li-Al(s) | LiCl-KCl(f) | Li-S-Fe

III

\[ a' \]

\[ a'' \]

528
It has been found that the above battery has a self-discharge current of 0.7 ma/cm² at open circuit. Results obtained from polarization measurements can be used to calculate the expected self-discharge current when convection is absent and the cell has a simple geometry.

From transport theory

\[ i_{Li^+} = -\frac{\sigma_{Li^+}}{F^2} \frac{\partial \eta_{Li^+}}{\partial x} \]  

(12)

\[ j_e = -\frac{\sigma e}{F^2} \frac{\partial \eta}{\partial x} \]  

(13)

where \( j \) is the flux in equivalents per unit area per second, and \( \eta \) is the electrochemical potential. \( Li^+ \) is assumed to carry all the cationic current which is not actually the case for LiCl-KCl, but it is convenient for the derivation and does not alter the results.

The following general relations hold

\[ \eta_{Li^+} = \mu_{Li^+} + F\phi \]  

(14)

\[ \mu_{Li} = \mu_{Li^+} + \mu_e \]  

(15)

where equation (14) is the definition of electrochemical potential, \( \mu_{Li^+} \) is the chemical potential of \( Li^+ \) and \( \phi \) the electrostatic potential. Equation (15) follows from the equilibria \( Li = Li^+ + le \). Electrical neutrality dictates that

\[ j_{Li^+} = j_e \]  

(16)

so that

\[ j_e \left( \frac{1}{\sigma_{Li^+}} + \frac{1}{\sigma_e} \right) = -\frac{1}{F^2} \left( \frac{\partial \mu_{Li^+}}{\partial x} + \frac{\partial \mu_e}{\partial x} \right) \]  

(17)
and

\[ j_e = - \frac{1}{F^2} \int_{\mu'}^{\mu''} \frac{\sigma_{\text{Li}^+} e}{\sigma_{\text{Li}^+} + \sigma_e} d\mu_{\text{Li}} \]  

(18)

where \( l \) is the thickness of the electrolyte in cell (III). A constant interelectrode distance is assumed here. When \( \sigma_e < \sigma_{\text{Li}^+} \)

\[ j_e = - \frac{RT}{F^2} \int_{a_{\text{Li}}'}^{a_{\text{Li}}} \sigma_e d\ln a_{\text{Li}} \]  

(19)

Since \( j = j F \) and \( \sigma = \sigma_e a_{\text{Li}} \), where \( \sigma_e \) is the electronic conductivity for \( a_{\text{Li}} \) at \( e \) and \( \sigma_{\text{Li}} \) is the self-discharge current according to equation (21) of 0.35 ma/cm² for a cell with interelectrode distance of 1 cm. The measured value was found to be 0.7 ma/cm² in fair agreement with the calculated value. This indicates that the mechanism of self-discharge is electronic conduction as measured by the polarization technique.

\[ i_e = - \frac{RT}{\mathcal{F} \mathcal{L}} \int_{a_{\text{Li}}'}^{a_{\text{Li}}} \sigma_e a_{\text{Li}} d\ln a_{\text{Li}} = - \frac{RT}{\mathcal{F} \mathcal{L}} \sigma_e (a_{\text{Li}} - a_{\text{Li}}') \]  

(20)

When \( a_{\text{Li}}'' \ll l \) which is the case for cell (III)

\[ i_e = \frac{RT}{\mathcal{F} \mathcal{L}} \sigma_e a_{\text{Li}}' = \frac{RT}{\mathcal{F} \mathcal{L}} \sigma_e \]  

(21)

where \( \sigma_e' \) is the electron conductivity for \( a_{\text{Li}}' \). Using data from Figure 5 and results from Argonne National Laboratory (28) one obtains \( \sigma_e = 5.6 \times 10^{-3} \) when \( a_{\text{Li}}' = 5.7 \times 10^{-3} \) giving a self-discharge current according to equation (21) of 0.35 ma/cm² for a cell with interelectrode distance of 1 cm. The measured value was found to be 0.7 ma/cm² in fair agreement with the calculated value. This indicates that the mechanism of self-discharge is electronic conduction as measured by the polarization technique.

LiCl-KCl eutectic is often used as an electrolyte in cells to measure the activity of metals in alloys. The results from polarization measurements can be used to decide if electronic conduction interferes with the determination of activities. According to Wagner (29) the emf of the cell...
is given by the expression

$$E = \frac{1}{F} \int_{\mu''}^{\mu'} \eta_{\text{ion}} \, d\mu_{\text{Li}}$$

(22)

where

$$\eta_{\text{ion}} = \frac{\sigma_{\text{ion}}}{\sigma_{\text{ion}} + \sigma_{\text{e}}}$$

(23)

so that

$$E = \frac{RT}{F} \int_{a''_{\text{Li}}}^{a'_{\text{Li}}} \frac{\sigma_{\text{ion}}}{\sigma_{\text{ion}} + \sigma_{\text{e}} a''_{\text{Li}}} \, d \ln a'_{\text{Li}} = -\frac{RT}{F} \ln \left( \frac{\sigma_{\text{ion}} + \sigma_{\text{e}} a''_{\text{Li}}}{a'_{\text{Li}}} \right) a'_{\text{Li}}$$

(24)

and

$$E = \frac{RT}{F} \ln \left| \frac{a'_{\text{Li}}}{a''_{\text{Li}}} \right| - \frac{RT}{F} \ln \left( \frac{\sigma_{\text{ion}} + \sigma_{\text{e}} a''_{\text{Li}}}{a'_{\text{Li}}} \right) a'_{\text{Li}}$$

(25)

$$E = \frac{RT}{F} \ln \left| \frac{a''_{\text{Li}}}{a'_{\text{Li}}} \right| - \frac{RT}{F} \ln \left( \frac{\sigma_{\text{ion}} + \sigma_{\text{e}} a''_{\text{Li}}}{a'_{\text{Li}}} \right) a''_{\text{Li}}$$

(26)

Using the results of Figures 5 and 6 one can calculate the effect of electronic conduction in the case of any alloys studied. The effect is very small in almost all cases studied at temperatures below 700°C.
If silver is heated at 500°C in an atmosphere of chlorine gas, a liquid layer of AgCl should be formed on the silver. It is proposed that the mechanism of this reaction is similar to the lower temperature case where a solid layer of AgCl is formed. In that case the electronic conductivity controls the kinetics of the film formation. In particular

$$\text{Ag(s)} | \text{AgCl(s)} | \text{Cl}_2(g)$$

$$j_{\text{electronic}} = \frac{k_r}{1} = \frac{1}{\sigma_{\text{electronic}}} \int \mu_{\text{Ag}}$$

(27)

where $k_r$ is the rational rate constant and represents the equivalents of AgCl formed per unit area per unit time for a unit product layer thickness. For calculations in the liquid state equation (27) must be expressed in terms of diffusion coefficients of subhalides and chlorine gas, thus

$$k_r = \frac{1}{\sigma_{\text{electronic}}} \int_{a''_{\text{Ag}}}^{a'_{\text{Ag}}} n_{\text{sub.}} \cdot D_{\text{sub.}} \cdot a_{\text{Ag}} \cdot \ln a_{\text{Ag}} - \frac{1}{1} \int_{a''_{\text{Ag}}}^{a'_{\text{Ag}}} n_{h} \cdot D_{h} \cdot a_{\text{Ag}}$$

(28)

where $n_{\text{sub}}$ and $n_h$ are the concentration of subhalide and electron holes in equilibrium with Ag.

$$k_r = n_{\text{sub.}} \cdot D_{\text{sub.}} \left( a'_{\text{Ag}} - a''_{\text{Ag}} \right) - n_h \cdot D_h \left( 1 - \frac{1}{a''_{\text{Ag}}} \right)$$

(29)

Since $a'_{\text{Ag}} = 1$ and $a''_{\text{Ag}} << 1$

$$k_r = n_{\text{sub.}} \cdot D_{\text{sub.}} - n_h \cdot D_h \left( 1 - \frac{1}{a''_{\text{Ag}}} \right)$$

(30)

Table 2 lists the solubility of Cl$_2$ in the salts for a pressure of one atmosphere, i.e., $n_{\text{Cl}_2}$

532
Equation (30) then reads

\[ k_r = n_{\text{sub.}}^0 D_{\text{sub.}} + n_h^\circ D_h \]  

or

\[ k_r = n_{\text{sub.}}^0 D_{\text{sub.}} + 2n_h^\circ D_{\text{Cl}_2} \]

Substituting values from Tables 1 and 2 one obtains

\[ k_r = 2.52 \times 10^{-10} \]

Experiments have not yet been performed on this system.

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Fig. 1: Experimental arrangement for polarization experiments.

Fig. 2: Results of polarization measurements on molten NaCl at 830°C. 
\[ G = 120 \quad a_{Na}^{ref} = 10^{-7} \]

Fig. 3: Electron, electron hole, and ionic conductivity of NaCl at 830°C as a function of sodium activity in the melt.

Fig. 4: Conductivity of NaCl with excess Na measured by Bronstein and Bredig. The square data point represents results from polarization measurements.
Fig. 5: Results of polarization measurements on molten LiCl-KCl eut. at several temperatures. G=100

Fig. 6: Electron, electron hole, and ionic conductivity of LiCl-KCl eutectic at 600°C.