Mixed Conduction in Ionic Crystals

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Mixed conductors are met in the chemical, metallurgical, and photographic processes. It is important that the properties of such ionic crystals must be studied. Recent advances made in the study of ionic crystals are given in this paper.

Mixed conduction is exhibited by the sulfides[1], oxides[2], and halides[3,4]. In this ionic crystals both ions and the electrons contribute to the conductivity. Thus the mixed conduction is obtained.

In the case of the ionic conduction electrochemical reaction is present at the boundary between the metal (Ag), which is an electronic conductor, and a solid ionic conductor like AgI. If the electrochemical reaction is absent at the boundary between the metal (Cu) and the solid electronic conductor(Cu_2O)[5], the current is carried by electrons.

Faraday's laws can be strictly applied to ionic conductors. The validity of Faraday's laws to ionic conductors was first shown by Warburg and Tegetmein[6], Habar and Tolloczko[7], and Burni and Scarpa[8]. Later Tubant and his associates[9] and Reinhold[10] conducted systematic studies on the determination of transport numbers in solid conductors.

Tubant[11] had shown that in the case of AgI only cationic conduction took place. That means only the cations are mobile through AgI. In fig. 1 the amount of silver deposited after passing certain coulombs is given:

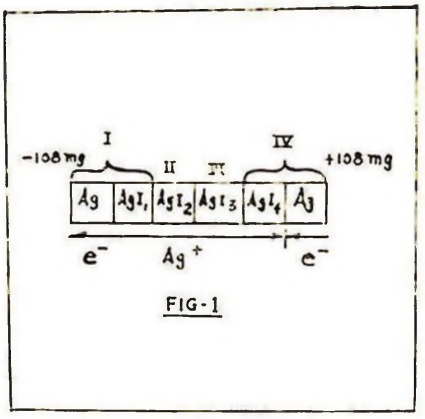


FIG-1

In the middle compartment AgI_2, and AgI_3, there was no increase or decrease of weight. In the cathode compartment (AgI_4/Ag) combination there was an increase in weight equal to the loss in weight in anode compartment. The pellet AgI_4 could not be separated from Ag while AgI_2 and AgI_3 could be separated.

On the contrary $PbCl_2$, $BaCl_2$, $BaBr_2$[12] exhibited anionic conduction.

The oxides[1] and sulfides exhibited the electronic conduction. In these conductors the current is carried by the electrons and thus the electronic conduction is obtained.

In some of the above conductors the ionic or electronic conduction is predominant, so that a small fraction of other conductivity can be neglected or is very small. Thus the ionic conductors exhibit the mixed conduction. In Cu_2O at 1000°C the cationic conductivity was found to be 0.05 percent and the rest was electronic conductivity[13,14]. Similarly the mixed conduction was obtained in case of silver sulfide[15] and silver oxide[16].

The mechanism of conduction is dependent upon the nature of the defects present in the ionic crystal. Frankel[17] had suggested the cationic conduction in the case of AgCl. According to him there is a thermodynamic equilibrium between the ions present in the lattice, the interstitial ions and the ionic vacancies. The interstitial ion can move to other interstitial positions. The interstitial ion can push the ion in the lattice to interstitial positions. The ion in the lattice can jump to the ionic vacancy. Thus the electrical conduction is obtained. In the case of the alkali salts there are both the anionic and cationic vacancies. The conduction is due to both the ions. That means the mobile anions and cations i. e., interstitial ions or vacancies must be present. On theoretical considerations Schottky[18] has concluded that the energy required for the formation of vacancies. Therefore he concluded that the diffusion in alkali salts is by the vacancy diffusion. The other theoretical limiting cases of defects[19] are A) Anti-Frankel defects where equal concentrations of interstitial anions and anion vacancies are present B) anti-

Schottky defects where equal concentrations of anions and cations occupy the interstitial positions

Just like the ionic defects facilitate the ionic conduction, the electron defects can facilitate the electronic conduction When the tonic vacancies are present the neutrality of the crystal is maintained by the removal of electrons corresponding to the valency of the metal. Thus the electron defects or holes in lattice are createed. When excess metal is present the quasifree electrons are present in the ionic crystal lattice. Thus the neutrality of the ionic crystal is maintained. The electrones moving through the defects or the electrones themselves exchanging with the quasifree electrons give rise to electronic conductivity.

Therefore the presence of both the ionic defects and electronic defects will be responsible for the mixed conduction in ionic solids. When the ionic conductivity is predominant the ionic solid is said to be ionic conductor and when the electronic conductivity is predominant the ionic solid is said to be electronic conductor.

There are a few other ionic solids which can exhibit electronic conduction without defects being present. In these solids e.g., CuO^{-o} the stoichiometric ratio of Cu/o is ideal and therefore no defects are present. The electrons are at their lattice positions and as the temperature is raised the electrons attain energy and move in randomness. Since the orbits of electrons in ionic crystals overlap a particular quantum state cannot be assigned. They enter into conduction band. Thus there will be an equilibrium between the lattice electrons, excess electrons and defect electrons.

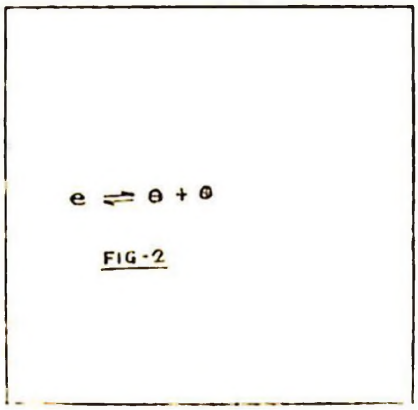


FIG-2

Thus electronic cohduction is obtained. The particular type of conductors are known as intrinsic conductors.

If σ_i and σ_e are the conductivities of ions and electrons, the following equations[21,22] can be arrived at by the energy considerations.

$$\sigma^-_i = \gamma BC \sqrt{NN_i} \frac{\nu a^2 e^2}{RT} \exp(-Ui)RT) \exp(-wi/2kT)$$

$$\sigma^-_e = A \cdot e^{B/Z}$$

The theory of mixed conduction was given by Hebb[4]. The current carried by ions and electrones is given by :

$$J_e = -\sigma^-_e \nabla \Psi$$

$$J_i = -\sigma^-_i \nabla(\Psi + z)$$

Hebb had shown that the electronic conductivity in mixed conductor could be suppressed by the introduction of other ionic solid as shown in Fig. 3 and 3.

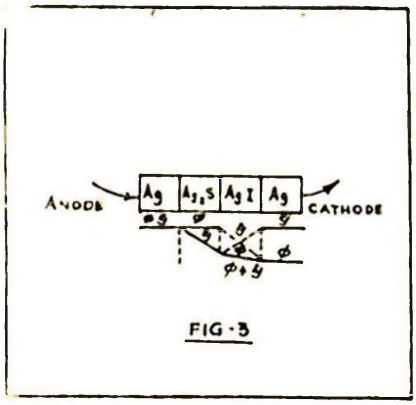


FIG-3

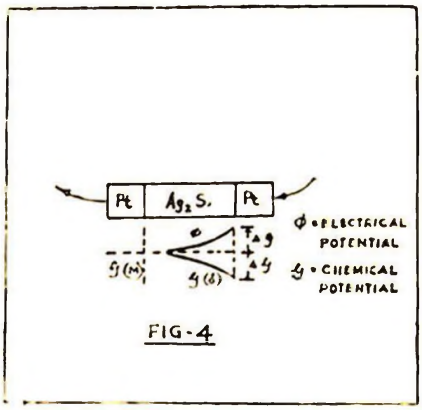


FIG-4

In can be seen from the above figure 3 that suppression of electronic conduction is obtained by the introduction of AgI, which is an ionic conductor. The drop in Ag_2S is equal to the drop in AgI. That is:

$$J_e = O = \sigma_e \nabla \Psi_e$$
$$J_i = -\sigma_i (\Psi + z) = \sigma_i \nabla(z)$$

Thus the electronic part is suppressed.

The Fig. 4 indicates the suppression of ionic conductivity. That is :

$$J_e = -\sigma_e \nabla (\Psi)$$
$$J_i = O = \sigma_i (\Psi + z)$$
$$\therefore \Psi = -z \text{[takin } \phi = \Psi = O \text{ at the Ag Cathode]}$$

Therefore the electrochemical potential of electron is equal to the chemical potential of silver in Ag_2S

The electronic conductivity and the ionic conductivity of mixed conductors can be measured by measuring the potential of the cells in Fig. 5 and Fig. 6.

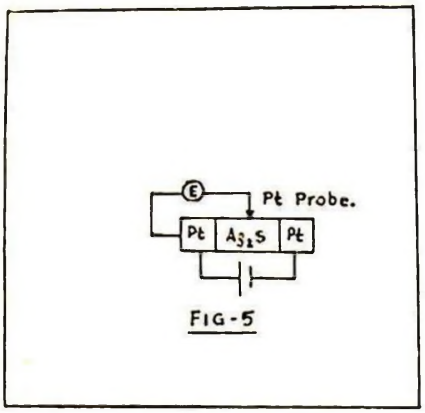


FIG-5

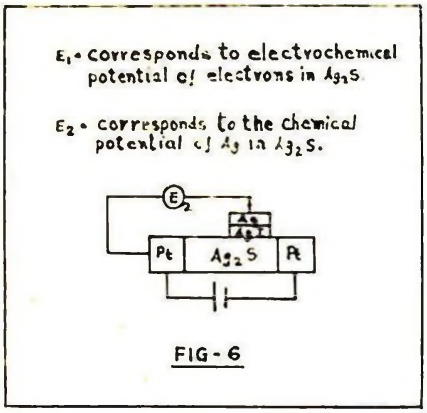


FIG-6

Other methods of measuring the ionic and electronic conductivity are dependent upon the determination of transport members[9,10,11] and the diffusion co-efficients. Making use of following Einstein law $\frac{\sigma}{D} = \frac{Ne}{RT}$

Wagner had determined the conductivity of silver ions in Ag_2S at 200°C making use of the diffusion co-efficients. The conductivity was found to be 0.8 to 2.1 ohm-cm.

A review of the solid electrolyte cells with ionic crystals which have mixed conduction was given by Wagner [1]. A short account of them is given below.

1. **Mixed conductors between similar reversible electrodes :**

Ag/AgI/AgI/Ag I (a)
$O_2/Cu_2O/Cu_2O/O_2$
0.05 atm. 0.05 atm.

In case of I (a) when the equilibrium is established between the silver and silver iodide the ionic conductivity was found to be 99.9% and the remaining was electron conductivity[26]. Similarly in Cu_2O [6] at 1000° and 0.05 atmospheres of oxygen pressure the ionic conductivity was found to be 5×10^{-4} and the rest of the conductivity was due to electrons.

2. **Cells with mixed conductor between different reversible electrodes :**

Cu/CuI/I_2 (gas)

The potential of the above cell is equal to the difference of chemical potential of metal. or non-metal [27].

3. **Cells with mixed conductor between reversible electrode and electronic conductor :**

Ag/Ag_2S/Pt

The ionic conductivity and the electronic conductivity of Ag_2S were determined by Wagner[2] and by Tubant and Reinhold [3].

4. **Cells with mixed conductor between a reversible electrode and an electronic conductor :**

Ag/Ag_2S/AgI/Ag

With this solid electrolyte cell Hebb[22] had determined the ionic conductivity suppressing the electronic conductivity

5. **Cells with mixed conductor between ionic conductor and electronic conductor :**

Ag/AgI/Ag_2S/Pt

The potential of the above solid electrolytic cell can be given by [9].

$$E = -\frac{(\mu Ag - \mu^{\circ} Ag)}{Z F}$$

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