DEVELOPMENT OF AN ELECTROCHEMICAL CELL FOR THERMODYNAMIC ACTIVITY MEASUREMENTS OF Agi IN xAgi(1-x)AgPO₃ GLASSES

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SUMMARY

The lonic conductivity in solids is well known since the 19th century, although the transport mechanisms in amorphous solids are not yet completely understood. The control of this property is important for the development of fast ionic conductors. Trough the dissolution of halogenated salts in a vitreous matrix, it is possible to foster an increase of many orders of magnitude in the ionic conductivity of some glasses. This effect is well exemplified in the glass family x Agl (1-x) AgPO₃ in which, the, ionic conductivity at room temperature increases 4 orders of magnitude when x vary from 0 to 0.5. To investigate this impressive variation in ionic conductivity, we propose a model based on the weak electrolyte theory. This theory proposes that the glass is a solution and the modifier is weakly dissociated in the glass matrix, the ionic conductivity being related to the thermodynamic activity of the solute. In this work, we will present the fundamentals of the proposed investigation, the experimental set up and preliminary results on thermodynamic measurements.

KEYWORDS:

Glass Ionic Conductivity, Weak Electrolyte Theory, Thermodynamic Activity measurements

INTRODUCTION

According to their electrical properties, solids can be classified as conductors, semiconductors or insulating in which the charge carriers can be electrons or ions. The materials in which the electrical conductivity is given mainly by ions motion are called solid electrolytes or fast ionic conductors (FIC) (1) in the case where their ionic transport reaches the values of usual electrolytic solutions. These materials can be used as electrolytes for energy storage in solid state batteries or fuel cells.

Most of the solid electrolytes conduct by only one charge carrier. For a monovalent positive charge carrier, the ionic conductivity σ_+ is given by:

$$\sigma_{+} = n_{+}e\mu_{+} \tag{A}$$

where σ_+ is the conductivity (in S cm⁻¹), n_+ is the charge carriers concentration (in atom cm⁻³), *e* is the electron charge (in C) and μ_+ is their electric mobility (in cm² V⁻¹ s⁻¹).

Unlike what happens in electronic semiconductors, the respective importance of mobility, μ_+ , and number of charge carriers, n_+ is difficult to be determined by Hall Effect measurements due to the weak signal provided by an ionic conductor submitted to a magnetic field.

Therefore, to overcome this experimental difficulty, Souquet *et al.* proposed a model to calculate the ionic mobility in alkali silicate glasses (2) by analysis of the discontinuity of the ionic transport mechanism above and below the glass transition temperature (T_g).

A similar study (3) in the x Agl (1-x) AgPO₃ system indicates that the increase of ionic conductivity when x vary from 0 to 0.5 could be due to an increase in the number of charge carriers, rather than to an increase of their mobility. Considering AgI as a weak electrolyte and, thus, partly dissociated in the glass solvent AgPO₃, dissociation equilibrium allows to correlate the number of charge carriers to the thermodynamic activity of AgI, a_{AgI} according to (3):

$$\log \sigma_{+} \propto \log n_{+} \propto \frac{\Delta \bar{G}_{AgI}}{2.3 \ 2k_{B}T} = \frac{1}{2} \log a_{AgI} \tag{B}$$

where $\Delta \bar{G}_{AgI}$ is the partial free energy of AgI and a_{AgI} is, by definition, the thermodynamic activity of AgI in the glassy system x AgI (1-x)AgPO₃.

In this work, we propose an experimental set-up to measure the thermodynamic activity of AgI in glasses of the system x AgI (1-x) $AgPO_{3.}$ Preliminary results on activity measurements will also be presented.

THEORITICAL BACKGROUND

For thermodynamic measurements, two different electrochemical cells are needed. The first one, called reference cell, uses pure Agl as electrolyte and corresponds to the electrochemical chain:

Ag (+) | Agl | C,
$$I_2$$
 (-) (C)

The electromotive force (*EMF*) of this cell, EMF_1 is given by:

$$EMF_1 = -\frac{\Delta G_{AgI}^0}{F}$$
(D)

where ΔG^0_{AgI} is the standard free energy of formation of pure AgI, and is expressed by:

$$\Delta G_{AgI}^{0} = G_{AgI}^{0} - G_{Ag}^{0} - \frac{1}{2} G_{I_{2}}^{0}$$
(E)

The second electrochemical cell is:

Ag (+) | x Agl (1-x) AgPO₃ | C,
$$I_2$$
 (-) (F)

In this case, the electrolyte is no longer pure AgI, but AgI dissolved in the vitreous AgPO₃. Since AgI is no longer in its pure reference state, the free energy of AgI formation is no longer ΔG^0_{AgI} , but ΔG_{AgI} , the free energy of formation of AgI in the glass. So, the resulting *EMF* for cell (F) is given by:

$$EMF_2 = -\frac{\Delta G_{AgI}}{F}$$
(G)

with:

$$\Delta G_{AgI} = G_{AgI}^{0} + \Delta \overline{G}_{AgI} - G_{Ag}^{0} - \frac{1}{2}G_{I_{2}}^{0}$$
(H)

The partial thermodynamic function $\Delta \overline{G}_{AgI}$ represents the difference between the free energy of AgI in its standard state and in the AgI-AgPO₃ glass

Therefore:

$$EMF_2 = -\frac{\Delta G_{AgI}}{F} = -\frac{\Delta G_{AgI}^0 + \Delta \overline{G}_{AgI}}{F}$$
(I)

The difference between EMF_2 and EMF_1 give, then, access to $\Delta \overline{G}_{AgI}$, the partial free energy of AgI in the glass:

$$EMF_{1} - EMF_{2} = -\frac{\Delta G_{AgI}^{0}}{F} + \frac{\Delta G_{AgI}^{0} + \Delta \overline{G}_{AgI}}{F}$$
(J)

or:

$$EMF_1 - EMF_2 = \frac{\Delta \overline{G}_{AgI}}{F} = \frac{RT}{F} \ln a_{AgI}$$
(K)

Thus, from electrochemical measurements EMF_1 and EMF_2 , we can determine $\ln a_{AgI}$. If we repeat the measurements with glasses from the system x AgI (1-x) AgPO₃ with x = 0.1, 0.2, 0.3, 0.4 and 0.5, we will have access to the variation of ln a_{AgI} with composition, x. Then, by comparison with variation of log σ_+ , we may verify the validity of relation (B).

The cell (D), as well as its EMF, may be estimated from literature data. Thus, this cell may be regarded as a reference, and the good agreement of experimental results of EMF_1 , with literature data, will validate our experimental setup.

EXPERIMENTAL

The electrochemical set up proposed for thermodynamic measurements is schematically represented on figure 1. The cell is made by successive compactions in a polymer mould (PTFE), of the electrolyte (Agl or an Agl-AgPO₃ glass) and a mixture of iodine and graphite. The contacts with a silver disc and iodine electrodes are platinum discs. The cell is introduced in a transparent *Buchi* furnace for *EMF* measurements as a function of temperature:



Figure 1 – Experimental set up for electromotive force (*EMF*) measurements.

RESULTS AND DISCUSSION

Using the relation:

$$\Delta G^{0}_{AeI} = \Delta H^{0}_{AeI} - T\Delta S^{0}_{AeI}$$
(L)

it is possible to calculate, using literature data, the variation of $\Delta G^0_{AgI\alpha}$ and consequently the variation of *EMF*₁, (equation (D)). Employing following data, at 298 K, from reference (5) and (6), cited in reference (7).

$$\Delta H^{0}_{AgI} = -62.2 \pm 0.8 \ kJ \ mol^{-1} \tag{M}$$

$$\Delta S^{0}_{AgI} = S^{0}_{AgI} - S^{0}_{Ag} - S^{0}_{I_{2}}/2 = 14 \pm 2 J K mol^{-1}$$
(N)

In Figure 2, we can see the variation of EMF_1 in previous published results (4) and results obtained in this work, for cell (C).

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Figure 2 - Electromotive force EMF_1 of the cell Ag (+) | Agl | C,I₂ measured by Bradley and Greene (4) and in this work.

It is possible, now, to calculate, from data presented in Figure 2, the variations of ΔG^0_{AgI} as a function of temperature, which are presented in Figure 3.

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Figure 3 – Values of ΔG^0_{AgI} (in kJ mole⁻¹) versus Temperature (in K).

Data from Figure 3, allow us to calculate ΔH^0_{AgI} (the intercept at T=0) and ΔS^0_{AgI} (the slope of the straight line), which are indicated at Table 1 together with the theoretical values from reference (5) and (6):

Table 1 - ΔH^0_{AgI} and ΔS^0_{AgI} values at 298K obtained from experimental data (Bradley and Greene and this work) as well as theoretical data from reference 5 and 6.

	This Work	Bradley & Greene	Thermodynamic
		(4)	Data
$\Delta H^0_{AgI} \ (kJ \ mol^{-1}) \ (298 \ K)$	- 55.0	- 61.9	- 62.3 ± 0.4 (5)
$\Delta S^0_{Agl} \left(J K mol^{-1} \right) $ (298 K)	27	15	14 ± 2 (6)

As we can see from Figure 3 and Table 1, the values obtained in this work are slightly different from tabulated data in (7) data and also from values obtained by Bradley and Green from similar electrochemical measurements

Figure 2 shows that our EMF_1 values are lower than the expected ones. This may be due to the degradation of the I_2 , C electrode caused probably by iodine sublimation, which in turn, may cause loss of contact to the Agl pellet or the platinum disc. We are currently working in the optimization of our cell, for instance in the N₂ flux to avoid those problems. We may also optimize the weight ratio of mixture I_2 , C to avoid the observed degradation of the electrode.

CONCLUSIONS

We described a method and the corresponding experimental set-up to determine the variations of the thermodynamic activity of AgI in the glass system x AgI (1-x) $AgPO_3$.

Preliminary results of the EMF_1 , of the cell Ag (+) | Agl | C, I₂ (-) show stable values of electromotive force within 24 hours. However, those values are slightly lower than those predicted from data in the literature. This fact may be due to the volatilization of lodine during heating and to a contact loss between the mixtures I₂, C and the Agl pellet or the cathode. We are currently working to solve these problems and to get closer values to the expected ones. Before any further measurements with a cell having x Agl (1-x) AgPO₃ glass as electrolytes, we must first optimize the values obtained with the reference cell using pure iodide.

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