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Equilibrium potential, enthalpy and entropy values for the cell Ag/ $Ag_{0.94}Cs_{0.06}I$/graphite, I_2 (g)

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Electrode potential measurements for the title cell are presented from which thermodynamic parameters are obtained. The E values are lower than those of the same cell with pure electrolyte which results from an increase in the entropy term. There is also a decrease in the α–β transition temperature, which is ascribed to a decrease in the formation energy of the Frenkel defects which in turn is associated with the entropic change.

Introduction

In previous studies, it was found that caesium-doped silver iodide exhibits a noticeable decrease in the β–α transition temperature (420 K). This means that the electrolyte retains the high conductivity characteristic of the α phase at much lower temperatures. The minimum temperature, about 380 ± 10 K, was observed for samples doped with up to 6 mol% of caesium iodide.[1] In order to gain further information on the influence of this homogeneous doping on the thermodynamic parameters of the electrolyte, with a view to using this electrolyte in an iodine-sensing cell, measurements of the equilibrium potential of the cell:

$$\mathrm{Ag} \,/\, \mathrm{Ag_{0.94}Cs_{0.06}I} \,/\, \mathrm{graphite, I_2\,(g)} \qquad (1)$$

were performed. Taking into account the relatively small amount of dopant, which is itself inert, it is to be expected that the cell reaction should be that of silver iodide formation: $Ag(s) + ½I_2(g) = AgI(s)$. Thus, any difference with respect to the pure electrolyte will be reflected in the corresponding entropy term.

Experimental

The solid electrolyte was prepared by mixing powders of AgI and CsI ($\geqslant$99.9% purity). After melting to ensure homogeneity, the samples were ground and the resulting powder pressed at 1000 kg cm^{-2} to form pellets of 1 cm diameter and 0.2–0.3 cm thickness. The cell was mounted by pressing the electrolyte pellet between silver and graphite disks with leads of platinum. The potential measurements were carried out by means of a high impedance digital voltmeter, under iodine partial pressures from 71 Pa to 4052 Pa (7.0×10^{-4} atm to 4.0×10^{-2} atm). It is to be noted that at this range of iodine partial pressures no noticeable electronic conductivity is to be expected.[2] The temperature range covered from 340 K to 440 K.

Results

Fig. 1 shows the results obtained at an iodine partial pressure of 71 Pa, plotted as E/T against $1/T$. In the same graph experimental values corresponding to pure AgI at the same iodine partial pressure are presented which coincide with the calculated values using the theoretical $E°$ and the Nernst equation.[3] The intersection point of pure AgI gives the transition temperature at 420 ± 5 K. The two straight lines corresponding to the doped electrolyte run parallel to the ones of pure silver iodide. To differentiate these lines from those of pure AgI, the high and low temperature phases are here indicated as **a**- and **b**-$Ag_{0.94}Cs_{0.06}I$, respectively. As expected, they give a low transition temperature between the high and low temperature phases, at about 390 ± 5 K.

According to the well known equation relating the cell potential to the enthalpy and entropy changes:

$$E/T = \Delta S/F - \Delta H/FT \qquad (2)$$

the parallelism of the straight lines confirms that the formation enthalpies are the same in both cases. Thus, as expected, the decrease in cell potential for the doped electrolyte should be ascribed to an entropic effect due to the presence of dopant.

Figs. 2 and 3 show potential cell measurements as a function of iodine partial pressure, from which the $E°$ values at different temperatures were extrapolated. The obtained values are plotted against temperature in Fig. 4, in which the figures corresponding to pure AgI are also included. From this plot the corresponding $\Delta H°$ and $\Delta S°$ values were obtained. Finally, in Table 1 the standard thermodynamic parameters are presented. Regarding the low temperature phase, it is evident that the introduction of the dopant promotes an increase of about

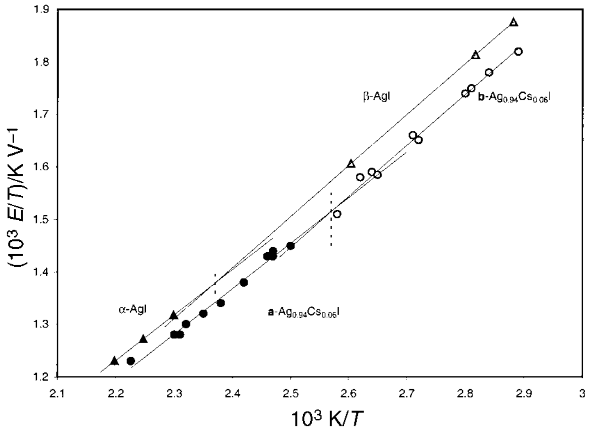

Fig. 1 E/T as a function of $1/T$ for AgI and $Ag_{0.94}Cs_{0.06}I$. Correlation factors: 0.9884 and 0.9913 for **a**- and **b**-$Ag_{0.94}Cs_{0.06}I$, respectively.

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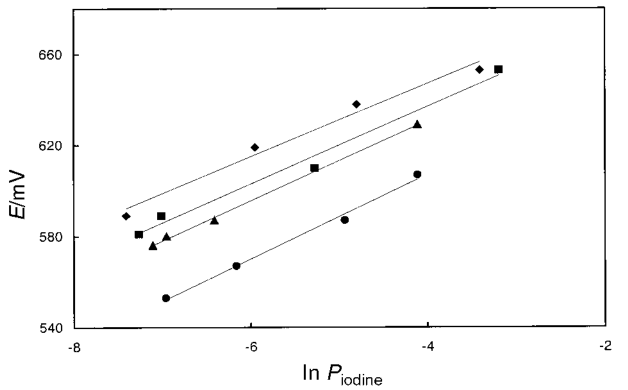

Fig. 2 Potential *vs.* ln P_{iodine} for **a**-$Ag_{0.94}Cs_{0.06}I$ at: 384 K (◆), 398 K (■), 408 K (▲) and 431 K (●).

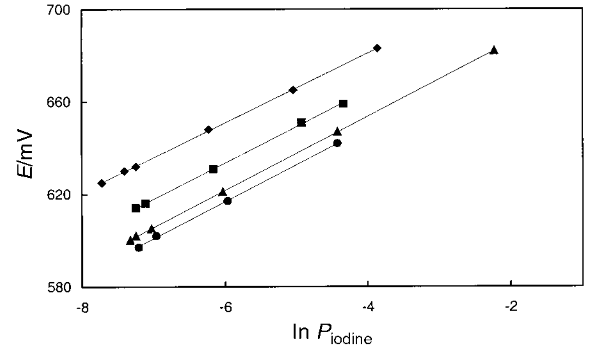

Fig. 3 Potential *vs.* ln P_{iodine} for **b**-$Ag_{0.94}Cs_{0.06}I$ at: 349 K (◆), 363 K (■), 374 K (▲) and 383 K (●).

15 J mol^{-1} K^{-1} in the entropy term. As found earlier,[4] the formation enthalpy change is independent of iodine partial pressure.

Discussion

The decrease in transition temperature should then be ascribed to an entropic effect which in turn should be related to the presence of the critical number of atomic defects needed to trigger the transition, as assumed earlier, on the basis of the model presented by Rice *et al.*[5]

In this sense, if the critical number of defects is reached at a lower temperature, it may well be assumed that their formation enthalpy is somewhat lowered by the dopant, by a purely entropic effect. Thus, the entropic contribution to the energy might be equated with the enthalpic variation in the formation energy of defects. On this basis, the following reasoning may be made. Firstly, the critical defect concentration of Frenkel-type defects, n_c, may be expressed as:

$$n_c = \text{constant} \cdot \exp\,(-\Delta h_F{}^{\circ}/2kT^{\circ}) \tag{3}$$

where $\Delta h_F{}^{\circ}$, the defect formation enthalpy[6,7] has a value of 63 ± 5 kJ mol^{-1}, k is the Boltzmann constant and T° the α–β transition temperature of pure AgI. For doped AgI, the same critical concentration would be given by:

$$n_c = \text{constant} \cdot \exp\,(-\Delta h_F{}'/2kT') \tag{4}$$

with different values of enthalpy and transition temperature.

Equating eqns. (3) and (4) gives:

$$\Delta h_F^{\circ}/T^{\circ} = \Delta h_F{}'/T' \tag{5}$$

Following the above reasoning, the value of $\Delta h_F{}'$ may be obtained by introducing the correction due to the entropy contribution. At 420 K, it results in a $\Delta h_F{}'$ value of 57 ± 5 kJ mol^{-1}. Now, introducing that value in eqn. (5), a value of 380 ± 10 K is obtained, in good agreement with that found experimentally.

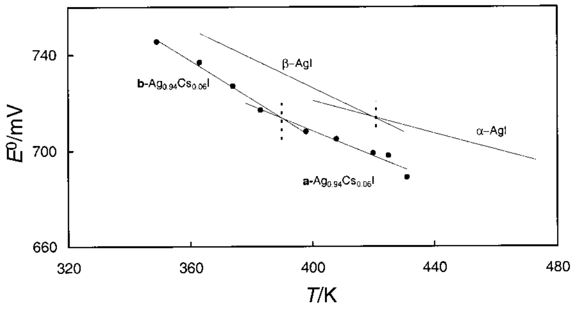

Fig. 4 Standard potential (E°) as a function of temperature for AgI and $Ag_{0.94}Cs_{0.06}I$. Correlation factors: 0.9016 and 0.9893 for **a**- and **b**-$Ag_{0.94}Cs_{0.06}I$, respectively.

Table 1 Standard thermodynamic parameters and transition temperatures for AgI and $Ag_{0.94}Cs_{0.06}I$

Electrolyte	Phase	$\Delta H_F{}^{\circ}$/kJ mol^{-1}	$\Delta S_F{}^{\circ}$/J K^{-1} mol^{-1}	T_{tr}/K
AgI	α	−83.3 ± 1.7	−34.3 ± 0.7	420
	β	−93.9 ± 2.0	−61.9 ± 1.2	
$Ag_{0.94}Cs_{0.06}I$	**a**	−84.2 ± 1.7	−50.4 ± 1.0	390 ± 5
	b	−94.9 ± 1.9	−77.2 ± 1.5	

Acknowledgements

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