

A Cu(I) ion conductor obtained by replacement of Ag(I) in α -AgI

J. C. BAZÁN, J. A. SCHMIDT

Laboratorio de Fisicoquímica, Departamento de Química e Ingeniería Química, Universidad Nacional del Sur, Bahía Blanca, Argentina

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A solid conductor for Cu(I) was obtained by introducing Cu(I) into the high temperature form of AgI. The cationic transport number is practically one with negligible electronic conduction. The formula of the compound may be expressed by $Ag_{(1-x)}Cu_xI$ with x varying with the temperature.

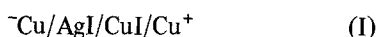
1. Introduction

In recent years there has been an increasing interest in obtaining new solid conductors by inducing modifications in the structures and/or compositions of solid conductors previously known. The great number of silver ion conductors obtained so far is by introducing foreign atoms or organic radicals into AgI [1]. Copper conducting compounds were also included since both Ag(I) and Cu(I) ions are very mobile in solid compounds [2]. Recently, Takahashi *et al.* [3] studied a copper ion conductor Cu(I) halide-organic halide double salt and Scrosati *et al.* [4] reported a copper ion conductor prepared by introducing Cu(I) into Ag_4I_5Rb .

The present work refers to the preparation and characterization of a solid conductor for Cu(I) obtained by partial replacement of Ag(I) by Cu(I) in the high temperature form of AgI.

2. Preparation of the Cu(I) conductor

The substitution of Ag ions by Cu(I) ions was carried out by short circuiting the cell:



in which pellets of CuI and AgI were pressed between copper electrodes.

The corresponding processes are: (a) copper dissolution in the anode as Cu(I); (b) introduction of Cu(I) into AgI; (c) passage of Ag(I) through the interface AgI/CuI, and (d) metallic copper depo-

sition on the cathode (Fig. 1). Interdiffusion between both salts also takes place [5].

The cell components were maintained in position by means of steel springs and pyrex glass rods inside a glass furnace. The temperature was kept constant to $\pm 1^\circ C$ and was measured by means of an iron-constantan thermocouple. To avoid spurious thermal potentials, copper leads from the electrodes to the external circuit were employed. A slow stream of purified N_2 swept the glass furnace during the experiments and during the heating and cooling stages.

The AgI was prepared from AR grade $AgNO_3$ and AR grade KI; CuI (Alfa Inorganics 'Ultrapure') was used without further purification. The copper electrodes were 99.99%. The pellets were made by pressing AgI and CuI powders at 1200 kg cm^{-2} .

The initial cell potential was about 300-400 mV, depending on the working temperature. It approached zero during the

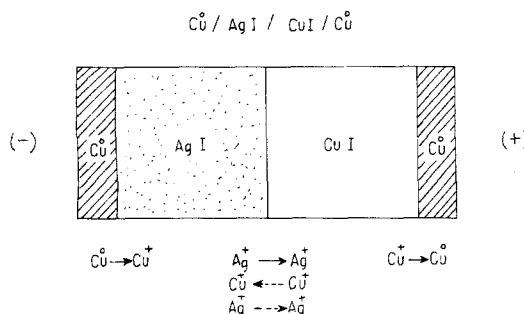


Fig. 1. Movement of ions during the substitution process. \rightarrow Electromigration; $\leftarrow \rightleftarrows \rightarrow$ Interdiffusion.

substitution process. The time needed to reach the stabilization point, as indicated by the null cell potential, was strongly temperature-dependent. For instance, at 250° C, the null e.m.f. was obtained after about 30 h, while at 350° C it was reached after about 3 h.

After cooling the cell, the AgI tablet remained stuck to the electrode and metallic copper dendrites appeared at the CuI/Cu interface.

The substitution was also attempted by direct electrolysis of a AgI tablet between Cu electrodes, but the attempt was not successful. During electrolysis, the cell potential was erratic and high. Even at relatively low values of the current, ~0.5 mA, the cell exhibited the decomposition potential of the solid electrolyte. This may be related to interfacial polarization phenomena. On the other hand, with AgI tablets totally or partially stabilized by short circuiting, electrolysis between copper electrodes proceeded readily at low cell potentials. Copper dendrites were deposited on the cathode, thus evidencing copper ion conduction in the substituted AgI.

When substitution was not complete, (this occasionally happened at temperatures below 300° C), the copper dendrites were covered with an 'head' of silver which was clearly visible with a microscope. For this reason, the full substitution was assured by electrolysis of the AgI tablet until a clear deposit of copper was present at the cathode.

3. Composition of the substituted AgI

The copper conducting compound can be represented by the formula $\text{Ag}_{(1-x)}\text{Cu}_x\text{I}$. The value of x was determined by atomic absorption spectroscopy analysis of the substituted AgI tablets. Data indicated a variation of x with the sample stabilization temperature. Thus, at 255° C the substi-

tuted AgI stabilized composition is $\text{Ag}_{0.558}\text{Cu}_{0.442}\text{I}$ and at 320° C it is $\text{Ag}_{0.473}\text{Cu}_{0.527}\text{I}$. These results are in agreement with the phase diagram of the AgI-CuI system [6].

4. Characterisation of the copper ion conductor

The total and the ionic conductivities were determined with a cell formed with a tablet of substituted AgI sandwiched between metallic copper electrodes.

The ionic transport was studied by experiments of the Tubandt-type by electrolysis of the Cu-substituted AgI between copper electrodes. The samples used were stabilized at 320° C. The copper electrodes were weighed before and after the passage of a measured charge. Results obtained at different currents and temperatures are shown in Table I. One concludes that the compound behaves as a pure ionic conductor for Cu(I) ion.

The total conductivity was determined with a conductivity bridge (Leeds and Northrup) at 1000 Hz between 150 and 400° C. Results are plotted in Fig. 2 as $\log(\text{conductivity})$ against the reciprocal of the absolute temperature. For the sake of comparison the conductivity values for pure CuI [7] and pure AgI [5] are also shown in the same figure. The error is about ± 0.2 logarithmic units. The tablets used were stabilized at three different temperatures but this did not affect the conductivity values.

The partial electronic conductivity of the substituted AgI was measured by applying Wagner's polarization method [8]. The cell consisted of a Cu-substituted AgI tablet pressed between a graphite anode (spectroscopic quality) and a copper cathode. The electronic conductivity of pure CuI was also determined. Measurements were made by controlling the potential and

Table I

Temp. (° C)	I (μ A)	Q (c)	Calculated mass change* (mg)	Anode loss (mg)	Cathode gain (mg)
328	1500	12.15	8.0	8.2	8.3
358	1200	9.72	6.4	6.6	6.4
303	1000	14.40	9.5	9.6	9.6

* Assuming that the electrode processes involve monovalent ions.

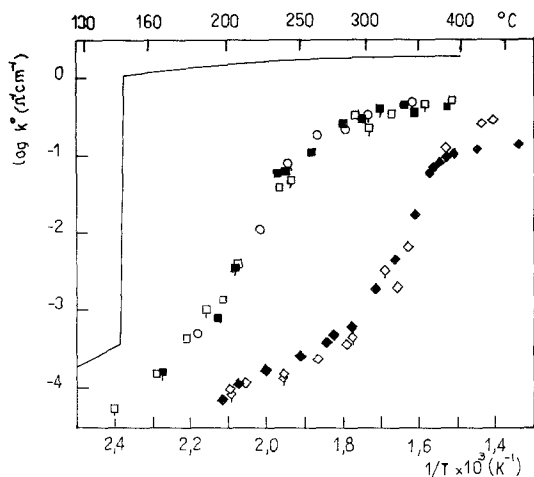


Fig. 2. Total conductivity as a function of temperature. — AgI, [5]; \blacklozenge CuI, [7]; \diamond CuI, this work. $\square, \blacksquare, \circ$, subst. AgI, stabilized at 300°C, 330°C, 269°C, respectively. Points with tail ($\square\square\square$) indicate measurements made during cooling.

measuring the current, which usually stabilized in a short time. Currents of the order of $1 \mu\text{A}$ were measured between 230 and 280°C. Hysteresis was not observed. The samples employed were stabilized at 320°C.

The electronic partial conductivity of pure CuI, as well as that of pure AgI is due to electron holes and the same type of charge carrier is suspected for the substituted AgI. Hence, the experimental data should be correlated with the equation:

$$\log I = \log(k_+^0 ART/LF) + \log [\exp(EF/RT) - 1] \quad (1)$$

where I is the current; k_+^0 the hole conductivity; A the cross-sectional area; L the thickness of the tablet of solid electrolyte and E the applied potential. T , R and F have their usual meanings.

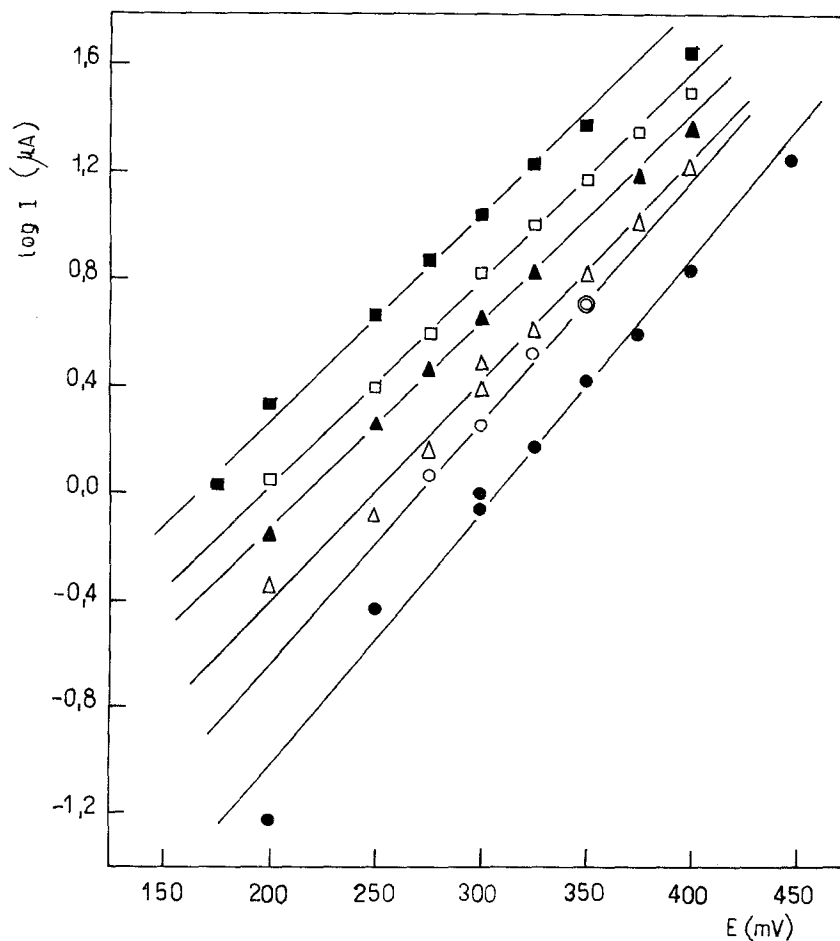


Fig. 3. Log I versus E for Cu-substituted AgI. \bullet : 232°C; \circ : 266°C; \triangle : 314°C; \blacktriangle : 336°C; \square : 360°C; \blacksquare : 384°C.

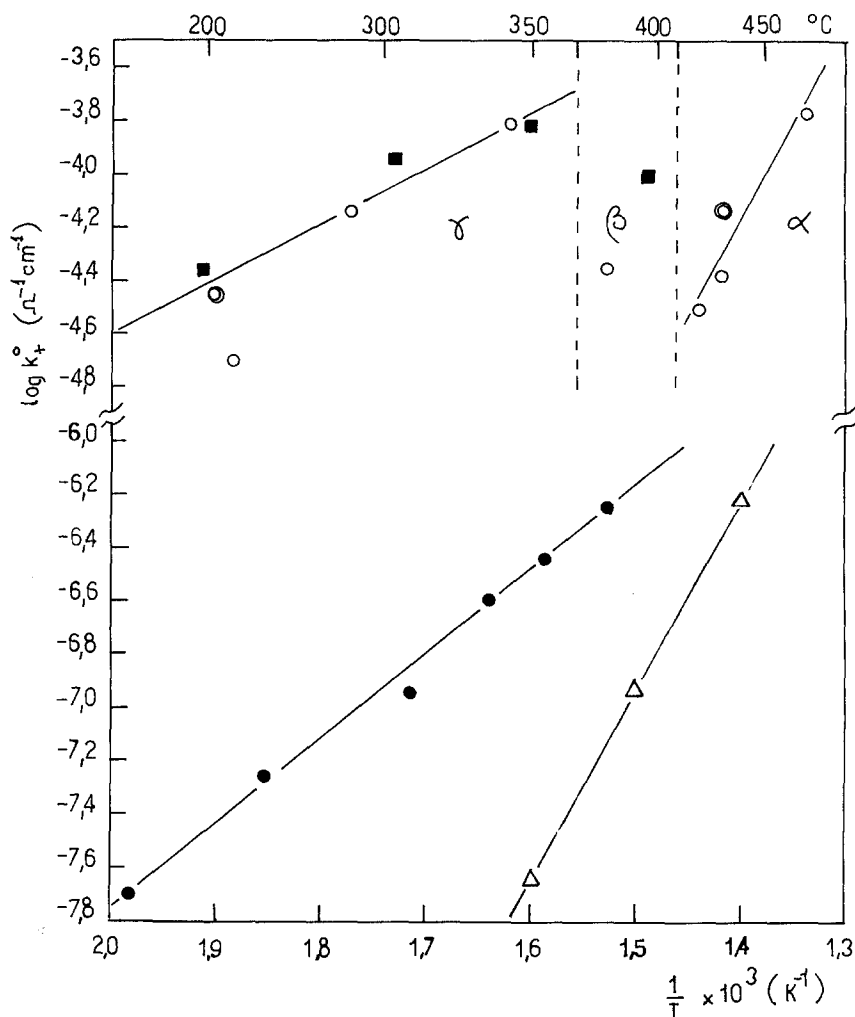


Fig. 4. Electronic conductivity as a function of temperature. \circ : CuI, [7]; \blacksquare : CuI, this work; \bullet : Cu-subst. AgI; \triangle : AgI, [9]; Greek letters correspond to the different CuI phases.

Table 2

Apparent activation energy (kcal mol ⁻¹)	Compound	Temperature range (°C)
14.20	Substituted AgI	200–400
9.15	Pure CuI	220–369
32.00	Pure AgI	254–332

Equation 1 results from the general expression describing the current–potential relationship for the cell with a mixed conductor between a reversible electrode and a blocking electrode [8] [9], for the case where the excess electron contribution is negligible.

Data for pure CuI fit a straight line with unit slope when plotted as $\log I$ versus $\log[\exp(EF/RT) - 1]$. The intercept of the line with the $\log I$ axis allows the calculation of the hole conductivity at the working temperature. The calculated values (Fig. 4) are in satisfactory agreement with those reported by Wagner and Wagner [7].

For the Cu-substituted AgI, the potential range of the polarization curve was between 200 and 450 mV. With these relatively high values of potential, the condition that $\exp(EF/RT) \gg 1$ is fulfilled thus allowing the use of the simplified form of Equation 1:

$$\log I = \log(k_p^0 ART/LF) + EF/2.3 RT. \quad (2)$$

Results obtained at different temperatures, plotted as \log (current intensity) versus potential, are shown in Fig. 3. Above 450 mV a growing faradaic contribution is evident, which may be attributed to the decomposition of the solid electrolyte.

From these straight lines the relevant hole conductivities were calculated. Fig. 4 shows plots of \log (hole conductivity) versus T^{-1} for CuI, the substituted AgI and pure AgI [9]. In Table 2 the values of the apparent activation energies for the hole conductivity in CuI, substituted AgI and pure AgI [9] are shown.

It is of interest to note that the activation energies for the hole conduction for the substituted AgI equilibrated with copper is about one half of that of pure AgI and somewhat higher than that for pure CuI. According to Ilschner [9] the activation energy can be attributed to hole formation. In this way, the decreasing values from AgI to substituted AgI and pure CuI would correspond to the increasing hole formation capacity which can arise from the further ionization of Cu(I) to Cu(II).

5. Conclusions

The experimental results presented in this work show that the Cu-substituted AgI is as good an ionic conductor for Cu(I) ions as pure CuI. The

former has a lower electronic conductivity than the latter and displays relatively high values of conductivity down to lower temperatures.

Acknowledgement

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