JOURNAL OF SOLID STATE CHEMISTRY 21, 73–78 (1977)

Solid-State Ionics: The Electrical Conductivity in the $Ag_{1-x}Cu_xI$-Substituted Ammonium Iodide Double Salts

TAKEHIKO TAKAHASHI, NOBORU WAKABAYASHI, AND
OSAMU YAMAMOTO

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya 464, Japan

Received October 12, 1976; in revised form December 29, 1976

The temperature dependence of the electrical conductivity in the $Ag_{1-x}Cu_xI$–QI ($Q = NH_4$, $(CH_3)_4N$, and $C_5H_5NCH_3$) systems were measured at temperatures ranging from −20 to 130°C under nitrogen gas flow. Temperature T_d, at which a high ionic conductivity compound decomposes to a poor conductivity compound, was determined as a function of x. Temperature T_d was raised with the increase of x in the $Ag_{1-x}Cu_xI$–NH_4I and $Ag_{1-x}Cu_xI$–$(CH_3)_4NI$ systems, but did not depend on the x value in the $Ag_{1-x}Cu_xI$–$C_5H_5NCH_3I$ system; that is, the disproportionation reaction in the $Ag_{1-x}Cu_xI$–NH_4I and –$(CH_3)_4NI$ systems was different from that in the $Ag_{1-x}Cu_xI$–$C_5H_5NCH_3I$ system.

Introduction

High conductivity solid silver ion conductors have been prepared by combining AgI with MI (M = K, Rb, and NH_4) (*1*, *2*), substituted ammonium iodides (*3*, *4*), and sulfonium iodide (*5*, *6*). Solid copper ion conductors have also been synthesized by the combination of copper(I) halides with substituted ammonium halides (*7*–*10*). Some typical solid electrolytes are presented in Table I. When NH_4I, $(CH_3)_4NI$, and C_5H_5NHI are added to AgI, high silver ion conductivity solid electrolytes are formed, but copper electrolytes are not obtained when the above substituted ammonium iodides are made to react with CuI, although Cu^+ and Ag^+ have similar properties.

In the present paper, the effects of substitution of silver by copper in the solid electrolytes of AgI-modified type; that is, $Ag_{1-x}Cu_xI$-substituted ammonium iodides systems on the ionic conductivities, are described, and by what parameter the presence of ion conductive compounds are determined is discussed. Of the above-mentioned substituted ammonium iodides and AgI systems, the AgI–NH_4I system was studied in detail by Bradley and Greene (*1*) and Topol and Owens (*2*). The system, AgI-completely substituted acyclic alkyl ammonium iodide, was described by Owens (*3*). Among these systems, the AgI–$(CH_3)_4NI$ system is examined here. The AgI-unsaturated azacyclic substituted ammonium iodide system was studied by Owens *et al.* (*4*); the AgI–$C_5H_5NCH_3I$ system is selected for study here.

Experimental

Silver iodide was precipitated by gradually adding an aqueous solution of KI to a solution of $AgNO_3$. The resulting product was washed several times with distilled water and ethyl alcohol, and then dried *in vacuo* on P_2O_5. Copper(I) iodide was purified by recrystallizing in hydroiodic acid. After drying under vacuum, the copper(I) iodide was annealed under oxygen-free nitrogen to remove the excess halogen.

(Ag, Cu)I solid solution was prepared by combining silver iodide with copper(I) iodide. The reaction was carried out as described by Nölting (*15*). The appropriate quantities

Printed in Great Britain

ISSN 0022-4596

TABLE I

SOME TYPICAL SOLID ELECTROLYTES

Added compound to AgI or CuI	AgI	CuI
Ag_2S	Ag_3SI (*11*)	
MI (M = K,Rb,NH_4)	MAg_4I_5 (*1, 2*)	MCu_2I_3 (no conductivity)
HgI_2	Ag_2HgI_4 (*12*)	Cu_2HgI_4 (*13*)
$(CH_3)_4NI$	$[(CH_3)_4N]_2Ag_{13}I_{15}$ (*3*)	
C_5H_5NHI	$[C_5H_5NH]Ag_5I_6$ (*4*)	
$C_6H_{12}N_4CH_3I$	$[C_6H_{12}N_4CH_3]Ag_5I_6$ (*14*)	$[C_6H_{12}N_4CH_3]_3Cu_{17}I_{20}$ (*7*)

of AgI and CuI were thoroughly ground together in an agate mortar and then heated in a sealed evacuated Pyrex vessel. According to X-ray investigation, homogeneous mixed crystals with zincblende type structure were produced.

$(CH_3)_4NI$ and $C_5H_5NCH_3I$ were prepared by the method used generally. The typical example of synthesis is as follows: To a solution containing 10 ml of pyridine in 50 ml of ethylalcohol were slowly added 15 g of a methyl iodide solution in 10 ml of ethylalcohol and the mixture was allowed to stand at 10°C for 1 day. After being filtered, the precipitate was dried *in vacuo.* on P_2O_5. The products were purified by recrystallizing in ethyl alcohol.

The phase diagram for the (Ag, Cu)I–NH_4I system has not been reported. In the AgI–NH_4I system, the high silver ion conductivity solid $NH_4Ag_4I_5$ was found at the composition of 80 mole% (m/o) AgI (*1, 2*). It was assumed in the present investigation that if the conductive phase were found, it would contain the same amount of (Ag, Cu)I. Therefore the (Ag, Cu)I–NH_4I double salts were obtained by heating a mixture of NH_4I and (Ag, Cu)I (1:4 molar ratio) in a sealed evacuated Pyrex vessel. The (Ag, Cu)I–$(CH_3)_4NI$ double salts were synthesized by mixing $(CH_3)_4NI$ and (Ag, Cu)I (2:13 molar ratio), and heating in a sealed evacuated Pyrex vessel. The electrical conductivity of the AgI–$(CH_3)_4NI$ system was measured by Owens (*3*) as a function of composition and the highest conductivity was found at a composition of about 87 m/o AgI, and the crystal structure of high silver ion conductivity compound $[(CH_3)_4N]_2Ag_{13}I_{15}$ was reported by Geller and Lind (*16*); therefore, the composition of 86.7 m/o (Ag, Cu)I was selected in the (Ag, Cu)I–$(CH_3)_4NI$ system. The (Ag, Cu)I–$C_5H_5NCH_3I$ system was prepared using a method similar to that above.

These solid-state reaction products were ground and pressed under a pressure of 4000 kg/cm^2 to form a conductivity cell of the configuration of Ag,S/S/Ag,S (S is the sample). The electrodes consisted of powdered silver mixed with the electrolyte in the weight ratio of 2:1. The emphasis is put on the conductivity change rather than on its absolute value and the conductivity was measured with a 1000-Hz ac bridge under nitrogen gas flow at different temperatures.

X-ray diffraction patterns were obtained using Cu$K\alpha$ radiation.

Results and Discussion

(Ag, Cu)I Solid Solution

Figure 1 shows the lattice constant a_0 of (Ag, Cu)I solid solution as a function of the mole percent of silver iodide. The relation between a_0 and AgI m/o in $Ag_{1-x}Cu_xI$ obeys Vegard's law. This result is in agreement with the phase diagram of the AgI–CuI system investigated by Hölting (*15*).

The solid-state reaction products were ground and pressed under a pressure of 4000 kg/cm^2 into a conductivity cell with the configuration graphite/(Ag, Cu)I/graphite. The conductivity was measured with a 1000-Hz ac bridge at different temperatures. The

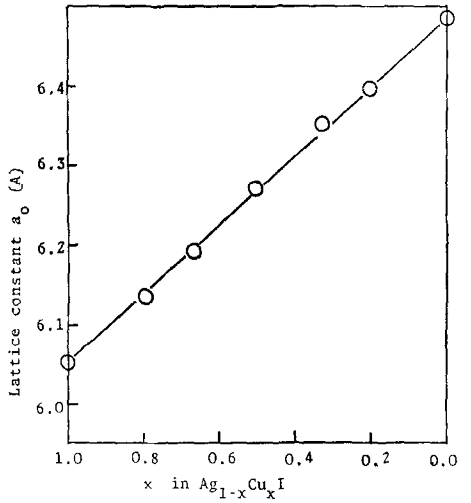

FIG. 1. The lattice constant a_0 as a function of x in $Ag_{1-x}Cu_xI$.

logarithmic conductivity vs the reciprocal of the absolute temperature curves for these samples are shown in Fig. 2. They are characterized by the phase transition of $\gamma \rightarrow \alpha$ phase in which the conductivity increases suddenly by several orders of magnitude. The larger the x value in $Ag_{1-x}Cu_xI$, the higher the $\gamma \rightarrow \alpha$ phase transformation temperature. The results are in agreement with the phase diagram (15).

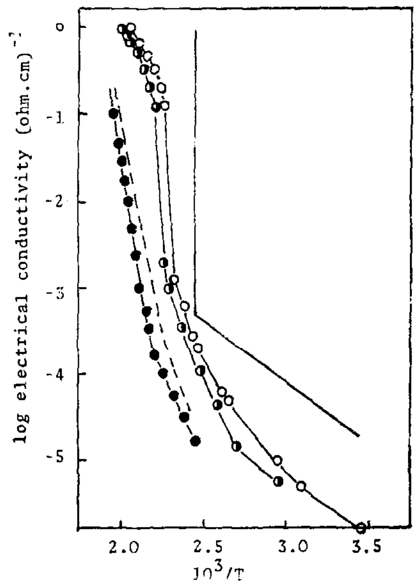

FIG. 2. Temperature dependence of the conductivity of $Ag_{1-x}Cu_xI$; at $x = 0.00$ (——) (18), $x = 0.102$ (o), $x = 0.133$ (◑), $x = 0.30$ (– – –) (19), and $x = 0.307$ (●).

$Ag_{1-x}Cu_xI$-NH_4I system

According to the phase diagram study and the electrical conductivity measurement in the systems AgI-MI (M = K, Rb, and NH_4) investigated by Bradley and Green (1) and Topol and Owens (2), these systems have high ionic conductivity compounds, MAg_4I_5 which decompose to poor conductivity compounds, M_2AgI_3 and AgI at 37°C for KAg_4I_5, at 27°C for $RbAg_4I_5$, and at 32°C for $NH_4Ag_4I_5$. In our study, silver in $NH_4Ag_4I_5$ was substituted by copper and the decomposition temperature of $NH_4Ag_{4-4x}Cu_{4x}I_5$ was measured as a function of x with the conductivity measurement and X-ray diffraction analysis.

The solid-state reaction products of the system $Ag_{1-x}Cu_xI$-NH_4I were stored for 3 weeks in an evacuated Pyrex vessel at room temperature before X-ray analysis and conductivity measurements. X-ray powder diffraction patterns of $NH_4Ag_{4-4x}Cu_{4x}I_5$ at room temperature gave strong peaks due to $Ag_{1-x}Cu_xI$ and weak peaks, which may be due to $(NH_4)_2Ag_{1-x}Cu_xI_3$; the peaks of AgI and CuI were not observed.

The logarithmic conductivity vs the reciprocal of the absolute temperature curves for $NH_4Ag_4I_5$ and $NH_4Ag_{4-4x}Cu_{4x}I_5$ ($x = 0.06$) are shown in Fig. 3. Each curve consists of three parts. The conductivity of $NH_4Ag_4I_5$ decreases suddenly on cooling at 32°C, and this temperature was in good accordance with that on heating. Temperature T_d, at which a sudden increase of the conductivity of $NH_4Ag_4I_5$ is shown, agrees with the disproportionation temperature of $NH_4Ag_4I_5$ reported by Topol (2). At low temperatures, the conductivity of $NH_4Ag_{4-4x}Cu_{4x}I_5$ ($x = 0.06$) was almost the same as that of $Ag_{1-x}Cu_xI$ ($x = 0.06$). This result corresponds to that of X-ray analysis, which showed the presence of the solid solution $Ag_{1-x}Cu_xI$ at room temperature. At high temperature, the conductivity and the activation energy for conduction (16.8 kJ/mole) of $NH_4Ag_{4-4x}Cu_{4x}I_5$ ($x = 0.06$) were the same as those of $NH_4Ag_4I_5$. For $NH_4Ag_{4-4x}Cu_{4x}I_5$ ($x = 0.06$), T_d is higher than that for $NH_4Ag_4I_5$.

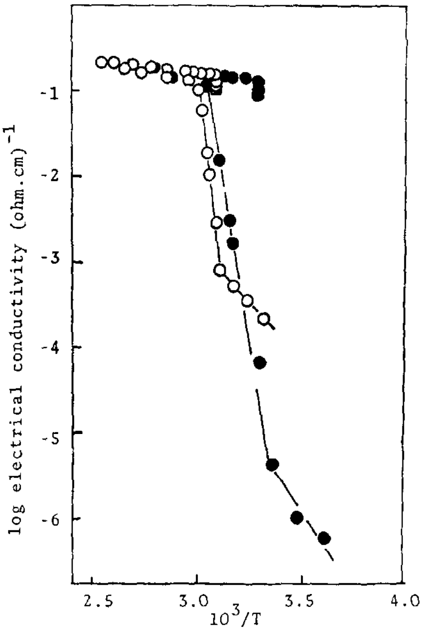

FIG. 3. Temperature dependence of the conductivity of $NH_4Ag_4I_5$ (●) and $NH_4Ag_{4-4x}Cu_{4x}I_5$ ($x = 0.06$) (○).

The temperature dependence of the conductivities of the systems $NH_4Ag_{4-4x}Cu_{4x}I_5$ with various values of x was measured and the disproportionation temperatures were determined. The results are shown in Fig. 4. These temperatures were found to become higher with the increase of the x value in $Ag_{1-x}Cu_xI$. The substitution for silver with copper in $NH_4Ag_4I_5$ did not appear at temperatures below 32°C; the disproportionation reaction of $NH_4Ag_{4-4x}Cu_{4x}I_5$,

$$2NH_4Ag_{4-4x}Cu_{4x}I_5 \rightleftharpoons 7Ag_{1-x}Cu_xI + (NH_4)_2Ag_{1-x}Cu_xI_3$$

occurs at temperatures below 32°C. According to the results given by Scrosati *et al.* (*17*), only 1.5 atom% of silver in $RbAg_4I_5$ is substituted by copper at room temperature. The disproportionation temperature, however, has not been reported. It is assumed from the present results that $RbAg_{4-4x}Cu_{4x}I_5$ ($x = 0.016$) decomposes to $Rb_2Ag_{1-x}Cu_xI_3$ and $Ag_{1-x}Cu_xI$ at room temperature, and the disproportionation temperature becomes higher with increasing x.

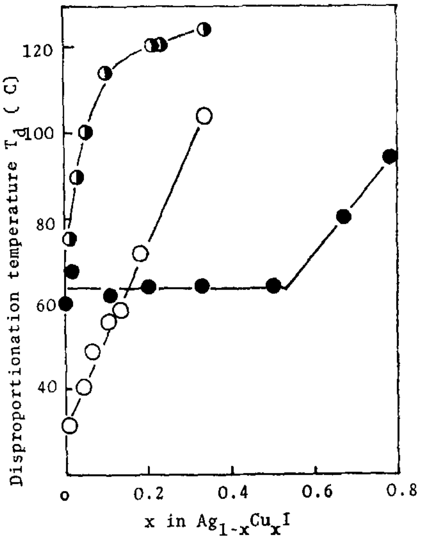

FIG. 4. The disproportionation temperature T_d as a function of x; for the $Ag_{1-x}Cu_xI$–NH_4I system (○), –$(CH_3)_4NI$ (◑), and –$C_5H_5NCH_3I$ (●).

$Ag_{1-x}Cu_xI$–$(CH_3)_4NI$ System

The solid-state reaction products were stored for 5 weeks in evacuated Pyrex vessels under ambient conditions before the experiment.

The electrical conductivity of the $Ag_{1-x}Cu_xI$–$(CH_3)_4NI$ system was measured at different temperatures. The typical results are shown in Fig. 5. The results may be

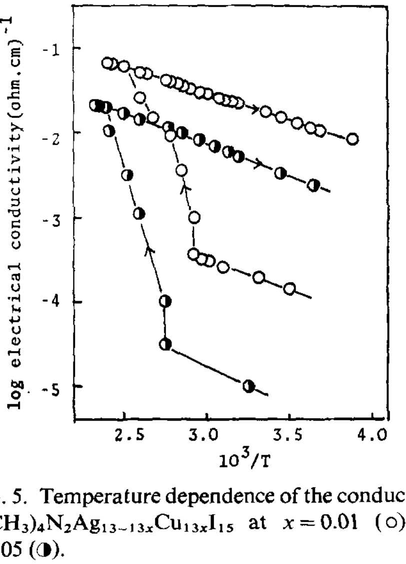

FIG. 5. Temperature dependence of the conductivity of $(CH_3)_4N_2Ag_{13-13x}Cu_{13x}I_{15}$ at $x = 0.01$ (○) and $x = 0.05$ (◑).

represented in terms of three distinct temperature regions. In each case, the logarithm of the conductivity increases linearly with the decrease of the reciprocal of temperature. At low temperatures, the conductivity was almost the same as that of $Ag_{1-x}Cu_xI$. X-ray analysis of the $Ag_{1-x}Cu_xI$-$(CH_3)_4NI$ system at room temperature gave the diffraction pattern of $Ag_{1-x}Cu_xI$ and unknown diffuse pattern which may be of $(CH_3)_4NAg_{2-2x}Cu_{2x}I_3$. A sharp jump in the conductivity for the $Ag_{1-x}Cu_xI$-$(CH_3)_4NI$ system is observed at T_d (for example, when $x = 0.01$, $T_d = 100°C$) on heating. The conductivity on cooling does not decrease to a considerable extent. For $[(CH_3)_4N]_2Ag_{13-13x}Cu_{13x}I_{15}$, the activation energy for conduction calculated from the log σ vs $1/T$ curve on cooling was almost the same as that of $[(CH_3)_4N]_2Ag_{13}I_{15}$, but the conductivity value decreases with the increase of x. The X-ray diffraction pattern of the samples annealed above T_d before quenching to room temperature was almost the same as that of $[(CH_3)_4N]_2Ag_{13}I_{15}$. At temperature T_d, therefore, the disproportionation reaction of $[(CH_3)_4N]_2Ag_{13-13x}Cu_{13x}I_{15}$ could result

$$[(CH_3)_4N]_2Ag_{13-13x}Cu_{13x}I_{15} \rightleftharpoons 9Ag_{1-x}Cu_xI + 2[(CH_3)_4NAg_{2-2x}Cu_{2x}I_3]$$

and the reaction was slow.

Temperature T_d is shown as a function of x in Fig. 4. T_d rises sharply with the increase of x in contrast with $NH_4Ag_{4-4x}Cu_{4x}I_5$. This result corresponds to Scrosati's conclusion (*17*) of the solubility of copper at room temperature being lower in this electrolyte, $(CH_3)_4NI \cdot 6AgI$, than in $RbAg_4I_5$.

$Ag_{1-x}Cu_xI$-$C_5H_5NCH_3I$ System

The AgI-$C_5H_5NCH_3I$ system was investigated by Owens *et al.* (*4*), but the composition dependence of the conductivity of this system has not been determined. In the present study, the $Ag_{1-x}Cu_xI$ (87 m/o)-$C_5H_5NCH_3I$ (13 m/o) was examined.

A logarithm of conductivity vs the reciprocal of the absolute temperature curve for $Ag_{1-x}Cu_xI$ ($x = 0.50$, 87 m/o) -$C_5H_5NCH_3I$ (13 m/o) is shown in Fig. 6. The conductivity increases sharply at 65°C on heating, and the cooling curve gives the straight line in the temperature range of 120 to 27°C. The conductivity and the activation energy were the same as those of 6.7 $AgIC_5H_5NCH_3I$. According to X-ray diffraction analysis at room temperature, the diffraction pattern due to $Ag_{1-x}Cu_xI$ was not observed, but the pattern of pure CuI and the diffused patterns which may be considered to be due to 6.7 $AgI \cdot C_5H_5NCH_3I$ were observed. Further, the conductivity at room temperature is higher than that of $Ag_{1-x}Cu_xI$. As shown in Fig. 4, T_d does not depend on x, in the range of 0.01 to 0.50 of x. At temperatures below T_d, therefore, the solid-state disproportionation reaction may be

$$6.7\ Ag_{1-x}Cu_xI \cdot C_5H_5NCH_3I \rightleftharpoons (1-x)[6.7\ AgI \cdot C_5H_5NCH_3I] + 6.7\ xCuI + xC_5H_5NCH_3I.$$

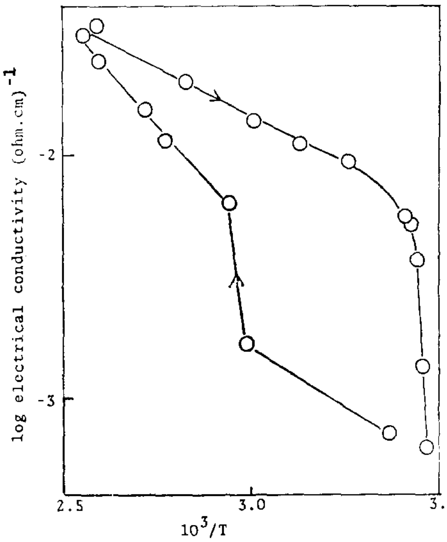

FIG. 6. Temperature dependence of the conductivity of $Ag_{1-x}Cu_xI$ ($x = 0.50$, 87 m/o) -$C_5H_5NCH_3I$ (13 m/o).

Conclusion

The disproportionation temperature in the $Ag_{1-x}Cu_xI$-QI ($Q = NH_4$, $(CH_3)_4N$, and $C_5H_5NCH_3$) systems was measured as a function of the value of x. Consequently, no high copper ion conductivity compound was found in the CuI–*QI* system. Further, we suggest that the conformation of substituted ammonium ion plays an important role in the disproportionation reactions.

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