

SILVER AND COPPER ION CONDUCTORS IN THE SOLID STATE

Takehiko Takahashi

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

Abstract— Materials exhibiting high ionic conductivities in the solid state at room temperature have mainly been found in silver ion conductors based on silver iodide and in copper ion conductors which are based on cuprous halide. Silver iodide and cuprous halide show low ionic conductivities at room temperature, while they are high conductivity solids at relatively higher temperatures. In order to obtain these high conductivity phases at room temperature, the introduction of foreign cations or anions into the lattice of silver iodide and cuprous halide has been attempted. In this paper, the various silver and copper ion high conductivity solids are reviewed and the proposed considerations for the mechanism of the ionic conduction are discussed.

INTRODUCTION

Despite the sweeping trend towards solid state components in the field of electronic engineering, the electrolyte had been used in the solid state at room temperature only in an extremely limited range till quite recently because few electrolytes have been found which were capable of being used practically in the solid state at room temperature. In the beginning of the 1960's, Ag_3SI was found to exhibit a relatively high silver ion conductivity in the solid state at room temperature and a galvanic cell was constructed using Ag_3SI as the electrolyte to obtain a current density of $1\text{--}2 \text{ mA/cm}^2$ with no appreciable polarization at room temperature (Ref. 1). This success was to add a new light to the application of ion conductors in the solid state at room temperature. Since Ag_3SI was found, various kinds of solid ion conductors exhibiting a high conductivity at room temperature have been discovered. These solid ion conductors have mainly been the silver and copper ion conductors which are stoichiometric materials exhibiting cation disordered phases.

SILVER ION CONDUCTORS

Room temperature silver ion conductors found up to the present have been limited to a certain compound based on silver iodide. Silver iodide shows a phase transition at 147°C and above this temperature, its silver ion conductivity increases suddenly by about six orders of magnitude above that at room temperature. The high temperature phase of silver iodide, α -phase, shows a body centered cubic structure with iodide ions which contains two silver iodide entities in a unit cell. From the X-ray investigation, the two silver ions in a unit cell are considered to be distributed over 42 available sites, thus taking an average structure. This structure corresponds to a "quasi-molten" or "liquid-like" state of the silver ions which are almost free to move. This model may be confirmed by the anomalously low entropy of fusion of silver iodide which is $11.3 \text{ J/degree, mole}$. There are regularities in the entropy of fusion, for example, the constant values for the alkali halides the mean value of which is about $24 \text{ J/degree, mole}$. The entropy of transition of silver iodide from β , the low temperature phase, to α phase is $14.5 \text{ J/degree, mole}$. These entropy values may suggest the liquid-like state of the silver ions in α silver iodide. Recent neutron diffraction experiments on α silver iodide (Ref. 2 & 3), however, indicated that the silver ions are preferentially found in

oblong ellipsoidal regions of space centered at the tetrahedral site, and there is a large anharmonic contribution to the thermal vibrations in the direction of the octahedral sites. This model suggests that the silver ions are not completely liquid-like and the $\langle 100 \rangle$ directions should be regarded as channel-like diffusion paths of the silver ions, while the $\langle 110 \rangle$ directions are regarded also as the channels of the silver ion diffusion (Ref. 4). The reason of this inconsistency is not clear.

Ag_3SI is stable in β -phase at room temperature which structurally resembles α silver iodide. In $\beta\text{-Ag}_3\text{SI}$, the body centered cubic lattice is composed of simple cubic iodide and sulfide ion sublattices. In a cube with iodide ions in the corners and the smaller sulfide ion in the center, there is a group of four voids in the vicinity of each face center of body centered cubic unit cell for the sites of the silver ions. The unit cell contains an entity of Ag_3SI and these three silver ions are considered to be distributed over 12 available interstitial sites in the (100) plane of the cube which correspond to the tetrahedral regions in α silver iodide. The structural resemblance of $\alpha\text{-AgI}$ and $\beta\text{-Ag}_3\text{SI}$ leads to the consideration that the partial substitution of the iodide ions by the sulfide ions might produce a high conductivity solid ion conductor of $\beta\text{-Ag}_3\text{SI}$ at room temperature. Stimulated by this consideration the partial substitution of the ions in silver iodide by foreign ions has been attempted.

Partial substitution of the iodide ions in silver iodide by foreign anions

By this time S^{2-} , CrO_4^{2-} , WO_4^{2-} , MoO_4^{2-} , Po_4^{3-} , AsO_4^{3-} , VO_4^{3-} and $\text{P}_2\text{O}_7^{4-}$ been successfully introduced into the lattice of silver iodide to obtain high silver ion conductivity compounds at room temperature (Ref. 5, 6 and 7). Of these solid silver ion conductors, the silver iodide and silver tungstate system is a conductor which is now in practical use in Japan. In Fig. 1, the electrical conductivity of the system $\text{AgI-Ag}_2\text{WO}_4$ is shown taking the content of Ag_2WO_4 as a parameter (Ref. 5). The structural formula of the highest conductivity compound is determined as $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ (Ref. 8). In this compound, the unit cell contains two $\text{Ag}_{26}\text{I}_{18}\text{W}_4\text{O}_{16}$ entities, and 90 iodide polyhedra and 56 mixed oxide-iodide polyhedra in a unit cell share faces to give the conduction passageways. The total number of sites of the silver ions per unit cell in the conduction passageway is 146 and an average of 44.5% of the 52 silver ions are in these polyhedra per unit cell, and these silver ions are considered to be mobile.

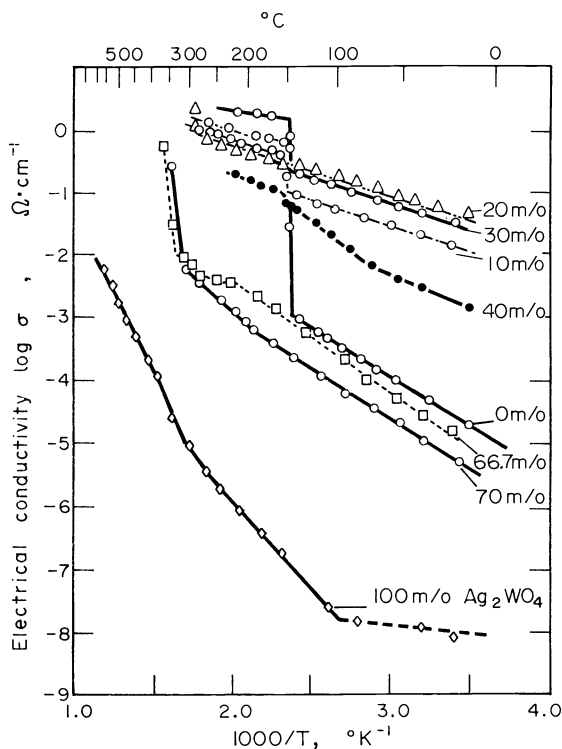


Fig. 1. Electrical conductivity of the system $\text{AgI-Ag}_2\text{WO}_4$ against the reciprocal of the absolute temperature.

Partial substitution of the silver ions in silver iodide by foreign cations

The alkali metal ions such as Rb^+ , K^+ , NH_4 (Ref. 9, 10 & 11), the substituted ammonium ions (Ref. 12, 13, 14 & 15), the sulfonium and selenonium ions (Ref. 16 & 17) and the carbonium ions (Ref. 18) have effectively been introduced into the lattice of silver iodide to give the high silver ion conductivity solids at room temperature. Of these silver ion conductors, RbAg_4I_5 is known to show the silver ion conductivity of $2.7 \cdot 10^{-1} \Omega^{-1} \text{cm}^{-1}$ at 24°C which is the highest ionic conductivity ever found in the solid state at room temperature. RbAg_4I_5 has a simple cubic structure and the iodide ions are arranged as tetrahedra which are interconnected by the sharing of faces so that there are continuous channels of connected iodide tetrahedra which extend throughout the crystal. The silver ions are located in the centers of these tetrahedra and easily diffuse through the tetrahedra faces to adjoining tetrahedral sites. The ratio of tetrahedra to the silver ions is 3.5 which means that there are 2.5 empty sites adjacent to each occupied site which permit fast silver ion diffusion (Ref. 19).

TABLE 1. Onium iodide-silver iodide solid electrolyte ($\text{QAg}_n\text{I}_m + \text{m}$)

Q	n	m	Ionic conductivity at 25°C ($\Omega^{-1} \text{cm}^{-1}$)
Tetramethylammonium (Me_4N)	6.5	1	0.04
Pyridinium (Py)	5	1	0.08
Dimethylpyrrolidinium	7	1	0.07
Benzyltrimethylammonium	8	1	0.01
Methane-1,1-bis-methyldiethylammonium	12	2	0.05
Octamethyldiethylenetriammonium	22	3	0.06
1-Methyl-1-thioniacyclohexane	7	1	0.06
Isopropyl dimethylsulfonium	7	1	0.05
Tropylium	4	1	0.006

Table 1 shows the conductivities of typical examples of onium silver iodide where Q is the onium cation and n the mole ratio of AgI to QI_m . In $[(\text{CH}_3)_4\text{N}]_2\text{Ag}_{13}\text{I}_{15}$, three tetramethylammonium silver iodide entities are there in a hexagonal unit cell and the iodide ions are at the corners of face sharing tetrahedra. These tetrahedra are arranged to show two kinds of channels, one of which may serve for the diffusion of the silver ions through the crystal. For 39 silver ions in a unit cell, there are 123 tetrahedra and the ratio of tetrahedra to the silver ions is 41/13 (Ref. 20).

In general, the structural investigations indicate that the cation substituted silver iodide solid electrolytes contain face sharing polyhedrons formed by the iodide ions, and the silver ions diffuse through the resultant passages. In these cases, an important function of the cations incorporated into a structure with silver iodide is to increase the degree of face sharing of polyhedra by coordinating a greater number of anions than the silver ions, which results in conductive structures.

Recently, the high conductivity silver ion conductors have been found in the bis-sulfonium diiodide or trimethyl selenonium iodide and silver iodide systems. The solid electrolytes of this group are represented by the general formulae $(\text{CH}_3)_2\text{S}^+(\text{CH}_2)_n\text{S}^+(\text{CH}_3)_2\text{I}^- \cdot x\text{AgI}$ where n is 3, 4 or 5 and $(\text{CH}_2)_m\text{S}^+(\text{CH}_2)_n\text{S}^+(\text{CH}_2)_m\text{I}^- \cdot x\text{AgI}$ where m is 4 or 5 and n is 2 or 3 and $(\text{CH}_3)_3\text{SeI} \cdot x\text{AgI}$. The highest conductivity of $1.10 \cdot 10^{-2} \Omega^{-1} \text{cm}^{-1}$ has been found in $\text{Ag}_{13}(\text{CH}_3)_2\text{S}(\text{CH}_2)_3\text{S}(\text{CH}_2)_3\text{I}_{15}$ at room temperature and $4 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$ in $(\text{CH}_3)_3\text{SeI}$ -85 mole % AgI at 21°C (Ref. 21).

Partial substitution of the ions in silver iodide by foreign cations and anions

High conductivity silver ion conductors have been prepared by introducing the mercuric ions and the chalcogenide ions (Ref. 22) or the alkali metal ions and the cyanide ions into the lattice of silver iodide (Ref. 23 & 24). In Fig. 2, the conductivities of the system $\text{AgI-HgI}_2\text{-Ag}_2\text{Chal}$ are shown as a function of temperature. These silver ion conductors have a body centered cubic structure, and an α - AgI type structure has been found in the sulfide

ion containing conductor which has 2.25 cations distributed over 42 available sites in a unit cell. The structures of the other conductors differ somewhat from that of α -AgI and the available sites for the cations in a unit cell are not 42 but 30. The mercuric ions have been found not to contribute to the conductance.

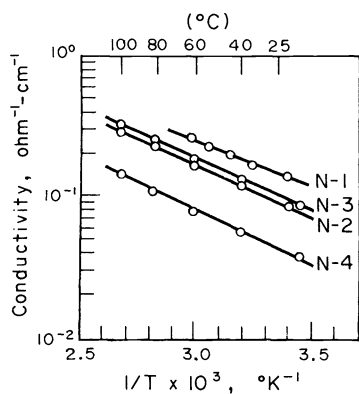
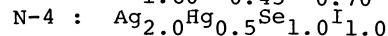
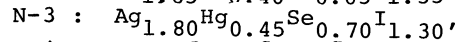
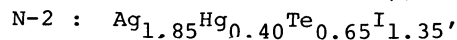
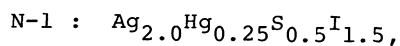





Fig. 2. Conductivity of the AgI-HgI₂-Ag₂Chal system.



Heat of transport of the silver ions

These silver ion conductors may be classified by comparing the heats of transport of the silver ions with the activation energies for silver ion conduction. In Table 2, these comparisons are shown. The heat of transport was calculated by measuring the relation between the thermoelectric power and the reciprocal of the absolute temperature (Ref. 25, 26 & 27).

TABLE 2. Heat of transport and the activation energy for conduction of the silver ions in various silver ion conductors

Electrolyte	Heat of Transport (eV)	Activation Energy for Conduction (eV)
α -AgI	<u>0.052</u>	<u>0.051</u>
RbAg ₄ I ₅	<u>0.086</u>	<u>0.092</u>
Ag ₆ WO ₄ I ₄	<u>0.14</u>	<u>0.16</u>
Ag ₂ Hg _{0.25} S _{0.5} I _{1.5}	<u>0.15</u>	<u>0.14</u>
aAgI·bQI		
Q	a/b	
Tetramethylammonium	6.5	0.115
Pyridinium  -H	3.6	0.091
1,3-dimethylpyridinium	6.7	<u>0.130</u>
1,2,6-trimethylpyridinium	6.7	<u>0.146</u>
1,2,4,6-tetramethylpyridinium	6.7	0.145
1-methylpyrrolidinium 	8	0.077
1-methylthioniacyclopentane 	5.25	0.146
N-methylhexamethylenetetramine	5	0.114

In the cases of α -AgI, the inorganic anion or cation substituted silver iodides and some of the organic ammonium cation substituted silver iodides, the heats of transport of the silver ion correspond to the activation energies for silver ion conduction while in most of the organic ammonium cation substituted silver iodides, the heats of transport are lower than the activation energies. From these results, the silver ions in the former group conductors may be considered to be all free to move, and in the latter group conductors they are not all mobile but need some energy of the sort of

formation energies for the mobile ions. For example, in tetramethylammonium silver iodide, face sharing tetrahedra are arranged in two kinds of channels, as mentioned earlier, one of which begins at one tetramethylammonium ion and ends at another. This channel may be less important for the diffusion of the silver ions through the crystal. The silver ions may diffuse from one channel to another via interconnecting face sharing tetrahedra which will need some energies.

COPPER(I) ION CONDUCTORS

Considering the success to obtain the room temperature high silver ion conductivity compounds by incorporating the appropriate foreign ions into the lattice of silver iodide and because of the similar properties of the silver ion and the copper(I) ion, it has naturally been tried to synthesize copper ion conductors by introducing foreign ions into the lattice of copper(I) halides. Up to the present, copper ion conductors exhibiting high conductivity at room temperature have been found only in the cation substituted copper(I) halides.

In the rubidium chloride and copper(I) chloride system, a compound $\text{Rb}_3\text{Cu}_7\text{Cl}_{10}$ has been found which exhibits a high copper(I) ion conductivity at room temperature. In Fig. 3, the conductivities of the RbCl-CuCl system is shown as a function of temperature (Ref. 28). The charge carriers in these conductors have been shown to be the copper(I) ions. Recent study on this system, however, showed that the highest copper(I) ion conductivity compound is not $\text{Rb}_3\text{Cu}_7\text{Cl}_{10}$ but RbCu_3Cl_4 which exhibits the copper(I) conductivity of $2.25 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 25°C (Ref. 29). The reason of this discrepancy has not been understood.

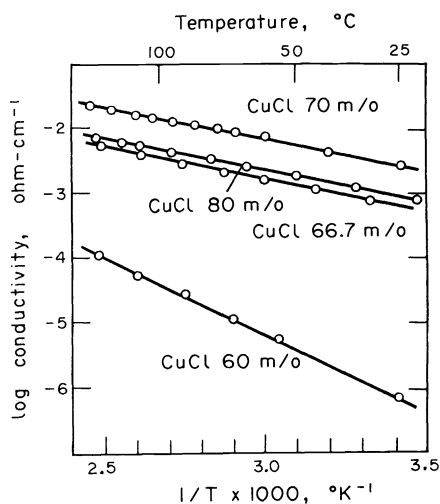


Fig. 3. Conductivity of the RbCl-CuCl system as a function of temperature.

The copper(I) ion conductors have been synthesized also by introducing organic substituted ammonium halides into the lattice of copper(I) halides (Ref. 30,31,32,33 & 34). Figure 4 shows the copper(I) ion conductivities of the bicyclic ammonium halides and copper(I) halides system (Ref. 30 & 31). The high copper(I) ion conductivity has been obtained also in the tricyclic ammonium halide and copper(I) halide system (Ref. 32). In Fig. 5, the composition dependence of the conductivities of the 1 methyl-piperidinium bromide and copper(I) bromide and other similar binary systems at room temperature is shown indicating that the highest conductivity appears at the composition of about 84 mole % of the copper(I) halides in each case (Ref. 33).

In addition, high copper(I) ion conductors have been found in the organic sulfonium iodide and copper(I) iodide system. The composition dependence

of the conductivities of these systems are shown in Fig. 6 and are compared with that of the corresponding ammonium iodide and copper(I) iodide system. These conductivity values show a maximum at 83.4 mole % of copper(I) iodide (Ref. 35).

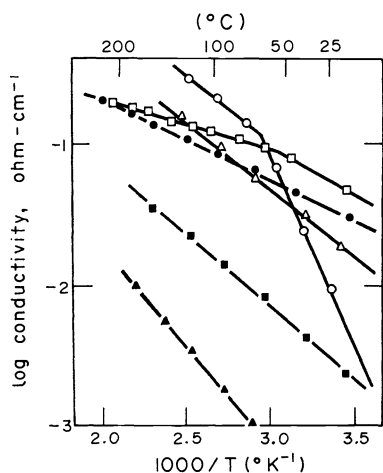


Fig. 4. Temperature dependence of the electrical conductivity of $17\text{CuCl}\cdot 3\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{HCl}$ (\circ), $4\text{CuCl}\cdot \text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{CH}_3\text{Cl}$ (Δ), $7\text{CuBr}\cdot \text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{HBr}$ (\square), $47\text{CuBr}\cdot 3\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{CH}_3\text{Br}$ (\bullet), $17\text{CuBr}\cdot 3\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{C}_2\text{H}_5\text{Br}$ (\blacktriangle), and $17\text{CuI}\cdot 3\text{C}_6\text{H}_{12}\text{N}_2\cdot 2\text{CH}_3\text{I}$ (\blacksquare).

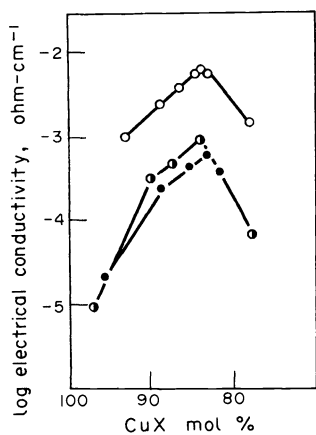


Fig. 5. Composition dependence of electrical conductivity of the binary systems $\text{C}_5\text{H}_{11}\text{NCH}_3\text{Br}-\text{CuBr}$ (\circ), $\text{C}_5\text{H}_{11}\text{NCH}_3\text{I}-\text{CuI}$ (\bullet), and $\text{C}_4\text{H}_9\text{ONCH}_3\text{I}-\text{CuI}$ (\bullet) at 25°C .

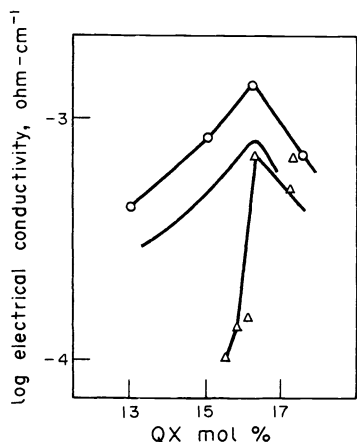


Fig. 6. Composition dependence of electrical conductivity of the $C_5H_{10}SCH_3I-CuI$ (\circ), $C_4H_8OSCH_3I-CuI$ (Δ), and $C_5H_{11}NCH_3I-CuI$ (-) systems.

Heat of transport of the copper(I) ions

In Table 3, the heats of transport of the copper(I) ions in some of the organic substituted ammonium bromide and copper(I) bromide systems are shown (Ref. 36). The heats of transport of the copper(I) ions are found to be smaller than their activation energies for conduction.

TABLE 3. Heat of transport of the copper(I) ions

	Heat of Transport (eV)	Activation Energy for Conduction (eV)	Conductivity at 20°C ($\Omega^{-1}cm^{-1}$)
31 $CuBr \cdot 4C_6H_{12}N_4CH_3Br$	0.092	0.147	0.024
7 $CuBr \cdot 4C_6H_{12}N_4CH_3Br$	0.094	0.178	0.016
37 $CuBr \cdot 3C_6H_{12}N_2 \cdot 2CH_3Br$	0.122	0.140	0.034
9 $CuBr \cdot C_6H_{12}N_2 \cdot 2CH_3Br$	0.122	0.155	0.020

From these results, the migration mechanism of the copper(I) ions in these copper(I) ion conductors may be considered to be similar to that of the silver ions in most of the organic ion substituted silver iodide.

SUMMARY

In general, the ionic migration in solids requires interconnected channels in which the mobile ions occupy partially the lattice sites having nearly equivalent site occupation energies. For fast ion transport, the activation energy for an ion jump from one site to another must be small.

In order to understand the conduction mechanism of the silver and copper(I) ions in solids more precisely, it will be necessary to accumulate a great deal of data in the field of solid state ionics.

Recent studies by NMR or Raman spectroscopy may add new information to these problems.

REFERENCES

1. T. Takahashi and O. Yamamoto, *Electrochim. Acta* **11**, 779-787, 911-917 (1966).

2. K. Funke, Progress in Solid State Chem. **11**, 345-402 (1976).
3. G. Eckold, K. Funke, J. Klaus and R.E. Lechner, J. Phys. Chem. Solids **37**, 1097-1103 (1976).
4. S. Hoshino, T. Sakuma and Y. Fujii, Techn. Rept. ISSP Ser. A. No. 804, 1-12 (March, 1977).
5. T. Takahashi, S. Ikeda and O. Yamamoto, J. Electrochem. Soc. **119**, 477-482 (1972), **120**, 647-651 (1973).
6. B. Scrosati, F. Papaleo and G. Pistoia, ibid **122**, 339-343 (1975).
7. G. Chiodelli, A. Magistris and A. Schiraldi, Electrochim. Acta **19**, 655-656 (1974).
8. L.Y.Y. Chan and S. Geller, J. Solid State Chem. **21**, 331 (1977).
9. J.N. Bradley and P.D. Greene, Trans Faraday Soc. **62**, 2069-2075 (1966), **63**, 424-430 (1967).
10. B.B. Owens and G.A. Argue, Science **157**, 308-310 (1967), J. Electrochem. Soc. **117**, 898-900 (1970).
11. D.O. Raleigh, J. Appl. Phys. **41**, 1876-1877 (1970).
12. B.B. Owens, J. Electrochem. Soc. **117**, 1536-1539 (1970), Adv. Electrochem. Electrochem. Eng., Ed. P. Delahay and C.W. Tobias vol. 8, 1-62 (1971).
13. B.B. Owens, J.H. Christie and G.T. Tiedeman, J. Electrochem. Soc. **118**, 1144-1147 (1971).
14. M.L. Berardelli, C. Biondi, M. De Rossi, G. Fonseca and M. Giomini, ibid, **119**, 114-118 (1972).
15. J. Coetzer and M.M. Thackeray, Electrochim Acta **21**, 37-38 (1976).
16. T. Takahashi, N. Wakabayashi, T. Miyazaki and O. Yamamoto, Nippon Kagaku Kaishi **1975**, 266-270.
17. R.G. Linford, J.M. Pollock and C.F. Randell, Nature **256**, [5516], 398-399 (1975).
18. J.H. Christie, B.B. Owens and G.T. Tiedeman, Inorg. Chem. **14**, 1423-1425 (1975).
19. S. Geller, Science **157**, 310-312 (1967).
20. S. Geller and M.D. Lind, J. Chem. Phys. **52**, 5854-5861 (1970).
21. R.G. Linford, J.M. Pollock and C.F. Randell, Nature **259** [5545], 656-657 (1976).
22. T. Takahashi, K. Kuwabara and O. Yamamoto, J. Electrochem. Soc. **120**, 1607-1612 (1973).
23. G.W. Mellors and D.V. Louzos, ibid, **118**, 846-850 (1971).
24. G.W. Mellors, D.V. Louzos and J.A. van Lier, ibid, **118**, 850-853 (1971).
25. T. Takahashi, O. Yamamoto and E. Nomura, Denki Kagaku **38**, 360-364 (1970).
26. K. Shahi and S. Chandra, Z. Naturforsch **30A**, 1055-1059 (1975).
27. K. Shahi, N. Sanyal and S. Chandra, J. Phys. Chem. Solids **36**, 1349-1352 (1975).
28. O. Yamamoto and T. Takahashi, Abst. 36th Spring Meeting, Chem. Soc. Japan (I) p. 263 (April, 1977) Osaka.
29. T. Matsui and J.B. Wagner, Jr., J. Electrochem. Soc. **124**, 941-944 (1977).
30. T. Takahashi, O. Yamamoto, ibid, **122**, 83-86 (1975).
31. M. Lazzari, R.C. Pace and B. Scrosati, Electrochim. Acta **20**, 331-334 (1975).
32. T. Takahashi, O. Yamamoto and S. Ikeda, J. Electrochem. Soc. **120**, 1431-1434 (1973).
33. T. Takahashi, N. Wakabayashi and O. Yamamoto, ibid, **123**, 129-132 (1976).
34. A.F. Sammels, J.Z. Gougotas and B.B. Owens, J. Electrochem. Soc. **122**, 1291-1296 (1975).
35. T. Takahashi, N. Wakabayashi and O. Yamamoto, J. Appl. Electrochem. **7**, 253-256 (1977).
36. T. Takahashi, O. Yamamoto and S. Yamada, Abst. 7th Chukaren Meeting, p. 105-106 (Oct. 1976) Nagoya.

Figures 1, 2, 4 and 5 are reprinted by permission of The Electrochemical Society, Inc.