JOURNAL OF APPLIED ELECTROCHEMISTRY 2 (1972) 51–57

Solid state ionics. High ionic conductivity solid in silver halide-silver sulphate system

T. TAKAHASHI, E. NOMURA and O. YAMAMOTO

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

Received 31 August 1971

The ionic conductivities and phase diagrams of AgI–Ag_2SO_4, AgCl–Ag_2SO_4 and AgBr–Ag_2SO_4 systems have been studied with the help of electrical conductivity, transport number, DTA and X-ray studies. In the AgI–Ag_2SO_4 system, the solid solution of α-AgI with Ag_2SO_4 was quenched to room temperature to have high ionic conductivity of $5{\cdot}0 \times 10^{-2}$ (ohm . cm)$^{-1}$ at room temperature and $1{\cdot}3 \times 10^{-3}$ (ohm . cm)$^{-1}$ at −78°C. The quenched solid solution was stable at −20°C, but gradually decomposed to β-AgI and β-Ag_2SO_4 at room temperature. The transport number of silver ion in this solid solution was about 1·0. In the AgCl–Ag_2SO_4 and AgBr–Ag_2SO_4 systems, the electrical conductivity was of the order of 10^{-4} to 10^{-6} (ohm . cm)$^{-1}$ at room temperature.

Introduction

In recent years, there has been considerable interest in high ionic conductivity solid electrolytes, and Ag_3SI [1], $Ag_2Hg_{0\cdot25}S_{0\cdot5}I_{1\cdot5}$ [2] and $RbAg_4I_5$ [3, 4], etc. have been found to have high ionic conductivity at ambient temperature. The ionic conductivity of these electrolytes is comparable to that of aqueous electrolyte solution, as shown in Table 1. Of these high ionic solid electrolytes, $RbAg_4I_5$, found by Bradley and Greene [3], and Owens and Argue [4], has very high ionic conductivity of 2×10^{-1} (ohm . cm)$^{-1}$ at 25°C. But this compound has the demerit of lability in moisture and iodine atmosphere [12]. The high ionic conductivity solids so far investigated have been double salts of silver iodide, and hence obtained by solid reaction of silver iodide and corresponding metal iodides or silver chalcogenides, for example, mercury iodide, rubidium iodide and silver sulphide. Further, the high ionic conductivity solids may be expected to be obtained by freezing higher temperature phases which have high ionic conductivities. A number of ionic compounds were investigated in our laboratory and it has been found that the higher temperature phase in the AgI–Ag_2SO_4 system can be frozen to maintain its high ionic conductivity.

Table 1. Ionic conductivity of solid electrolyte at room temperature

Substance	σ (ohm . cm)$^{-1}$
Ag_3SI	1×10^{-2}
$Ag_2Hg_{0\cdot25}S_{0\cdot5}I_{1\cdot5}$	7×10^{-2}
$RbAg_4I_5$	$2{\cdot}1 \times 10^{-1}$
α-AgI (150°C)	1×10^{0}
β-AgI	2×10^{-6}
AgCl	3×10^{-8}
AgBr	4×10^{-9}
α-Ag_2SO_4 (420°C)	5×10^{-3}

The object of this paper is to study the electrical conductivity of the frozen phase of the AgI–Ag_2SO_4 system and to decide the phase diagrams of this system and other silver halide–silver sulphate systems.

As is well known, AgI has four different modifications. Under ordinary temperature and pressure, it crystallizes in wurzite type (β-AgI) and zinc blende type (γ-AgI), and at 146°C it transforms to the higher temperature phase (α-AgI) which has a body-centred cubic structure. This β–α transformation is accompanied by an abrupt electrical conductivity change of four orders of magnitude. α-AgI is a high ionic conductor with silver ion as the mobile species, and its ionic conductivity is 1×10^{0} (ohm . cm)$^{-1}$ at 150°C [5].

Under high pressure, AgI is stable in a phase with NaCl type structure.

Ag_2SO_4 is a polymorphic compound and has two different modifications which are β-phase below 416°C and α-phase above 416°C. α-Ag_2SO_4 has high ionic conductivity of 1×10^{-2} $(\text{ohm}\,.\,\text{cm})^{-1}$ at 500°C and 3×10^{-3} $(\text{ohm}\,.\,\text{cm})^{-1}$ at 420°C, and the charge carriers in it are silver ions and electrons. According to the study of Hauffe *et al.*, its electronic transference number is $2{\cdot}5 \times 10^{-3}$ at 602°C under a partial pressure of oxygen of 100 torr [6] [13].

Experimental

Precipitation of the starting materials and samples for conductivity measurement

AgI was precipitated by adding 1N $AgNO_3$ aqueous solution to 1N KI aqueous solution with constant stirring. The precipitated AgI was washed 10 times by distilled water and with methyl alcohol and ethyl ether. Drying treatment carried out in vacuo was followed by heat drying at 110°C for 8 hours. All these procedures were carried out in a dark room.

AgCl and AgBr were precipitated by adding 1N $AgNO_3$ aqueous solution to 1N HCl or HBr solution, respectively. Washing and drying procedures were identical to the case of AgI.

The mixture of the weighed quantities of silver halide and silver sulphate was thoroughly ground and sealed in a Pyrex glass tube in vacuo. Then it was heated at 400°C for 2 hours in electrical furnace and cooled rapidly to −20°C.

Conductivity measurement

Samples for conductivity measurement were formed in the shape of pellets, about 0·3 cm thick and 1·3 cm in diameter, by pressing under a pressure of about 4 ton/cm^2. The cell assembly for conductivity measurements is shown in Fig. 1. In order to reduce the contact resistance, electrodes made of a mixture of 2 parts of powdered silver and 3 parts of sample were used. For measurement of the conductivity, an 1000 Hz impedance bridge was used.

The transport number of the ion was determined by the electrolysis method [7] using the cell constructed by the series arrangement of silver amalgamated anode, electrolyte and silver cathode. For the emf measurement, the cell constructed of silver anode, electrolyte, and iodine cathode, was also used.

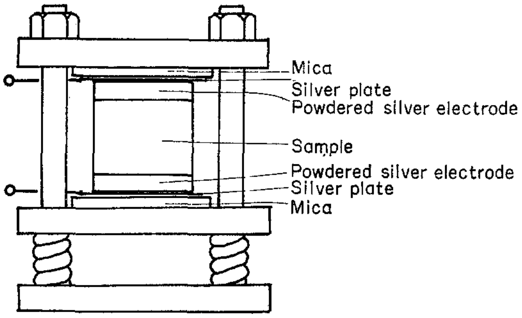

Fig. 1. Apparatus for conductivity measurement.

X-ray diffraction

The powder method was used in this study. The anode used in this experiment was Cu and the filter was Ni. The goniometer scanning speed selected was 1°/min in the qualitative analysis and ¼°/min in the lattice constant determination.

Differential thermal analysis

In order to measure the melting point and transition point, differential thermal analysis (DTA) was employed. The samples for DTA were used after storing for 6 months at room temperature. About one gramme of the sample was weighed and powdered in an agate mortar. This was put into a Vycor glass tube of 0·5 cm diameter and 4 cm length. The standard material α-alumina was also packed in another Vycor glass tube, and these tubes were held in a sample block made of nickel. The temperature change rate was controlled; 4°C/min for heating and 2°C/min for cooling respectively.

Results and Discussion

AgI–$AgSO_4$ system

Electrical conductivity

The electrical conductivities of the compounds containing Ag_2SO_4 from 10 mole% to 80 mole%, which have been cooled rapidly to −20°C are illustrated in Fig. 2. This figure shows that the samples containing 18–25 mole% Ag_2SO_4 have the high electrical conductivity of $5{\cdot}0 \times 10^{-2}$ $(\text{ohm}\,.\,\text{cm})^{-1}$ at room temperature and $1{\cdot}3 \times 10^{-3}$ $(\text{ohm}\,.\,\text{cm})^{-1}$ at −78°C. As the composition deviated from this range, the electrical conductivity gradually decreased. On the other hand, the electrical conductivity of the sample cooled slowly from 200°C to room temperature was found to be lower by about two orders of magnitude than the values shown in Fig. 2. When the quenched sample was annealed for several hours at 60°C, the electrical conductivity also decreased, especially in the range of composition from 18 mole% to 25 mole% Ag_2SO_4. In the lower temperature region, the logarithm of conductivity decreased linearly with the reciprocal of the absolute temperature, indicating Arrhenius behaviour. The activation energy for conduction of the sample containing 22 mole% Ag_2SO_4 was about 5·4 kcal/mol in the temperature range from 0°C to −80°C. At temperatures higher than room temperature, the conductivity decreased with increasing temperature. In order to evaluate the stability of this quenched sample, the time dependence of resistance was studied at each temperature. This result is shown in Fig. 3. At lower temperatures than −20°C, the resistance stayed constant for 300 days whereas at room temperature, the resistance increased with time, from 1·9 to 230 ohms, for 280 days. At 0°C and 10°C, it increased slowly with time from 6·2 to 9·6 ohms for 100 days, and 3·1 to 24 ohms for 233 days, respectively. It is concluded from these results that the quenched samples are stable below 0°C but markedly unstable above room temperature. The decrease of the electrical conductivity with increasing temperature above room temperature would be understandable as follows. When the sample containing 22 mole% Ag_2SO_4 was cooled rapidly from 200°C to −20°C, the higher temperature phase of α-AgI solid solution would be frozen to keep high electrical conductivity at −20°C. As temperature increased, the rate of oscillation of the lattice vibrations increased and the probability of a transformation from the higher temperature phase to the lower phase would increase. As a result, conductivity decreased with increasing temperature, as seen in Figs. 2 and 3.

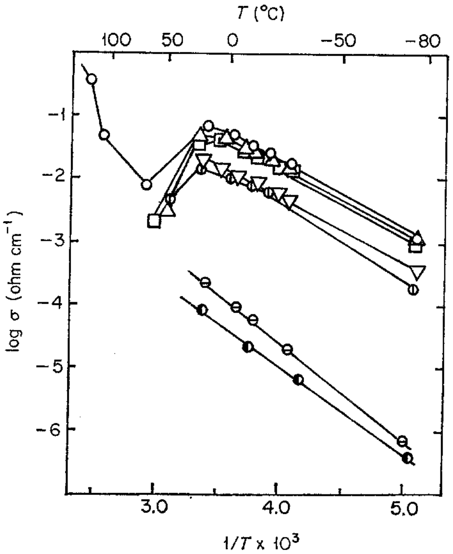

Fig. 2. Electrical conductivity of the AgI–Ag_2SO_4 system. ○ = 78 mole% Ag_2SO_4, △ = 80 mole%, ▽ = 90 mole%, ⦶ = 70 mole%, ⊖ = 40 mole%, ◐ = 20 mole%, □ = 85 mole%.

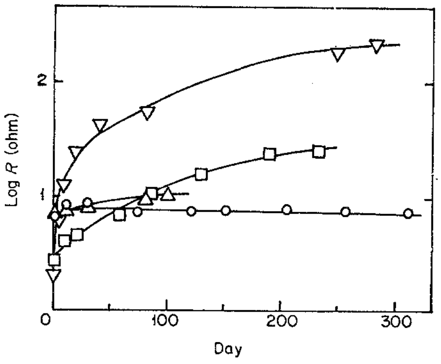

Fig. 3. Stability of the solid solution of 22 mole% Ag_2SO_4–78 mole% AgI. ▽ = room temperature, □ = 10°C, △ = 0°C, ○ = −20°C.

Transport number

It is important to determine the ionic transport number of solid electrolytes. In this study, the electrolysis method and the emf measurement of a silver-iodine cell were employed. In the former method [7], three pellets of 78 mole% AgI–22 mole% Ag_2SO_4 sample were used. As seen in Fig. 4, these pellets were held between two electrodes. In order to reduce the overvoltage for dissolution of silver ion, the amalgamated silver electrode was used as the anode,

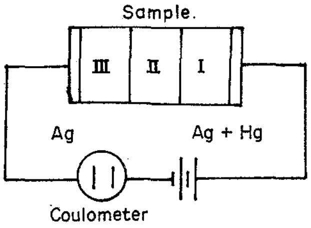

Fig. 4. Determination of transport number in the 22 mole% Ag_2SO_4 sample.

Table 2. Transport number in the 22 mole%Ag_2SO_4 sample

Electrolysis method		
Cell arrangement		*Change in mass*
Ag-Hg anode		—
22 mole% Ag_2SO_4–78 mole% AgI	I	—
22 mole% Ag_2SO_4–78 mole% AgI	II	−0·49 mg
22 mole% Ag_2SO_4–78 mole% AgI	III	+14·83 mg
Ag cathode		+0·03 mg
Ag in coulometer		14·39 mg
Transport number of silver ion		1·00
Current density		0·6–0·4 mA/cm^2
Emf measurement method of silver-iodine cell		
Theoretical emf		681 mV
Observed emf		671 mV
Transport number of silver ion		0·985

and a silver plate electrode was used as the cathode. A silver coulometer was used to determine the coulombs passed through the cell. The experiment was carried out at −20°C. The current density was 0·6–0·4 mA/cm^2 and cell voltage was about 180 mV. After a definite amount of current was passed, the change of the weight of each plate was measured. This result is shown in Table 2 to indicate that the transport number of silver ion is 1·00. In the latter measurement, a 22 mole% Ag_2SO_4 pellet was used as the electrolyte, silver plate as the anode, and the iodine and graphite mixture pellet as the cathode, the ratio of which was 2 : 1 in weight. The theoretical emf of this cell is calculated using thermodynamic data to be 681 mV at −20°C [8]. The experiment was carried out at −20°C and the open circuit voltage of the silver-iodine cell was measured as 671 mV. This result is shown in the latter half of Table 2. The ionic transport number is given by the ratio of the theoretical value to the measured one [9]. By this measurement, the transport number of a 22 mole% Ag_2SO_4 sample was estimated to be 0·99, and this value nearly agreed with that obtained by the electrolysis method. Therefore, it was concluded that the transport number of silver ion in this sample was about 1·0.

Phase diagram

The phase diagram of the AgI–Ag_2SO_4 system determined by DTA and X-ray analysis is shown in Fig. 5. Samples for this experiment were stored for 3 months at room temperature before the experiment, in order to achieve thermal equilibrium at room temperature. In the DTA patterns, the peak melting point of the sample containing 10 mole% Ag_2SO_4 appeared at 420°C which was lower than that of AgI (547°C), and was not observed in the range from 10 mole% to 60 mole% Ag_2SO_4. In this region, therefore, the liquidus and solidus lines are shown by broken lines in Fig. 5. Though Platonov [10] has shown that the AgI–Ag_2SO_4 system had a eutectic point of 142°C at 48 mole% Ag_2SO_4, the eutectic point measured in this study was 158°C. The lattice constants of α-AgI solid solutions were measured at 151°C as a

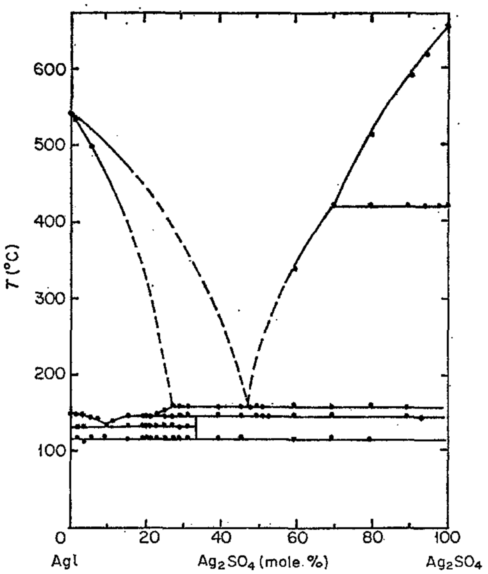

Fig. 5. Phase diagram of the AgI–Ag_2SO_4 system.

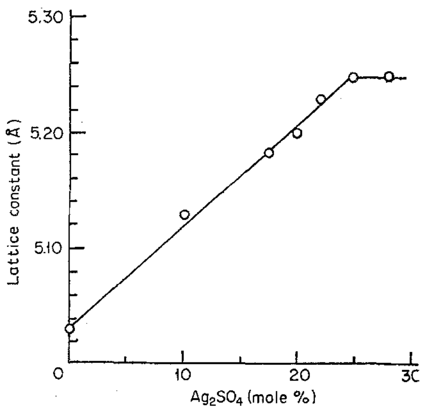

Fig. 6. Lattice constant of the AgI solid solution.

function of the concentration, in order to find the limit of solubility of Ag_2SO_4, and the result is shown in Fig. 6. The lattice constant of α-AgI solid solution increases linearly from 5·03 Å of α-AgI [11] to 5·25 Å corresponding to the Ag_2SO_4 content from 0 to 25 mole%; above 25 mole% Ag_2SO_4 it becomes constant. Therefore, it can be concluded that Ag_2SO_4 dissolved in α-AgI up to 25 mole% at 151°C. $Ag_4I_2SO_4$ is a stable compound from 119°C to 148°C; above 148°C it decomposes to α-AgI solid solution, and β-Ag_2SO_4, and below 119°C β-AgI and β-Ag_2SO_4 precipitate.

On the high ionic conductivity region

At ambient temperature, as seen in Fig. 2, there is a high ionic conductivity region in 22–15 mole% Ag_2SO_4, but no intermediate compound can be found in the phase diagram of Fig. 5. In order to know the reason why the high ionic conductivity region was found in the composition of about 22 mole% Ag_2SO_4, DTA and X-ray studies on the following samples were made: (1) the sample obtained by cooling rapidly from 200°C to −20°C, (2) annealing sample (1) at 100°C for 2 days, and (3) storing sample (1) for 6 months at room temperature. The results of the DTA study of these samples are shown in Fig. 7, where A is the heating curve of sample (1), B is that of sample (3), and C is the cooling curve of sample (3). The curve B has four endothermic peaks at 119°, 135°, 148° and 158°C. The first peak at 119°C corresponds to the solid reaction;

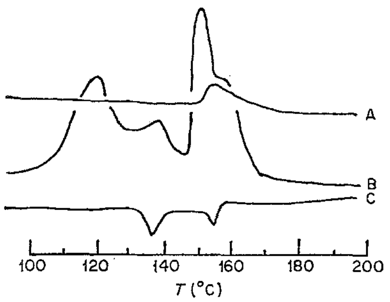

Fig. 7. DTA pattern of the 28 mole% Ag_2SO_4 sample obtained with various conditions.

$$\beta\text{-AgI}+\beta\text{-Ag}_2\text{SO}_4\rightarrow\text{Ag}_4\text{I}_2\text{SO}_4 \qquad (1)$$

The second peak at 135°C and third peak at 148°C are due to the eutectoid reaction and the peritectoid reaction, respectively;

$$\beta\text{-AgI}+\text{Ag}_4\text{I}_2\text{SO}_4\rightarrow\alpha\text{-AgI(S.S.)} \qquad (2)$$

$$\text{Ag}_4\text{I}_2\text{SO}_4\rightarrow\alpha\text{-AgI (S.S.)}+\beta\text{-Ag}_2\text{SO}_4 \qquad (3)$$

where α-AgI (S.S.) is the solid solution of AgI. The final peak at 158°C is due to the eutectic reaction. In the cooling curve C, the cooling rate of which was 2°C/min, there are two peaks due to the eutectic reaction and the peritectoid reaction of Equation (3); whereas, as seen in the curve A, the quenched sample has only one broad peak at about 155°C, which may be due to the eutectic reaction. One can conclude from the DTA study described above and the phase diagram of Fig. 5, that when cooled rapidly from a higher temperature than 158°C, α-AgI solid solution will be quenched without the eutectoid reaction of Equation (2) and peritectoid reaction of Equation (3). Also, the high ionic conductivity of the sample containing about 22 mole% Ag_2SO_4, as described previously, may be due to the quenched α-AgI phase, which has a very high ionic conductivity. The results of an X-ray study of the 22 mole% Ag_2SO_4 sample were α-AgI plus β-AgI and β-Ag_2SO_4 for sample (1), β-AgI plus β-Ag_2SO_4 for samples (2) and (3). These results also support the above argument.

AgCl–Ag_2SO_4 System

The phase relation in the AgCl–Ag_2SO_4 quasi-binary system has been studied. As shown in

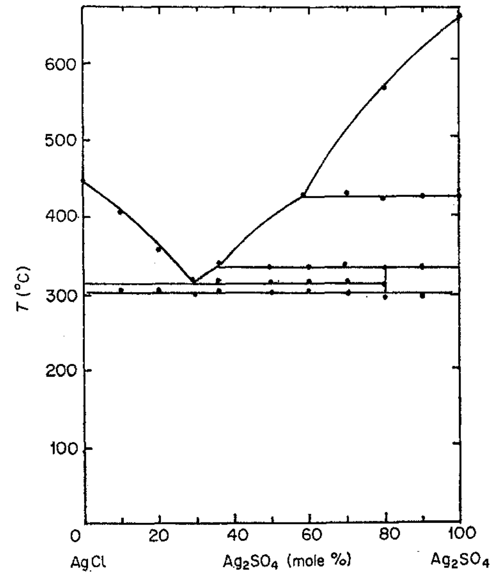

Fig. 8. Phase diagram of the AgCl–Ag_2SO_4 system.

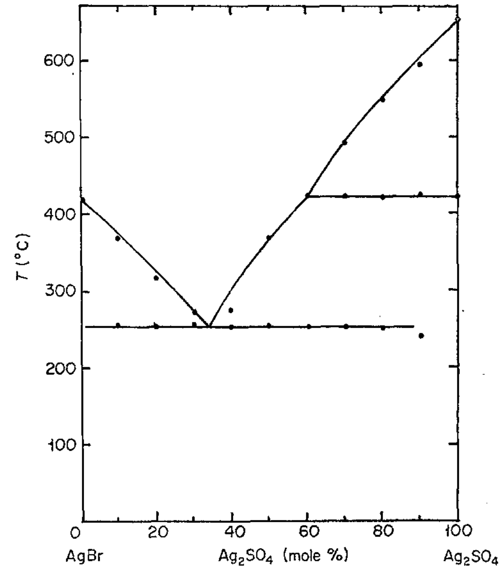

Fig. 9. Phase diagram of the AgBr–Ag_2SO_4 system.

Fig. 8, the liquidus curve in this system first descends gently from the melting point of AgCl at 455°C to the eutectic point at 303°C (29 mole% Ag_2SO_4) and then rises to the melting point of Ag_2SO_4 (652°C) through the three steps at 316°, 336° and 428°C. This system contains one intermediate compound, $Ag_9Cl(SO_4)_4$ between 305°C and its incongruent melting point of 336°C. $Ag_9Cl(SO_4)_4$ decomposes to AgCl and β-Ag_2SO_4 at 305°C. The transition temperature of β-Ag_2SO_4 to the α-phase is 428°C. The absence of the intermediate compound at room temperature was confirmed by the X-ray pattern.

The electrical conductivity of this system at room temperature was of the order of magnitude from 10^{-6} to 10^{-7} (ohm . cm)$^{-1}$.

AgBr-Ag_2SO_4 System

As shown in Fig. 9, this phase diagram is a simple eutectic system as opposed to the previously described AgI–Ag_2SO_4 and AgCl–Ag_2SO_4 systems. A eutectic point appeared at 255°C (35 mole% Ag_2SO_4). A break in the slope of the liquidus line at 425°C is due to the transformation of β-Ag_2SO_4 to the α-phase. The absence of the intermediate compound was confirmed by the observation of the X-ray powder pattern through overall concentrations.

The electrical conductivity of this system at room temperature is less than 10^{-4} (ohm . cm)$^{-1}$.

Conclusion

The results obtained from the experiments and the discussion on the silver halide–silver sulphate systems lead to the following conclusions.

1. In the AgI–Ag_2SO_4 system, the high ionic conductivity was obtained at room temperature at about 78 mole% AgI–22 mole% Ag_2SO_4.
2. The electrical conductivity of 78 mole% AgI–22 mole% Ag_2SO_4 was 5×10^{-2} (ohm.cm)$^{-1}$ at room temperature and $1{\cdot}3 \times 10^{-3}$ (ohm.cm)$^{-1}$ at −78°C.
3. The ionic transport number of 78 mole% AgI was estimated to be 1·00 by electrolysis method and 0·99 by the emf measurement of silver-iodine cell at −20°C.
4. The stability of the 78 mole% AgI solid solution was very high below 0°C, and at −20°C the initial electrical conductivity value was maintained for a year.
5. In the AgCl–Ag_2SO_4 and AgBr–Ag_2SO_4 systems, the electrical conductivity was of the order of 10^{-4} to 10^{-6} (ohm . cm)$^{-1}$ at room temperature.

References

[1] T. Takahashi and O. Yamamoto, *Denki Kagaku*, **32** (1964) 610.

[2] O. Yamamoto and T. Takahashi, *Denki Kagaku*, **35** (1967) 651.

[3] J. N. Bradley and P. D. Greene, *Trans. Faraday Soc.*, **63** (1967) 424.

[4] B. B. Owens and G. R. Argue, *Science*, **157** (1967) 308.

[5] K. H. Lieser, *Z. Phys. Chem. N.F.*, **9** (1956) 302.

[6] K. Hauffe and D. Hoeffgen, *Z. Phys. Chem. N.F.*, **49** (1966) 94.

[7] C. Tubandt, H. Reinhold and G. Liebold, *Z. anorg. allg. chem.*, **197** (1931) 225.

[8] T. Takahashi and O. Yamamoto, *Electrochim. Acta*, **11** (1966) 779.

[9] S. P. Mitoff, *J. Chem. Phys.*, **36** (1962) 1383.

[10] F. P. Platonov, *Trudy Moskov. Solsko-Khoz. Akad., im K.A. Timiyazeba*, **36** (1946) 13.

[11] L. W. Srok, *Z. Phys. Chem.*, **B25** (1934) 411.

[12] B. B. Owens, in 'Advances in Electrochemistry and electrochemical Engineering', Vol. 8 Interscience, New York, (1971) p. 1.

[13] A. Kvist, *Z. Naturforshg.*, **22a** (1966) 208.