JOURNAL OF SOLID STATE CHEMISTRY **20**, 315–321 (1977)

Physicochemical Investigation of the Silver Iodide–Silver Polymolybdate Systems in the Solid State

F. BONINO, M. LAZZARI, A. LONARDI, AND B. RIVOLTA

Centro Studi Processi Elettrodici del C.N.R., Polytechnic of Milan, Milan, Italy

AND

B. SCROSATI

Istituto di Chimica Fisica, University of Rome, Rome, Italy

Received August 24, 1976; in revised form November 8, 1976

The systems AgI–$Ag_2Mo_2O_7$ and AgI–$Ag_2Mo_4O_{13}$ have been investigated by differential scanning calorimetry, X-ray analysis, and conductivity to characterize intermediate compounds with fast ion transport in the solid state. The results indicate that in the first system there is a new phase, at about 75 mole % AgI, which initially contains a small amount of an Ag_2MoO_4, 4AgI phase in a metastable condition. In the AgI–$Ag_2Mo_4O_{13}$ system no formation of highly conductive intermediate compounds was detected but rather a decomposition in $Ag_2Mo_2O_7$, 75 m/o AgI, and MoO_3 was observed. The results have been qualitatively discussed in terms of the role of the minority substituting polymolybdate anions leading to the formation of open-structured compounds of the AgI-modified type.

Introduction

The majority of solid conductors of the silver iodide–silver oxosalt type have a vitreous structure characterized by peak-free X-ray diffraction patterns (*1*). The $Ag_2Mo_2O_7$, 75 m/o AgI conductor exhibits instead a very well-defined X-ray spectrum which maintains its crystalline character independently of the preparation procedure, as was pointed out in a previous paper (*1*) and shown in Fig. 1. Therefore we were interested in investigating further the AgI–$Ag_2Mo_2O_7$ system in order to define its peculiar properties and compare them with those of the "parent" AgI–Ag_2MoO_4 and AgI–$Ag_2Mo_4O_{13}$ systems. This investigation has been carried out with detailed differential scanning calorimetry (DSC) and conductivity studies.

Experimental

Silver iodide and silver molybdate were prepared by precipitation from silver nitrate and sodium iodide and sodium molybdate solutions, respectively (*2*). Silver dimolybdate was obtained, following the procedure described by Kohlmuller and Faurie (*3*), by a solid state reaction between MoO_3 and Ag_2MoO_4 in stoichiometric proportion. The final product was checked by X-ray analysis and the results closely agreed with those reported by Kohlmuller and Faurie for $Ag_2Mo_2O_7$. A similar procedure was also followed for the preparation of $Ag_2Mo_4O_{13}$. The X-ray analysis of the final product, however, beside the lines reported by Kohlmuller and Faurie for $Ag_2Mo_4O_{13}$ (*3*), also showed those related to MoO_3. This seems to be ascribable to the fact that, under the preparative conditions, the stable phase could be $Ag_6Mo_{10}O_{33}$, instead of $Ag_2Mo_4O_{13}$, as also suggested by Gatehouse and Leverett (*4*). The intermediate solid materials in the systems examined were formed by melting, under vacuum or inert gas, intimate mixtures of weighed amounts of silver iodide and the appropriate silver molybdate. The melt was subsequently cooled or quenched in one of the

Printed in Great Britain

ISSN 0022-4596

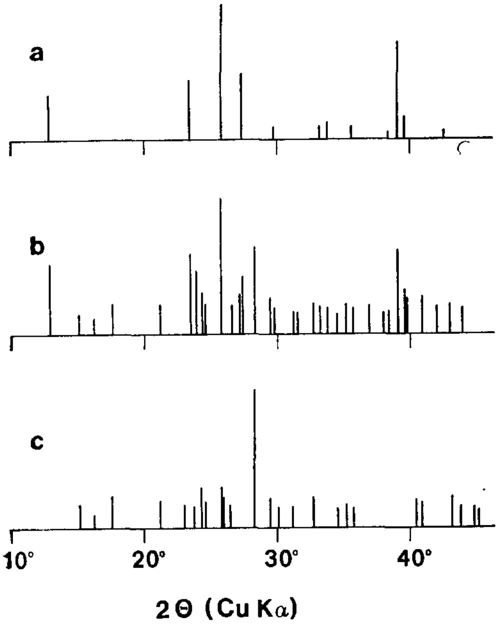

FIG. 1. X-Ray diffraction patterns of AgI–$Ag_2Mo_2O_7$ (75 m/o AgI) samples prepared by quenching in liquid nitrogen (a), by slow cooling (b), and after annealing at 140°C (c).

following three ways: (a) slow cooling under an inert gas stream at 1°C/min; (b) "spontaneous" cooling to room temperature under an inert gas stream; (c) quenching in liquid nitrogen.

X-Ray powder diffraction patterns were obtained with Cu$K\alpha$ radiation at 30 kV and 20 mA (JEOL diffractometer, Model JDX-8S). Differential scanning calorimetry studies were carried out at a scan rate of 15°C/min using a calorimeter Perkin–Elmer, Model DSC 1B. For comparison purposes the same sample amount was always used for these studies. For the conductance measurements, samples were pressed at about 2500 kg cm^{-2} into pellets with geometric surface areas of 1.25 cm^2. These pellets were sandwiched between two electrodes formed by mixing silver powder with the sample in a weight ratio of 1 : 2 and pressing it into pellets, also at 2500 kg cm^{-2}. The resistance of the resulting symmetrical cells was then measured using an ac bridge (Wayne Kerr) operating at 1.592 kHz. For measurements above room temperature, the cells were maintained at the desired value, with an accuracy of ±0.2°C using a recirculating thermostatic bath or a Pyrex cell in a controlled furnace.

Results

AgI–$Ag_2Mo_2O_7$

In a previous paper (*1*), it was shown that in this system there is an intermediate compound at 75 m/o AgI having at 25°C a conductivity of 0.008 ohm^{-1} cm^{-1}. The electrochemical characterization indicated that the observed conductivity was almost purely ionic and due to silver ion movements only. It was therefore concluded that the material may be regarded as a silver electrolyte. As already mentioned, however, this electrolyte shows some deviations from the general properties of the silver iodide–silver oxosalt class of conductors, the most peculiar of these being the type of structure which appears to be crystalline independent of the method of preparation. Furthermore, this structure does not seem to change, even after long annealing of the material at high temperatures. For example, the X-ray spectra of samples annealed at 140 (see Fig. 1), 180, and 220°C do not show drastic changes with respect to that of freshly prepared samples, but some weak reflections of silver iodide and a few unidentified reflections do appear in the case of samples annealed at 180°C. This would indicate that the transformations which take place in these temperature ranges are reversible or involve only a limited amount of the substance. To further investigate this aspect a detailed thermal study was carried out on $Ag_2Mo_2O_7$, 75 m/o AgI, samples obtained with method (c) (see Experimental). The DSC traces for such samples show a small endothermic peak at about 50°C, followed by two broad exothermic ones (at about 90 and 135°C respectively) and a strong endothermic peak at 176°C. No thermal effects were observed in the following cooling scan.

Similar samples were then submitted to various thermal cycles and the results are reported in Fig. 2. The first heating and cooling cycles up to 130°C (Figs 2a–d) show that the effects observed at about 50 and 90°C are irreversible. The following heating scan (e) to 200°C reveals a peak at 145°C, ascribable to the presence of silver iodide

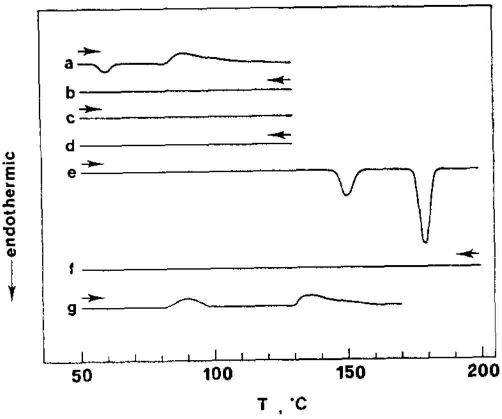

FIG. 2. Subsequent heating and cooling DSC traces of $Ag_2Mo_2O_7$, 75 m/o AgI quenched samples.

($\beta \rightarrow \alpha$ transition), followed by the strong peak at 176°C. The cooling trace (f) does not show any effect while in the subsequent heating scan (g) the broad exothermic peaks at 90 and 135°C appear again, thus showing that the existence of these latter is obviously connected to a heating treatment of the material at temperatures higher than 130°C. It must be pointed out that observation under the microscope during the heating scans above discussed showed that to the endothermic effect at 176°C is associated the melting of a small part of the sample. The complete fusion of the 75 m/o AgI sample takes place progressively between 250°C and 320°C, while for samples at higher (90 m/o) and lower (60 m/o) AgI content it occurs around 400°C.

In an attempt to clarify the complex thermal properties described above, we have also examined the behavior of the "parent" solid conductor, found by Chiodelli *et al.* (*5*), in the $AgI-Ag_2MoO_4$ system. This electrolyte, when prepared by quenching in liquid nitrogen a melted mixture at 80 m/o AgI, presents a vitreous structure characterized by a peak-free X-ray spectrum.

In Fig. 3 are shown various heating and cooling DSC traces of Ag_2MoO_4, 80 m/o AgI samples prepared by method (c). The initial heating shows a small endothermic peak at about 50°C, and two exothermic peaks starting at 75 and 100°C, respectively. These are followed by the AgI peak (150°C) and a large peak of melting at 176°C. In the second heating cycle the first two peaks disappear. Finally the peaks at 150 and 176°C are absent if the previous cooling is interrupted before the large exothermic effect at 90°C, as shown by the third cycle of the figure.

These results, together with the observations reported by Chiodelli *et al.* (*5*), allow one to conclude that the Ag_2MoO_4, 4AgI conductor undergoes at around 90°C an irreversible amorphous → crystalline transformation. This transformation leads to the decomposition of the material to silver iodide and a second phase, which together form an eutectic mixture melting at 176°C. The presence of this decomposition transformation has also been ascertained by X-ray analysis. The X-ray diffraction pattern of an Ag_2MoO_4, 80 m/o AgI sample which had been annealed at 140°C shows, in fact, the presence of silver iodide and of an intermediate phase Ag_2MoO_4, xAgI of unknown composition.

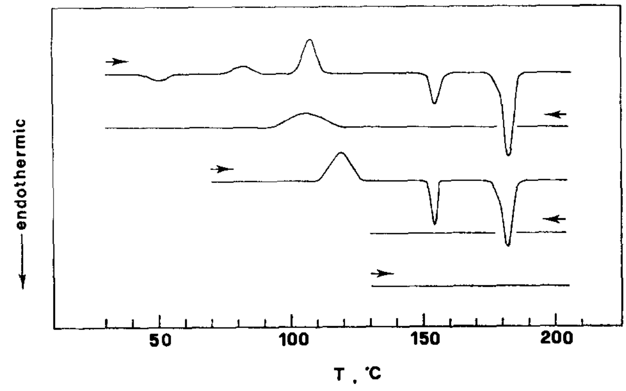

FIG. 3. DSC traces of Ag_2MoO_4, 80 m/o AgI quenched samples.

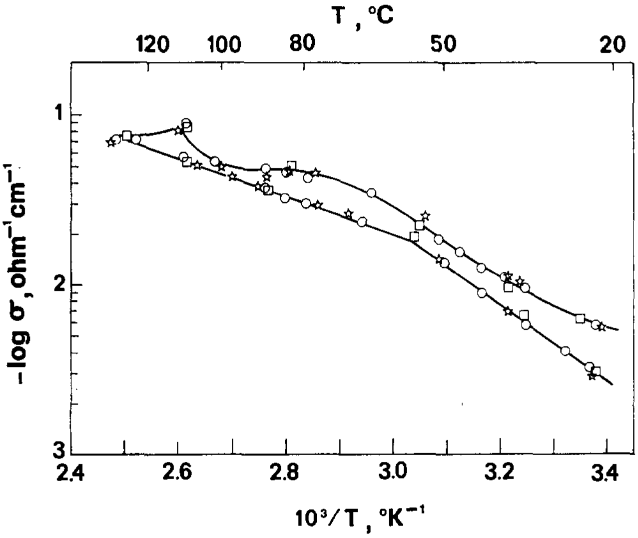

FIG. 4. Conductivity cycles (20–130°C) of various $Ag_2Mo_2O_7$, 75 m/o AgI quenched samples.

The comparison between the termal behavior of Ag_2MoO_4, 80 m/o AgI and that related to $Ag_2Mo_2O_7$, 75 m/o AgI, indicates that the latter contains a certain amount of the former. This minor constituent is probably responsible for the endothermic peak at 176°C which is always noticed in the heating DSC scans of the silver iodide–silver dimolybdate solid conductor.

This hypothesis is further validated when the conductimetric behaviors of the two materials are considered. Figure 4 shows the temperature dependence of the conductivity of a series of $Ag_2Mo_2O_7$, 75 m/o AgI samples obtained with method (c). The first heating curve, from 20 to 130°C, is nonlinear, and the following curve shows two different slopes. This peculiar hysteresis disappears in the subsequent thermal cycles which all assume the two-slope configuration of the first cooling curve.

These results indicate that, in the temperature range examined, the material undergoes an irreversible transformation. This conclusion is further confirmed by the fact that a sample obtained by slow cooling from the melt (method (a)), shows an initial temperature dependence of the conductivity which is identical to that presented by the cooling curve of the quenched sample, i.e. the two-slope trend.

To better confine the range of stability of the material, the conductometric behavior during the first heating process has been further investigated in a restricted temperature range from 20 to 80°C. Typical results related to two subsequent heating-cooling cycles are reported in Fig. 5. In this case the S-shaped trend is perfectly reproducible, thus indicating that the irreversible transformation takes place at temperatures higher than 80°C and, very likely, at about 90°C, a temperature associated with

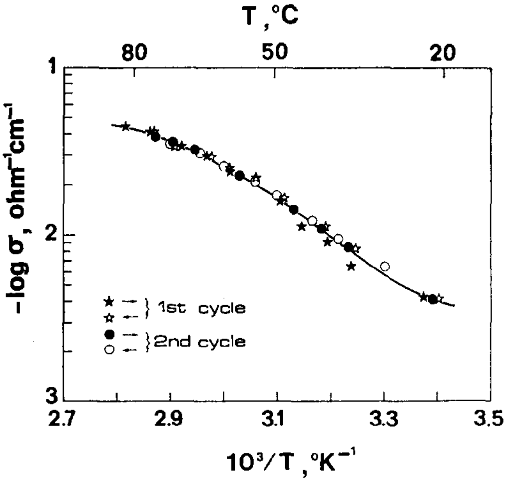

FIG. 5. Conductivity cycles (20–80°C) of various $Ag_2Mo_2O_7$, 75 m/o AgI quenched samples.

an exothermic effect in the DSC trace of the material. One may then conclude that the "irregularities" presented during the first heating of the $Ag_2Mo_2O_7$, 75 m/o AgI quenched samples are related to a situation of instability which disappears after a heating treatment at 120–130°C, as again indicated by the DSC studies (see Fig. 2).

In Fig. 6 is shown the initial conductometric behavior of a Ag_2MoO_4, 80 m/o AgI, sample, prepared with method (c). Up to about 80°C this behavior is qualitatively similar to that presented by the $Ag_2Mo_2O_7$, 75 m/o AgI samples under the same conditions. Near 90°C the sample softens or would even appear to partially fuse.

At this temperature, therefore, there is a spurious increase in conductivity. As discussed in the course of the analysis of the thermal results, to the above process is associated a decomposition reaction into poorly conductive materials (AgI and Ag_2MoO_4, xAgI). In fact, the conductivity of Ag_2MoO_4, 80 m/o AgI samples, after annealing at temperatures higher than 90°C, results strongly decreased.

Considering these results along with the others reported already, one may assume that the quenched $Ag_2Mo_2O_7$, 75 m/o AgI samples contain initially a certain amount of a metastable phase. This phase, which may be identified as Ag_2MoO_4, 80 m/o AgI, may originate from a partial decomposition of $Ag_2Mo_2O_7$ followed by a combination with AgI. It has to be pointed out that this decomposition must be induced by silver iodide. Silver dimolybdate as such is in fact thermodynamically stable (*3*) at the temperatures of treatment of the AgI–$Ag_2Mo_2O_7$ mixtures considered here (450–480°C).

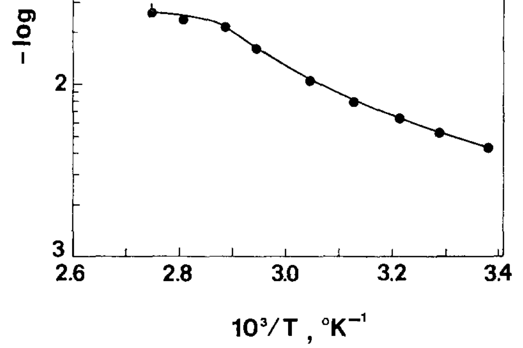

FIG. 6. Temperature dependence of the conductivity of Ag_2MoO_4, 80 m/o AgI quenched samples.

The conductivity behavior of the material after the first heating cycle up to 120°C (or of a material obtained by method (a)) is instead qualitatively representative of a solid conductor whose composition, even if not exactly definable because of the decomposition phenomena mentioned, is close to 0.25 $Ag_2Mo_2O_7$, 0.75 AgI.

AgI–$Ag_2Mo_4O_{13}$ System

The composition–conductivity plots of AgI–$Ag_2Mo_4O_{13}$ samples, obtained by method (b), do not show very well-defined maxima, as may be seen from Fig. 7. It is not therefore possible to determine from these plots the precise composition of the eventual intermediate conductive phase. A more exact definition of this composition has been attempted with DSC studies by measuring the area of the AgI peak (150°C) for various mixtures. As shown in Fig. 8, this area reaches zero for samples at 78 m/o AgI. This would appear to be the composition of the intermediate phase in the system.

The X-ray analysis of samples with this composition, however, surprisingly showed a pattern entirely ascribable to 0.75 AgI, 0.25 $Ag_2Mo_2O_7$, and MoO_3, as schematically indicated in Fig. 9. Such a pattern was definitely confirmed with a series of analyses performed under various conditions, such as on samples of compositions slightly different from 80 m/o AgI and/or obtained with different procedures. One has therefore to conclude that during the heating of the mixtures, $Ag_2Mo_4O_{13}$ (or, eventually, $Ag_6Mo_{10}O_{33}$) decomposes in MoO_3 and $Ag_2Mo_2O_7$. This latter combines then with silver iodide to give the conductive material

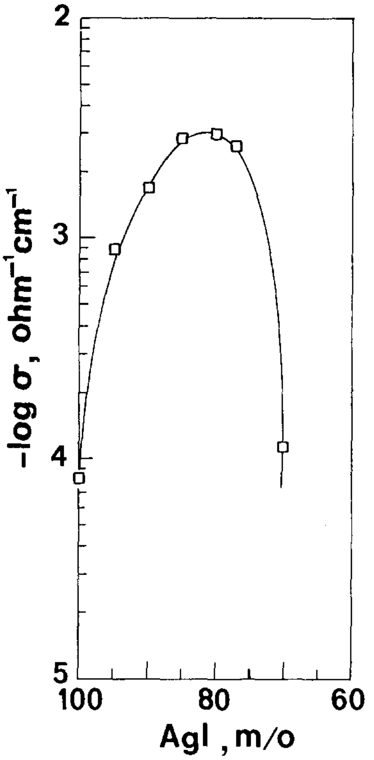

FIG. 7. Composition dependence of the conductivity in the $Ag_2Mo_4O_{13}$–AgI system at 25°C.

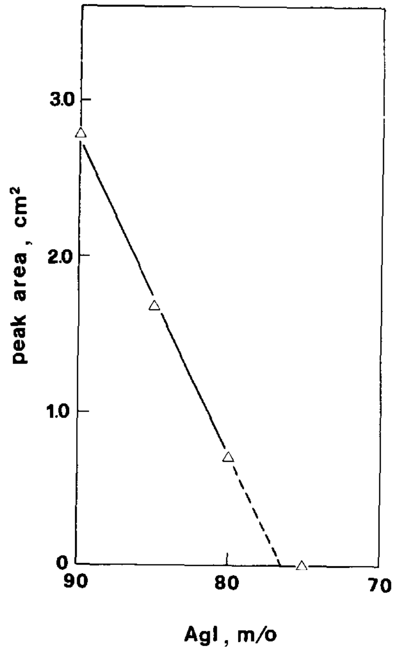

FIG. 8. Silver iodide peak area for $Ag_2Mo_4O_{13}$–AgI samples at various AgI contents.

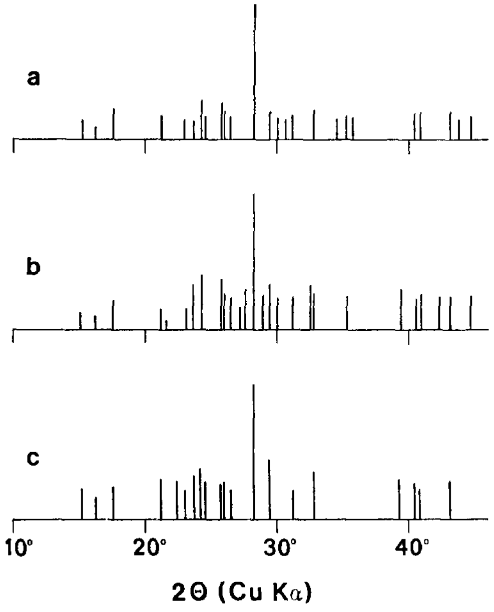

FIG. 9. X-Ray diffraction patterns of MoO_3 (a); $Ag_2Mo_4O_{13}$–AgI (80 m/o AgI) (b); and $Ag_2Mo_2O_7$, 75 m/o AgI (c), samples.

(0.75 AgI, 0.25 $Ag_2Mo_2O_7$) described in the previous section.

Also in this case it has to be remarked that the decomposition is related to the presence of silver iodide. Both $Ag_2Mo_4O_{13}$ and $Ag_6Mo_{10}O_{33}$ (*3*, *4*) are in fact thermodynamically stable at the temperatures at which they are heated in mixture with AgI.

Discussion

As already pointed out, the solid conductor found in the AgI–$Ag_2Mo_2O_7$ system has various properties which deviate from the general behavior of the silver iodide–silver oxosalt electrolytes. The samples obtained with the most common procedure, i.e., quenching the melted mixtures, show a crystalline structure and contain a certain amount of Ag_2MoO_4, 4AgI in metastable conditions. Furthermore the temperature dependence of the conductivity of this material shows a change in slope (Fig. 4) which does not correspond to any detectable thermal effect in the DSC traces (Fig. 2).

Even more atypical is the AgI–$Ag_2Mo_4O_{13}$

system, where the attempts to obtain an intermediate compound failed completely because of the total decomposition of the polymolybdate. In this respect, one must again mention how this decomposition occurs only when the polymolybdate is heated with silver iodide.

It would therefore seem from these results that the formation of open-structured, highly conductive compounds of the AgI-modified type is strongly related to the characteristics of the minority substituting polymolybdate anion.

The effect of the substituting ion in the formation of conductive phases has been pointed out already for other classes of silver solid electrolytes. A typical example is the family of tetraalkylammonium iodide–silver iodide conductors, QAg_nI_{n+1}, studied by Owens (*6*, *7*).

The role of the substituting cation was well evidenced here by the fact that materials in which the Q^+ ions contained less than nine carbon atoms were good conductors while those where the Q^+ ions contained more than nine atoms were insulators (*6*). One may then conclude that, even if the size relationship is not the sole factor which regulates the formation of intermediate open structures (*7*), certainly the volume effect of the substituting ion may be crucial in certain cases.

From this aspect, the results obtained in this work indicate that in passing from $Mo_2O_7^{2-}$ to $Mo_4O_{13}^{-2}$ one goes from a "transient" situation, where the formation of the intermediate compound seems to be just barely possible, to a total instability. In this respect, the behavior of the systems examined here appears very similar to that of the silver pyridinium–silver iodide systems, studied by Owens and coworkers (*8*, *9*). For instance, highly conductive electrolytes were obtained with 1–3 and 3–5 dimethyl-pyridinium iodides while with 2–6 dimethyl-pyridinium iodide no intermediate compound was formed (*8*). Furthermore the temperature dependence of the conductivity of the compound found in the pyridinium iodide–silver iodide system, $(C_5H_5NH)Ag_5I_6$, shows a change in slope at 50°C (*9*), which is qualitatively very similar to that observed in this work for the 0.75 AgI, 0.25 $Ag_2Mo_2O_7$ conductor. The transition of $(C_5H_5NH)Ag_5I_6$ is not associable to any detectable change in structure, as shown by Geller and Owens (*9*). These authors concluded that the transition may be related to a transformation from a region of low disorder, in which there is an increasing fraction of mobile Ag ions with increasing temperature, to one of high disorder, in which essentially all the Ag ions are mobile.

Due to the similarities between the two systems, this conclusion would somewhat sustain the idea of a "transient" situation, where the role of the minority ion is crucial for the stabilization of intermediate open structures, as suggested for the silver iodide–silver polymolybdate systems. On the other hand it is obvious that further studies, especially directed toward clarifying the structures, would certainly be necessary to confirm this assumption.

Acknowledgments

This work has been supported by the Consiglio Nazionale delle Ricerche (C.N.R.).

References

1. M. LAZZARI, B. SCROSATI, AND C. A. VINCENT, *Electrochim. Acta* **22**, 51 (1977).
2. B. SCROSATI, F. PAPALEO, G. PISTOIA, AND M. LAZZARI, *J. Electrochem. Soc.* **122**, 339 (1975).
3. R. KOHLMULLER AND J. P. FAURIE, *Bull. Soc. Chim. Fr.* **11**, 4379 (1968).
4. B. M. GATEHOUSE AND P. LEVERETT, *Chem. Comm.* **1093** (1969).
5. G. CHIODELLI, A. SCHIRALDI AND A. MAGISTRIS, *Electrochim. Acta* **19**, 655 (1974). *J. Appl. Electrochem.* **6**, 251 (1976).
6. B. B. OWENS, "Advances in Electrochemistry and Electrochemical Engineering" (P. Delahay and C. W. Tobias, Eds.), p. 57, Interscience, New York, 1971.
7. B. B. OWENS, "Fast Ion Transport in Solids" (W. van Gool, Ed.), p. 593, North Holland, Amsterdam (1973).
8. B. B. OWENS, J. H. CHRISTIE, AND G. T. TIEDERMANN, *J. Electrochem. Soc.* **118**, 144 (1971).
9. S. GELLER AND B. B. OWENS, *J. Phys. Chem. Solids*, **33**, 1241 (1972).