



# Electrical Conductivity Studies of AgCl:KCl (RbCl, CsCl) Composites and a Novel Method of Obtaining Highly Porous Materials

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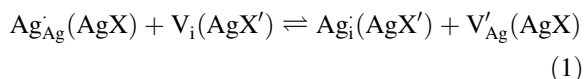
**Abstract.** Two phase systems consisting of AgCl and KCl (or RbCl, CsCl) have been studied with respect to morphology and electrical properties. As expected from the contact of such Frenkel and Schottky disordered ionic conductors, substantial enhancement effects were not observed. In the case of AgCl:KCl, eutectic lamellar structures have been obtained and their conductivities measured using both macroscopic electrodes as well as microelectrodes. Leaching the alkali chloride out of the lamellar composite leads to a porous solid network. Potential applications of such microporous ionic silver halides as a gas sensor as well as a solid envelope for liquid electrolytes are considered.

**Keywords:** composites, ionic conductivity, silver halide, eutectics, heterogeneous doping

## 1. Introduction

Ever since the work on LiI:Al<sub>2</sub>O<sub>3</sub> composite electrolyte [1], the studies on composite electrolytes [2–12] consisting of an ionic conductor and a second insulating phase or of two co-existing ionic conductors attracted much attention with respect to both potential application and theoretical understanding. A general explanation is based on the alteration of the defect chemistry [10–12] at the interface (“Heterogeneous Doping”). Of course, it has to be borne in mind that many effects may appear at solid-solid interfaces depending on the individual chemistry. Thus, in the case of AgI:Al<sub>2</sub>O<sub>3</sub> the formation of an “interfacial phase” or more precisely a pronounced stacking fault arrangement was observed, which is in agreement with the polytypism of AgI [13]. Alkali as well as silver halides doped “heterogeneously” [10,12] have attracted much attention mainly due to the improved transport properties. In these cases the contact phase is either a surface active insulator enabling the internal adsorption of cations or anions, or a second ion conductor of similar defect chemistry. Concerning the latter case, the disorder

reaction at the contact of two phase compatible silver halides can be written as a heterogeneous Frenkel equilibrium



Here we report the results obtained from studying systems in which a Frenkel disordered solid (AgCl) has been heterogeneously doped with Schottky disordered solid(s) KCl (RbCl, CsCl). The carriers on the AgCl side are Ag<sup>+</sup>-vacancies and interstitials, while chlorine and alkali-metal ion vacancies form the decisive carriers in KCl (RbCl, CsCl). Here a carrier distribution like Eq. (1) and also an internal adsorption of ions at the interface appears less probable.

Moreover, we shall discuss our results obtained on the eutectic structure in AgCl:KCl composite with special emphasis on its potential for “sensing” NH<sub>3</sub> and “trapping” aqueous AgNO<sub>3</sub>. The AgCl-KCl is known to exhibit very low mutual solubilities [14]. Electrical studies on that system are very limited. In [15] morphological changes of moving interfaces

were studied. In [16] conductivities of liquid AgCl-KCl mixtures (1100 K) have been investigated.

Microstructure and homogeneity of such composite systems play a decisive role in controlling the overall conductivity. A highly anisotropic topology (e.g., a lamellar microstructure) is expected for eutectic mixtures. Such structures are widely studied in metallurgy and are of interest since they are known to exhibit singular properties as far as mechanical strength or thermal shock resistance are concerned. In such anisotropic systems it is desirable not only to measure the overall electrical response in different directions but also to study local conductivities.

## 2. Experimental

Polycrystalline AgCl:KCl (AgCl:RbCl, AgCl:CsCl) samples were prepared by the conventional method, as e.g., denoted in [12], i.e., by mixing/grinding the appropriate compositions for 1 h, melting them in a preheated furnace for 15 min and then again grinding the mixture for 2 h. Pellets of diameter of  $\sim 1$  cm were obtained by uni-axially pressing the powder at pressure  $\sim 30$ KN/cm<sup>2</sup>. The reagents used were AgCl (Alfa, 99.99%), KCl (Merck, 99.5%), RbCl (Alfa, 99.9%) and CsCl (Merck, 99.5%). Silver paste was employed to fabricate the electrodes for conductivity measurements. The samples were prepared under red safety light.

AC conductivity measurements were performed using a Solartron 1260 impedance analyzer. The measurements were done in Ar atmosphere in a thermostat (Eurotherm) controlled furnace with a heating/cooling rate of 0.5°C/min. The point electrode method applied herein is described in [18].

Scanning electron micrographs were obtained using a Leo Steroscan 420 microscope and atomic force micrographs using a Topometrix TMX 2000 Discoverer microscope.

Porosity measurements were performed by porosimetry density measurements (Micromeritics Accupyc 1330), gravimetry and BET analysis. Since homogeneity and particle size distribution of the composite sensitively influence the conductivity, EDAX and SEM were employed to check the same.

## 3. Results and Discussions

The composites were found to be homogeneous on a length scale of  $\sim 1$   $\mu$ m with typical grain sizes of 100 nm to 1  $\mu$ m and porosities of typically 5%.

Conductivity measurements for all composites were performed from room temperature to 200°C. Heating and cooling cycles were found to be identical after sufficient annealing.

Figure 1(a) shows the temperature dependence of overall conductivity for different AgCl:KCl composites. It is clearly seen that the two phase effect, i.e., the enhancement in conductivity with respect to the “physical” superposition of the two bulk values

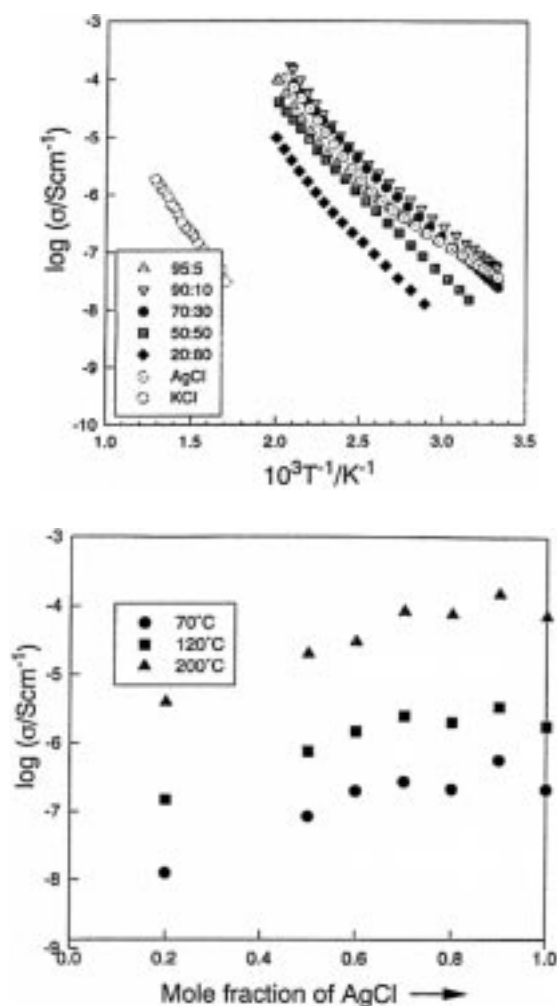


Fig. 1. (a) Variation of conductivity with temperature for different AgCl:KCl molar ratios. (b) Conductivity isotherms for AgCl:KCl composites.

( $\sigma_\infty$ ), is by far not as significant as in AgCl:Al<sub>2</sub>O<sub>3</sub> [10,12] or AgCl:AgI composites. The AgCl:RbCl and AgCl:CsCl composites did not show an enhancement at all. Note that the upper bound for a pure “physical” mixing effect is given by ( $\varphi$  = volume fraction of AgCl),  $\varphi\sigma_{\text{AgCl},\infty} + (1 - \varphi)\sigma_{\text{KCl},\infty}$ . Figure 1(b) shows three isotherms for AgCl:KCl, revealing only a slight conductivity enhancement ( $\lesssim$  a factor of 2) in KCl composites or even less in the other composites. The precise values are affected by the grain size. (It is well-known that in pure AgCl at  $T < 400$  K, the grain boundaries contribute significantly to the overall conductivity  $\sigma_m$  [12].) Moreover, a finite solubility of KCl in AgCl may contribute to the decrease of  $\sigma_m$  with  $\varphi$  near  $\varphi \simeq 1$ .

Figure 2(a) shows an atomic force micrograph of the lamellar structure obtained for the 0.7 AgCl:0.3 KCl, which is a characteristic result of eutectic kinetics. Figure 2(b) displays a 3-dimensional atomic force micrograph of the same sample. From EDAX analysis we could infer that the structure consists of networks of the two components, a lamellar AgCl structure with typical dimension of  $\sim 5\text{--}8\ \mu\text{m}$  length,  $\sim 350$  nm width and  $\sim 25$  nm depth (see Fig. 2), separated by thin KCl lamellae (typical width 100 nm).

It is expected that in such directional structures, the conductivity will be anisotropic. Hartmann et al. [21] have reported a highly anisotropic conductivity in LiF:NaF and NaF-CaF<sub>2</sub> single crystal eutectics, the high  $\sigma$ -value being parallel to the direction of the lamellar growth. Another relevant example in this context are directionally solidified zirconia samples reported on in [14]

Our system, being polycrystalline, was subjected to a more sensitive technique to study the direction dependence of conductivity. Microelectrodes (silver coated tungsten tips) with tip radius of  $\sim 2\ \mu\text{m}$  were used for surface conductivity measurement. Figure 3(a) shows the schematic representation of the experimental setup and 3(b) the variation of conductivity with temperature, in parallel and perpendicular direction to the lamellar structure. The microelectrode measurement yielded conductivities lower than the bulk values if the nominal contact area is taken into account. Tips placed parallel and perpendicular to the structure gave the same values of conductivity. If we correct for the effective contact area (essentially shifting up the values in Fig. 3(b) by one order of magnitude), a rough agreement with the macroscopic measurements over the entire T-range is obtained. The apparent isotropy in conductivity is due to the fact that in the polycrystalline lamellar structures, there are enough percolating pathways in each direction making the conductivity approximately directionally independent.

Since the structure consists of interpenetrating lamellae of AgCl and KCl, and since KCl, in contrast to AgCl, can easily be dissolved by water, a selective removal of one of the constituents appeared possible. Figure 4(a) shows the SEM picture of the structure (thick white regions are AgCl and thin black regions are KCl) which is free of major porosities. Figure 4(b) displays the porous structure obtained after leaching out the KCl from the composite. Typical pore sizes are  $2\text{--}3.5\ \mu\text{m}$  in length and  $550\ \text{nm}\text{--}1.2\ \mu\text{m}$  in width. The porosities measured correspond to the KCl content (e.g., 40%).

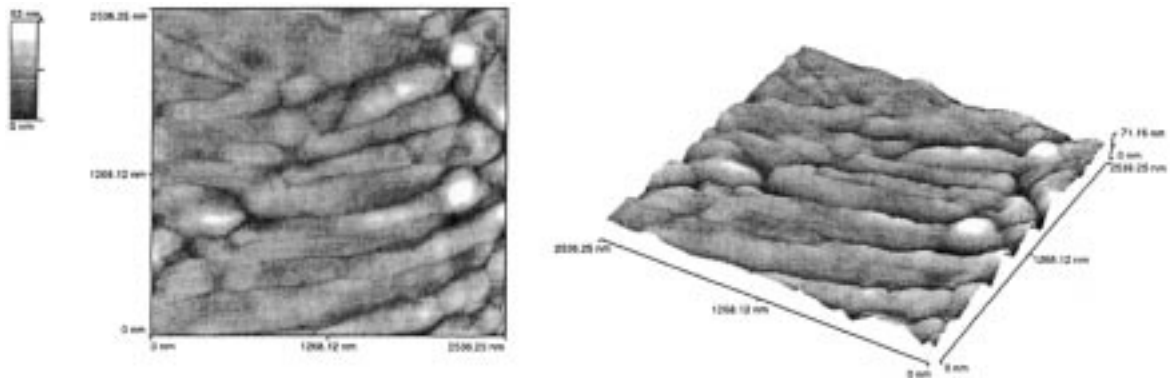


Fig. 2. (a) Lamellar structure obtained in a 0.7 AgCl:0.3 KCl composite electrolyte observed by Atomic Force Microscopy. (b) Magnified 3-d view of the lamellar structure.

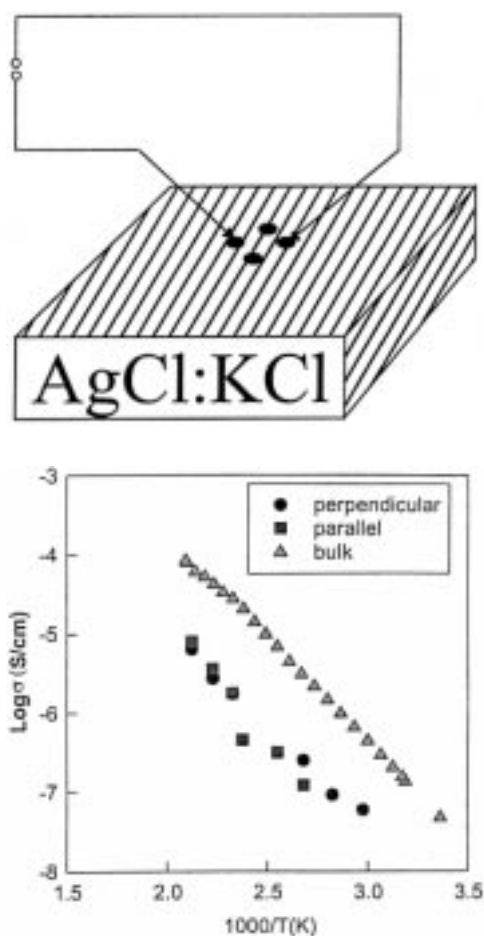


Fig. 3. (a) Schematic representation of the experimental setup for conductivity measurement using microelectrodes. (b) Variation of conductivity with temperature when microelectrodes are placed parallel and perpendicular to the lamellar structure.

With respect to the first point,  $\text{NH}_3$  is expected to increase the  $\text{Ag}^+$ -vacancy concentration at the outer and inner surfaces available to  $\text{NH}_3$  according to [19,20].

To our knowledge, this is the first time that a porous structure has been obtained in this way. A variety of applications can be thought of. We checked the possibility of using it as an improved  $\text{NH}_3$  sensor as well as a “container” for liquid electrolytes.

This effect can be used to sense  $\text{NH}_3$  with a significant selectivity. Experiments with  $\text{AgCl}$  films showed such an enhancement only in a very restricted parameter window, otherwise an increased transfer resistance was dominating the overall conductance. Microelectrode experiments on  $\text{AgCl}$  crystals nicely

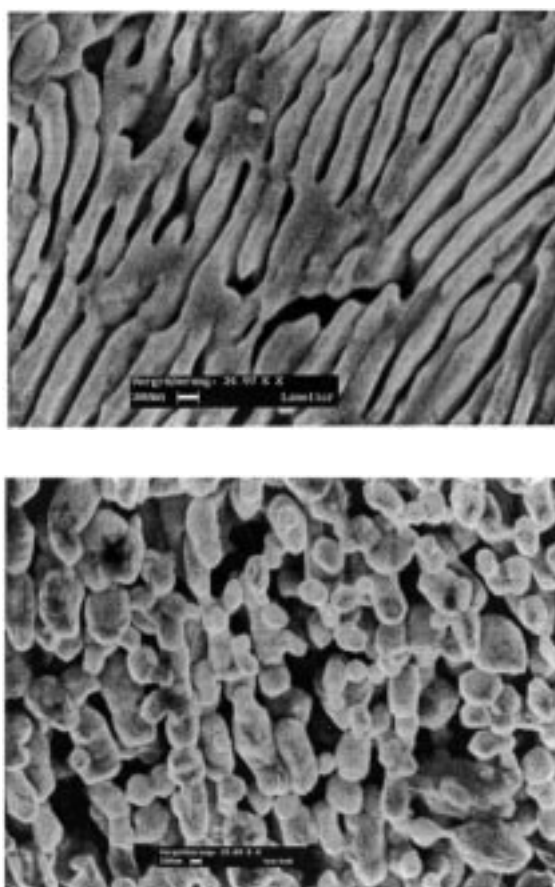


Fig. 4. (a) Scanning electron micrograph of the lamellar structure. (b) Porous  $\text{AgCl}$  network obtained by leaching out the  $\text{KCl}$  lamellae.

proved the expected increase of ionic conductivity roughly characterized by the migration energy of the  $V'_{\text{Ag}}$  defects as predicted. Also the response time was much improved by the use of microelectrodes [22]. The highly porous structure obtained in this work was shown to offer a percolating pore network, thus appearing to be a good candidate for a  $\text{NH}_3$  sensor material. As shown in Fig. 5 reproducible and reversible conductivity increase was indeed measured, the major response occurred comparatively quickly within only a few minutes. The time for achieving steady state, however, was one order of magnitude larger, possibly due to pure pore diffusion which can be improved by further structural optimization.

The second point refers to the strategy of combining the high conductivity of liquid electrolytes with the mechanical strength of a solid container. While nanoscopic containers are prone to lose the

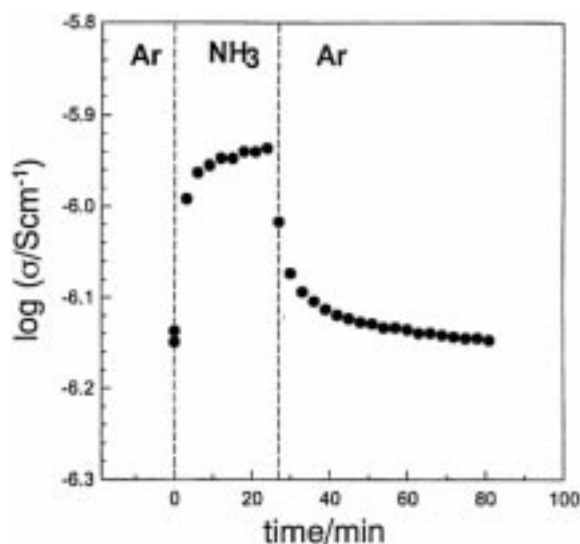


Fig. 5. Variation of conductivity with time in Ar and  $\text{NH}_3$  atmosphere in a porous AgCl network.

liquid if not tightly sealed, in the case of a solid “containing” liquid phase in pores of the size of nm to  $\mu\text{m}$ , local morphological stability of the composite is maintained by capillary forces. Situations like this are frequently met in biological systems in nature and, to some extent, in polymer electrolytes such as Nafion or in gel electrolytes.

Figure 6 proves the feasibility of using such a porous structure as a solid envelope for liquid electrolytes. Nevertheless, even in cases where the  $\text{AgNO}_3$  solution, filled nearly all the available pore volume, the conductivity increase is obviously limited by percolation problems (c.f. activation enthalpy). At about 400 K water leaves the system. The final conductivity is lower than the initial one, obviously reflecting microstructural damage. Further optimization of the microstructure is desirable and certainly possible.

#### 4. Conclusions

- Consistent with the heterogeneous doping theory, the composites consisting of AgCl and Schottky disordered materials such as KCl, RbCl, CsCl do not show significant conductivity anomalies resulting from a defect redistribution.
- Lamellar eutectic mixtures of AgCl and KCl were obtained and transformed into a highly porous AgCl network by leaching out the KCl phase. In

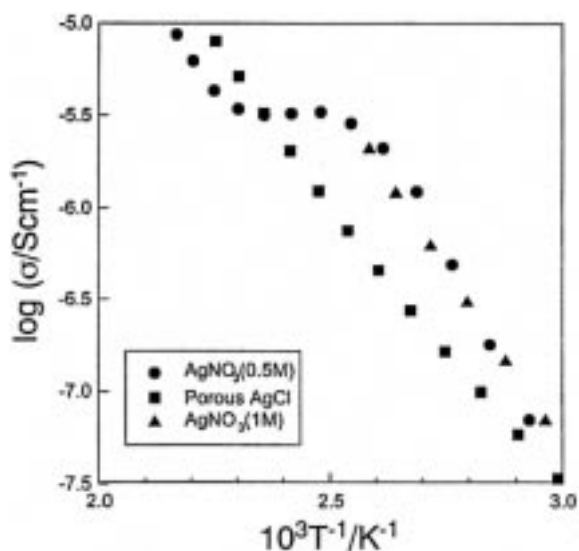


Fig. 6. Variation of conductivity with temperature in porous AgCl and with  $\text{AgNO}_3$  (0.5 M and 1 M) inserted into the structure.

this way a highly porous inorganic matrix was produced. The potential for applications was evidenced by using it as a  $\text{NH}_3$  sensor as well as a solid container for liquid electrolytes.

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