CHEMISTRY LETTERS, pp. 1261-1264, 1988.

Highly Ion-selective and Super Ion-conductive Solid Electrolyte Thin Films of AgCl Supported in a Porous Glass

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A solid electrolyte thin film of AgCl was prepared in a porous silica plate by supplying silver nitrate and sodium chloride aqueous solutions to the opposite faces of the porous plate. The film showed an extremely selective conductivity of silver ion, greater than that in AgCl crystal by seven orders of magnitude.

Because of their selective ion conductivity, some solid electrolytes have potential as separating membranes for application to ion-sensitive devices or batteries. The poor ionic conductivity of solids, however, has limited the practical applications to high-temperature uses as exemplified by an oxygen sensor using stabilized zirconia. The present letter has two purposes: to propose a novel method of preparing pinhole-free thin films, and to show that a thin film of AgCl thus prepared is highly and selectively conductive to silver ion. The essential feature of the method is that two reactant species are brought into contact through a porous plate, plugging the pores with the precipitate produced by the reaction, as shown schematically in Fig. 1.

The experimental apparatus, schematically shown in Fig.2, consisted of two glass vessels separated by a porous silica plate with average pore size of 4 nm, porosity of 28 volume% and thickness of 1 mm. The vessels were filled with 1 M of sodium chloride aqueous solution and 1 M of silver nitrate aqueous solution respectively. Potassium nitrate was added to the silver nitrate solution as a tracer of the permeability of the silica plate. The increase of potassium ion concentration in the opposite vessel was monitored on an ion meter by an electrochemical method. Figure 3 shows the concentration of K^+ in vessel 1 normalized by that in vessel 2 as a function of time. The potassium ion did

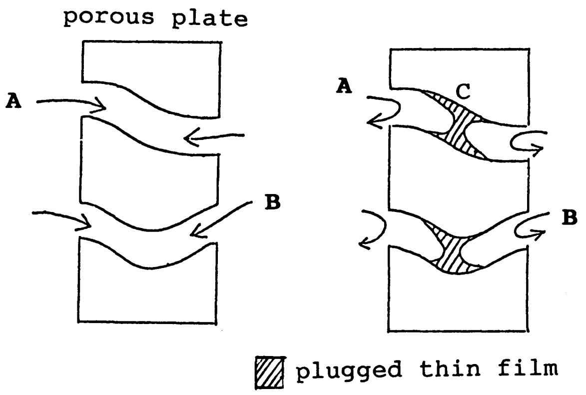

Fig.1. Conception of the method.
$A + B \rightarrow C$
(C: Solid electrolyte)

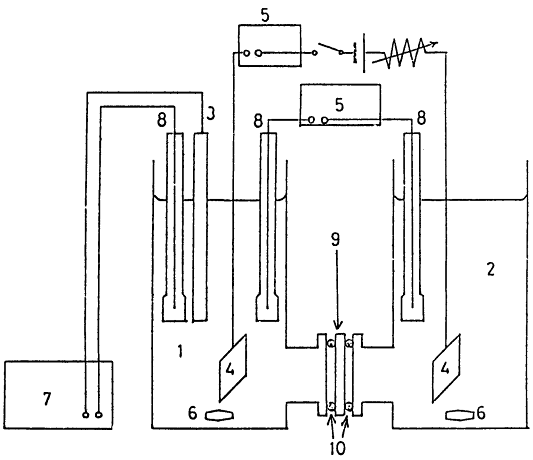

Fig.2. Experimental apparatus. 1. 1 M NaCl 2. 1 M $AgNO_3$, 1 M KNO_3 3. Ion selective electrode for potassium ion 4. Platinum electrode 5. Electormeter 6. Stirring bar 7. Ion meter 8. Reference electrode 9. Porous silica plate 10. O -ring seal

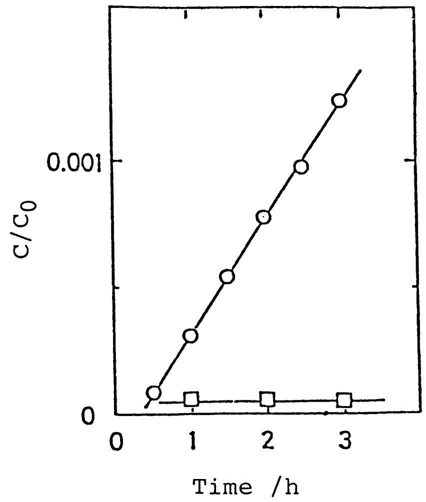

Fig.3. Permeated amount of potassium ion vs. reaction time.

○ : before reaction

□ : during reaction

not permeate through the porous plate during reaction although it permeated steadily when the solutions did not contain the reactants. This indicates that the pores were plugged by precipitated AgCl. The liquid junction potential of sodium chloride solution to silver nitrate solution, measured by two reference electrodes inserted in the solutions, increased up to 170 mV withtime during the reaction. This is due presumably to the selective permeation of silver ion through the AgCl precipitate produced in the pores.

Next, two platinum electrodes were inserted in the two solutions and a certain voltage was applied to prevent the occurrence of the liquid junction potential. The electric current flowing between the two electrodes during the reaction was monitored on an electrometer. The cross section of the porous plate after a run was observed by scanning electron microscopy (SEM). The amount of product was determined by the following procedure. The porous plates after several runs were put into a sodium thiosulfate aqueous solution to solve the AgCl precipitate, and then, the silver ion concentration in that solution was measured by the inductively coupled plasma method (I.C.P.).

Figure 4 shows SEM photographs of the cross section of porous plates after several runs. It shows that AgCl, which was identified by X-ray diffraction pattern, begins to form at the middle and then grows only in the direction of the sodium chloride solution. This means that the silver ion can penetrate the AgCl plug layer, but that the chloride ion cannot do so. The average size of the AgCl precipitate produced in the porous plate was estimated to be 100 angstroms from the full-width-at-half-maximum of the X-ray diffraction line (Rigaku RAD-B) using the Scherrer formula. The occupation ratio of the AgCl precipitate to the pore volume in the AgCl layer was calculated by the following equation:

$$\text{Occupation ratio} = \frac{\text{amount of AgCl / AgCl crystal density}}{\text{porosity} \times \text{AgCl layer thickness} \times \text{cross-section area}}$$

The results are summarized in Table 1. The difference of the observed occupation ratios from 100% may be attributed to the existence of dead-end pores, the smaller densities of the precipitated AgCl, and/or experimental inaccuracies.

The electric current flowing from the silver nitrate solution to the sodium chloride solution through the porous plate is shown in Fig.5. The current was generated in the initial 40 min, approached a maximum value, and then decreased gradually. The integration of the current along this curve, which is equivalent to the amount of electricity, is plotted against the amount of product determined from the I.C.P. measurement in Fig.6. The slope of this figure is unity, and therefore the transference number of silver ion is unity. This fact, as well as the fact that potassium ion did not permeate through the film, demonstrates that the AgCl layer has an extremely high selectivity for silver ion in a solution of 1 M of silver, chloride, sodium, and potassium ions and 2 M of nitrate ions.

Since the transference number of silver ion is unity, the value of the electric current represents directly the flux of silver ion through the cross section of the porous plate. Using this value, the mobility of the silver ion in the AgCl layer was calculated in the form of the effective diffusion coefficient according to the first Fick's law. The results are summarized in Table 2.

Table 1. Ratio of pore volume occupied by AgCl to total pore volume

Reaction time min	AgCl volume / pore volume %
10	64
40	92
90	81
150	84

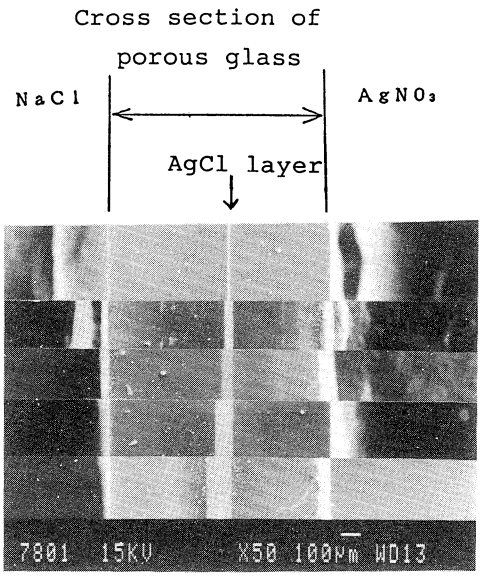

Fig.4. SEM photographs of cross section of porous glass after several runs (from the top: reaction times are 10, 20, 40, 90, and 150 min respectively).

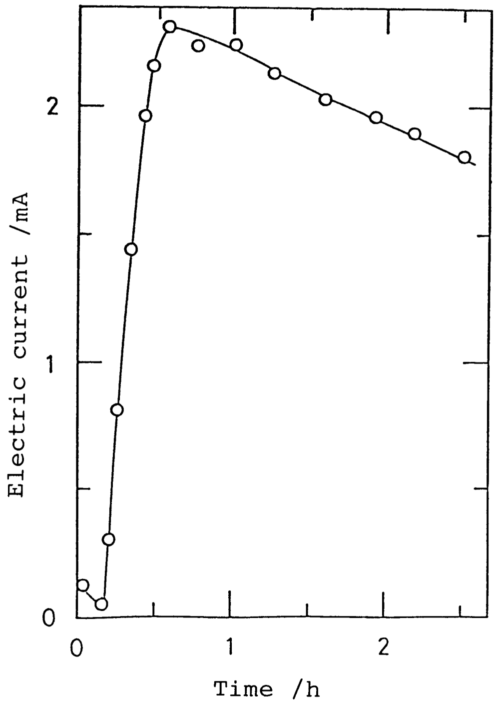

Fig.5. Electric current flowing between two platinum electrodes vs. reaction time.

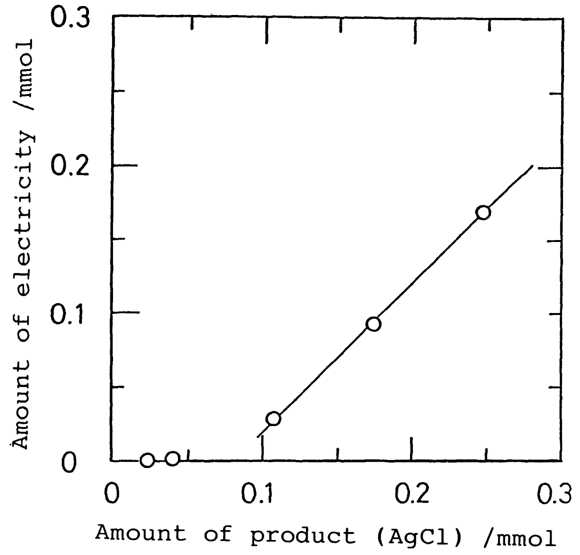

Fig.6. Integrated amount of electricity vs. AgCl produced.

Table 2. Effective diffusion coefficiet of silver ion in AgCl layer

Reaction time min	Diff. in AgCl layer m^2s^{-1}
40	1.6×10^{-11}
90	1.7×10^{-11}
150	2.2×10^{-11}
Diffusivity in bulk AgCl crystal	10^{-18}

Compared with the diffusivity in the bulk crystal, silver ion rapidly moves in the precipitated AgCl layer. The possibility that some unplugged space in the AgCl layer is responsible for the large diffusivity can be excluded, because potassium ion, which has a smaller hydrated ionic radius than that of silver ion, cannot pass the layer. Hence, silver ion migration is presumably due to solid-phase diffusion due to lattice defect of AgCl crystal. It is surprising that, in spite of the solid phase diffusion, the mobility is larger than that in the AgCl crystal by seven orders of magnitude. When ceramic particles (usually silica or alumina) are added to a variety of alkali halides, the ionic conductivity is enhanced by several orders of magnitude.[1-3] These investigators conclude that the rapid ion migration along the two-phase interfacial paths is responsible for the enhanced conductivity. So the rapid ion migration in the present material may be attributed tentatively to the AgCl-SiO_2 interfacial paths, since this silica substrate has as wide a surface area as 200 m^2/g. The details are now being studied.

In conclusion, we have successfully prepared a AgCl thin film in a porous plate by the method of supplying silver nitrate aqueous solution and sodium chloride aqueous solution to the opposite faces of a porous plate. They diffuse into the pores, react to precipitate AgCl at the middle of the plate and plug the pores. The AgCl thin film is characterized by two remarkable features: a high selectivity for silver ion among silver, potassium, sodium, chloride and nitrate ions, and a high mobility of silver ion, higher than that in AgCl crystal by seven orders of magnitude.

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(Received April 19, 1988)