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HIGH-CONDUCTIVITY SOLID PROTON CONDUCTORS: DODECAMOLYBDOPHOSPHORIC ACID AND DODECATUNGSTOPHOSPHORIC ACID CRYSTALS

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The electrical conductivities of dodecamolybdophosphoric acid $H_3Mo_{12}PO_{40}.29H_2O$ and dodecatungstophosphoric acid $H_3W_{12}PO_{40}.29H_2O$ crystals were measured. Remarkably high conductivities of 0.18 and 0.17 mho cm^{-1} at 25°C, and low activation energies of 15.5 and 13.7 kJ/mol were observed for the former and the latter, respectively.

Many studies of the solid proton conductors have been reported.[1] All of them show such poor conductivity ($<10^{-4}$ mho cm^{-1}) that enough current density cannot be drawn when they are applied to the solid electrolyte for a H_2-O_2 fuel cell. We searched for a new solid electrolyte applicable to fuel cells for practical use and found that the dodecamolybdophosphoric acid crystal (12-MPA) and dodecatungstophosphoric acid crystal (12-WPA) show high protonic conductivities.[2]

Large octahedral single crystals (about 15 mm in diameter) were grown by very slow cooling from aqueous solutions. Then the crystals were crushed under an atmosphere of 80 % relative humidity at room temperature.[3]

The electrical conductivity was measured by using a cell: graphite|sample|graphite. The sample, 12-MPA or 12-WPA of about 1 gram was sandwiched between flake graphite powder and pressed into a pellet of 12.5 mm diameter under a pressure of 1000 kg/cm^2. The resistance of the cell was measured by means of a conductance bridge at 1000 Hz, under an atmosphere of 80 ± 5 % relative humidity.[3] Frequency dependence of the conductance was scarcely observed for all samples investigated. The temperature dependence of electrical conductivities in the range from 9 to 48°C is shown in Fig.1. The electrical conductivities of 12-MPA and 12-WPA are 0.18 and 0.17 mho cm^{-1} at 25°C, respectively. These values are remarkably larger in comparison with those of the reported proton conductors.[1] The observed activation energies are 15.5 kJ/mol for 12-MPA and 13.7 kJ/mol for 12-WPA. A sudden decrease of the conductivity for 12-WPA below 288K will result from the phase transition.[4] Figure 2 shows the resistivity versus the thickness of 12-MPA. It demonstrates that the observed resistivity results entirely from the solid electrolyte.

The proton transport number was determined to be unity by electrolysis.

The observed high conductivity can be understood on the basis of the following structural viewpoints. Both 12-MPA and 12-WPA have a cubic unit cell of large *a* values.[5,6,7] All waters of crystallization are located in the interstice of the big and globular (about 12 Å in diameter) anion $[Mo_{12}PO_{40}]^{3-}$, and the acidic protons

may be hydrated. Furthermore, the motional narrowing in the proton magnetic resonance spectra[8] indicates that the protonic motion is very fast. The proton can be transported through the hydrogen-bond network as fast as in the liquid water.

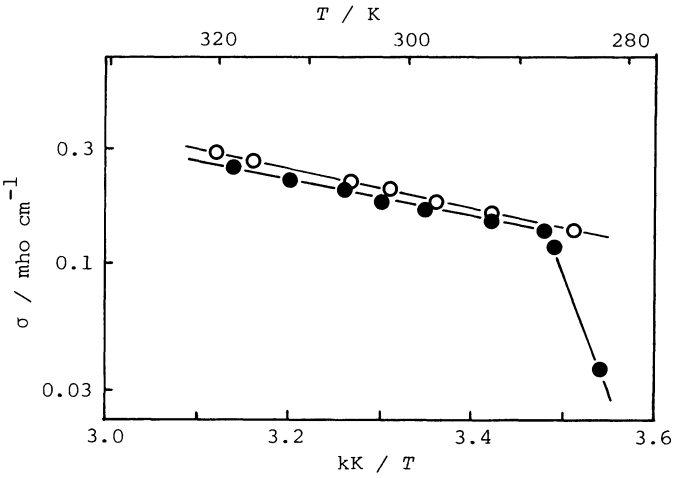

Fig.1. Temperature dependence of the electrical conductivities (σ) of 12-MPA ○ and 12-WPA ● .

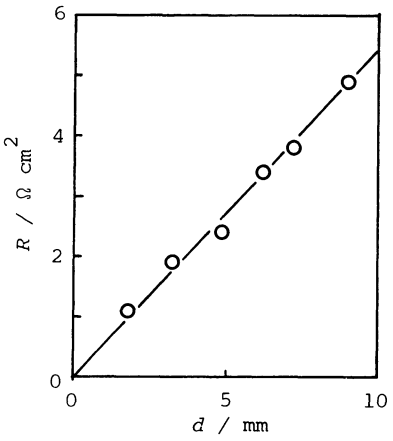

Fig.2. Resistivity(R) vs. thickness(d) of the 12-MPA pellet at 25°C.

The current density of 100 mA/cm^2 was obtained at the cell voltage of 0.5 volt,[2] by use of the fuel cell: graphite(containing Pt-black), H_2| 12-MPA(pellet)| O_2, graphite(containing Pt-black), with an active electrode area of 0.9 cm^2.

These results indicate that both 12-MPA and 12-WPA are promising solid electrolytes, applicable to fuel cells operating at room temperature, since these pellets show high electrical conductivities comparable to those of an acid solution, very low gas permeabilities, and no electronic conductivities.

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4) A small peak was observed in differential scanning calorimetric measurement. To be published.
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