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PROTON CONDUCTION IN ANTIMONIC ACID AT MEDIUM TEMPERATURES IN THE PRESENCE OF WATER VAPOR

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Antimonic acid was found to exhibit a relatively high proton conductivity at medium temperatures of 100 - 300 °C in the presence of water vapor. For example, the conductivity as high as 1×10^{-4} S·cm^{-1} could be maintained for 8 h at 200 °C under the water vapor pressure of 13 kPa. This stable conductivity at medium temperature was found to be attributable to the thermal stability of the water of constitution of $Sb_2O_5 \cdot 2H_2O$.

Inorganic fast proton conductors are being sought for potential applications in many electrochemical systems such as water electrolysis,1,2) electrochromic devices,3) hydrogen separators,4) fuel cells,5) and gas sensors.6) Although some compounds, e.g., $H_3PMo_{12}O_{40} \cdot nH_2O$,7) $HUO_2PO_4 \cdot 4H_2O$,8) $Sb_2O_5 \cdot nH_2O$,9) $Zr(HPO_4)_2 \cdot H_2O$,10) etc., have been reported to exhibit high proton conductivities at lower temperatures, only few examples11) are known of good proton conductors which are stable in the temperature range 100 - 300 °C. Good proton conductors which can be used at medium temperatures are very important from a viewpoint of technological applications.

In the previous publications12-15) we demonstrated that the antimonic acid samples thermally treated up to 620 °C exhibited high proton conductivities at room temperature when the relative humidity was high. This result implies not only water plays an important role in proton conduction in antimonic acid, but also one can expect a stable proton conductivity at higher temperatures if sufficient amounts of water are maintained in the sample. This comunication deals with the thermal stability and the conductivity for antimonic acid at medium temperatures in the presence of water vapor.

Antimonic acid ($Sb_2O_5 \cdot nH_2O$) was prepared by stirring Sb_2O_3 powder in a 31% (by weight) H_2O_2 solution as reported before.13) Thermal behavior of the sample obtained was examined by thermogravimetry using a Cahn R-100 electrobalance in the presence of water vapor. Nitrogen gas containing water vapor (P_{H_2O} = 0.07 - 67 kPa) was continuously passed over the sample powder of ca. 200 mg at 100 cm^3/min. Water was fed to nitrogen gas stream by use of a microfeeder. The weight change was recorded as the sample was heated at 2 °C/min.

The ac proton conductivity was measured as follows. The powder sample was isostatically cold-pressed at 2700 kgf/cm^2 into a compact disc 10 mm in diameter and 2 mm thickness with bulk density ranging from 60 to 70% of the theoretical density. Platinum black powder was applied on both ends of the disc as electrodes. The disc

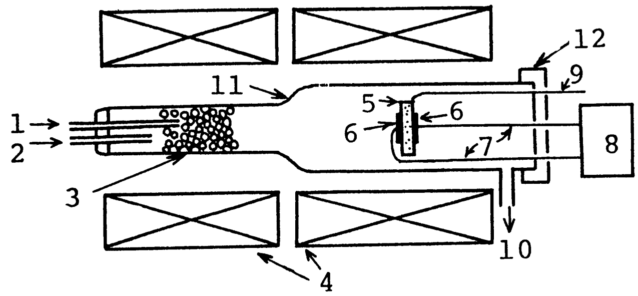

Fig.1. Apparatus for conductivity measurement.

1, Water from a microfeeder; 2, N_2 gas; 3, Glass beads; 4, Electric furnace; 5, Sample disc; 6, Pt gauze; 7, Pt wire; 8, Vector impedance meter; 9, Thermocouple; 10, Gas outlet; 11, Pyrex glass tube; 12, Brass seal.

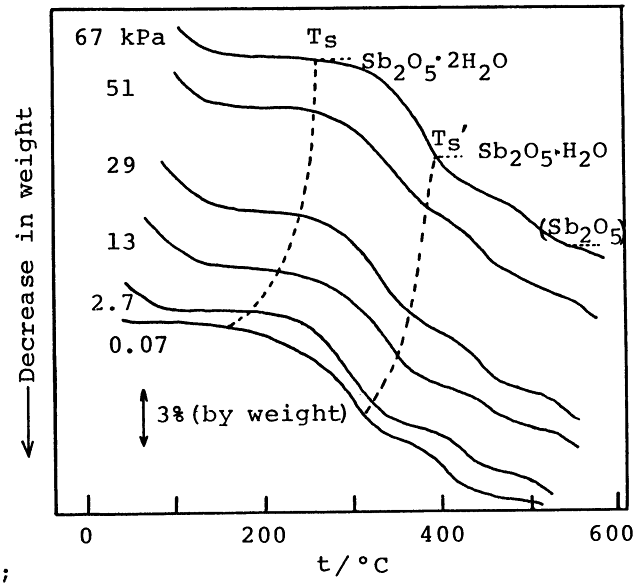

Fig.2. TGA curves for antimonic acid under various water vapor pressures.

with Pt electrodes was then fastened between two sheets of Pt gauze, which were connected to an impeadance meter as shown in Fig.1. After the disc having been left in dry nitrogen stream at 120 °C for ca. 30 min, the conductivity of the disc was monitored over a temperature range from room temperature to ca. 280 °C in the wet nitrogen gas stream. Hewlett Packard 4800 A and 4815 A vector impedance meters with a frequency range of from 5 Hz to 110 MHz were used for all conductivity measurement.

Figure 2 shows TGA curves for antimonic acid under various water vapor pressures. Water loss occured in three stages in all cases except $P_{H_2O} = 0.07$ kPa. The first stage, occuring at lower temperatures, was reversible and attributable to the desorption of physisorbed water. The stable form of antimonic acid, $Sb_2O_5 \cdot 2H_2O$, was produced after this stage. The second stage was related to the irreversible dehydration of $Sb_2O_5 \cdot 2H_2O$ to $Sb_2O_5 \cdot H_2O$. The onset temperature of the dehydration, T_s, depended on the water vapor pressure (P_{H_2O}) as shown by a dotted line: the higher the P_{H_2O}, the higher the T_s. For example, T_s (230 °C) at 29 kPa was ca. 60 °C higher than that at 0.07 kPa. This means that the water of constitution of $Sb_2O_5 \cdot 2H_2O$ becomes more stabilized as P_{H_2O} increased. Similar behavior was observed for the onset temperature (T_s') of dehydration of $Sb_2O_5 \cdot H_2O$, the third stage of water loss.

Although the water of constitution of antimonic acid is relatively stable at medium temperatures especially in the presence of water vapor as shown above, the conductivity above ca. 80 °C has not yet been reported.[16)] We carried out the impedance measurement for antimonic acid up to 280 °C. Characteristic complex impedance plot (Z′ vs. -Z″) of a sample disc (60 °C) at $P_{H_2O} = 2.7$ kPa are shown in Fig. 3 as a typical example. The impedance plot consisted of a semi-circle, as is typically observed for a fast ion conductor.[17)] Similar semi-circles were also obtained at other temperatures and water vapor pressures. Extrapolation of the semi-circle to the Z′ axis was used to obtain the resistance (R) of the disc. The conductivity

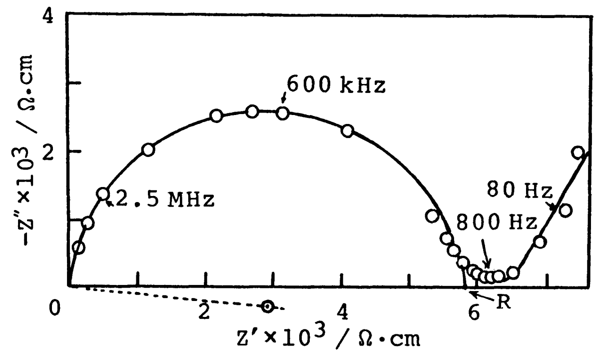

Fig.3. Complex impedance plots for antimonic acid at 60 °C and P_{H_2O} = 2.7 kPa.

was obtained from R and the disc dimensions. The frequency for the -Z'' minimum was in the range ca. 0.5 - ca. 2 kHz.

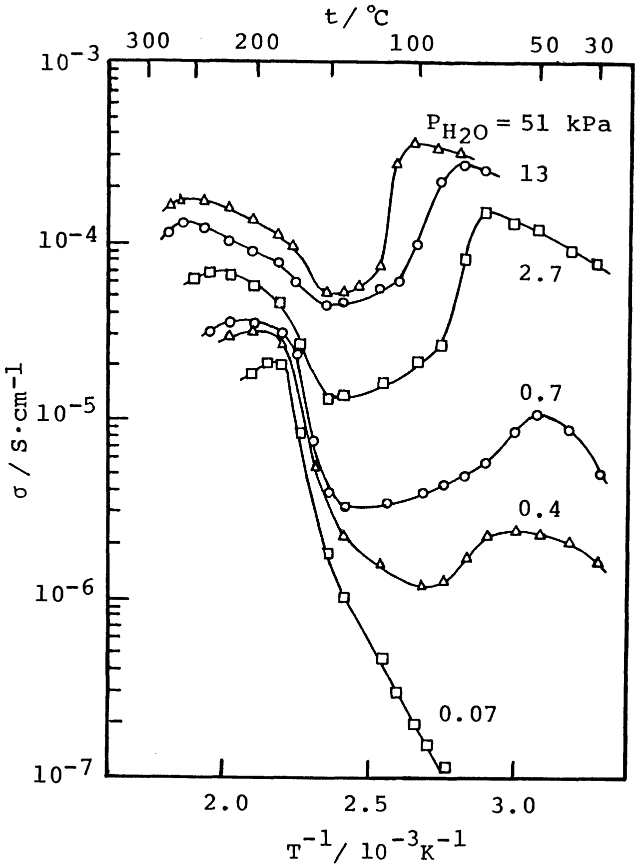

Fig.4. Dependence of conductivity of antimonic acid on temperature under various water vapor pressures.

Figure 4 shows plots of the conductivity for antimonic acid vs. temperature under various water vapor pressures. The impedance measurements were carried out at 800 Hz, by raising the disc temperature at 1 °C/min. It is seen that the conductivity plots have two peaks in the presence of water vapor (above 0.4 kPa). The appearance of the first peak at lower temperature will be ascribed to the loss of the physisorbed water, which plays an important role in the Grotthus type proton conduction mechanism.[13,16] As we reported before,[12] the remarkable effect of water vapor to increase the conductivity of antimonic acid was observed at temperatures below ca. 100 °C. At 80 °C, for example, the conductivity of 1×10^{-4} $S\cdot cm^{-1}$ at P_{H_2O} = 2.7 kPa was about 10^3 times as high as that at 0.07 kPa. The descent of the second peak suggests the decrease of proton concentration due to the loss of the water of constitution of $Sb_2O_5\cdot 2H_2O$. The temperature of the second peak rose with an increase in P_{H_2O}. It is to be noted that a conductivity as high as 1.3×10^{-4} $S\cdot cm^{-1}$ was obtained even at 250 °C under a high P_{H_2O} (13 kPa).

On the other hand, the conductivity in the dry nitrogen stream (P_{H_2O} = 0.07 kPa) increased sharply with a rise in the temperature and reached a maximum value of 2×10^{-5} $S\cdot cm^{-1}$ at 180 °C. The proton transfer in this case seems to be conducted mainly by proton hopping from one lattice oxygen site to another,[15] because the Grotthus mechanism cannot be applicable to the case owing to the lack of the physisorbed water.

A short-term stability test was carried out at medium temperatures. Figure 5 shows the time courses of the conductivities at the P_{H_2O} of 13 kPa (200 °C) and the P_{H_2O} of 2.7 kPa (140 °C), respectively. In both cases little change of the conductivity was observed for 8 h except the initial stage at which a small decrease of the conductivity ocurred. It is of practical importance that a conductivity as high as 1 × 10^{-4} $S \cdot cm^{-1}$ can be maintained at a temperature as high as 200 °C.

In conclusion, antimonic acid was found to exhibit a high proton conductivity even at 200 - 250 °C when the water of constitution of $Sb_2O_5 \cdot 2H_2O$ could be stabilized under enough water vapor pressures. This finding may contribute to wider applications of antimonic acid at medium temperatures in the presence of water vapor.

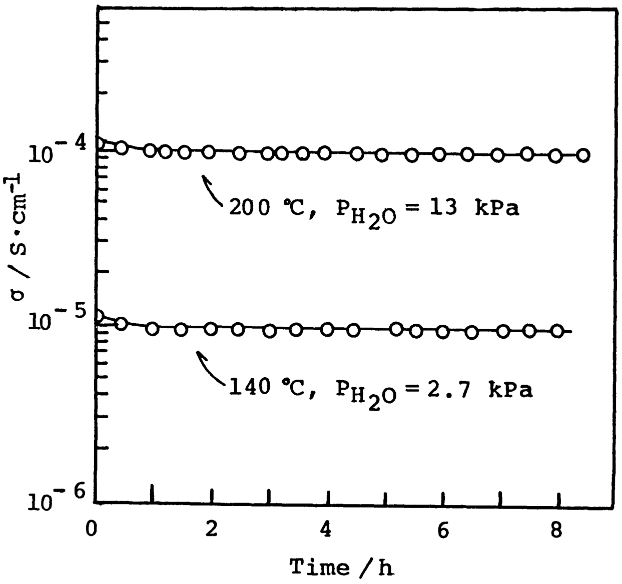

Fig.5. Time dependence of conductivity of antimonic acid under different conditions.

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