CHEMISTRY LETTERS, pp. 1741-1742, 1982.

PROTON CONDUCTION IN THERMALLY TREATED ANTIMONIC ACID SAMPLES

Yoshihiro OZAWA, Norio MIURA, Noboru YAMAZOE*, and Tetsuro SEIYAMA
Department of Materials Science and Technology, Graduate School of
Engineering Sciences, Kyushu University, Kasuga-shi, Fukuoka 816

Antimonic acid samples thermally treated up to 893 K exhibited high proton conductivities of order of 10^{-1} S·m^{-1} at room temperature when the relative humidity was high. The humidity dependence of the conductivities changed with the heat treatment temperature, in coincidence with the changes in fine structure of the antimonic acid samples.

Fast proton conductors can be widely used in many electrochemical systems such as fuel cells, water electrolysis, hydrogen separators,[1)] and electrochromic displays. Although some compounds[2)] are known to show high proton conductivities at ambient temperature, they often lack thermal stability: heat treatment at a high temperature often results in irreversible loss of proton conductivity because of structural destruction. It is reported that antimonic acid is a high proton conductor exhibiting a conductivity of 3×10^{-2} S·m^{-1} at room temperature.[3)] We have found that the high proton conductivity in the antimonic acid system can be maintained even after thermal treatments up to 893 K. Such a thermal stability seems to be attributable to its pyrochlore framework which is reportedly maintained up to 1120 K.[4)] This communication deals with the proton conductivity of the thermally treated antimonic acid samples.

Antimonic acid was prepared by stirring Sb_2O_3 powder in a 31% (by weight) H_2O_2 solution for 30 h at 333 - 353 K. The resulting precipitate was then separated on a centrifuge, washed repeatedly with deionized water, and dried under a reduced pressure at 323 K for 3 days. The thermally treated samples were obtained by calcining the antimonic acid at 513, 593, 773, and 893 K for 1 h in air, respectively. The proton conductivities were measured as follows. Each powder sample was cold-pressed into a compact disc 20 mm in diameter and 2 mm in thickness at 845 kgf·cm^{-2}, on which platinum powder was applied as electrodes. Each disc was subjected to the measurement of a.c. conductivity by means of a conductance bridge at 800 Hz, after conditioning in a stream (50 cm^3·min^{-1}) of nitrogen of a known relative humidity at 303 K for 10 h.

Figure 1 shows the proton conductivity of each sample as a function of relative humidity in the nitrogen stream. The proton conductivities of the thermally treated samples were stable and well reproducible. No hysteresis effects of the conductivity were observed on changing the relative humidity upward or downward. The proton transference number measured separately by constructing a hydrogen concentration cell was close to unity for all the samples, confirming that they are pure proton conductors. It is evident from the figure that the thermally treated samples as well as the untreated sample exhibit high proton conductivities of order of 10^{-1} S·m^{-1} at a relative humidity (h_{rel}) of 83%. Treatments at 593 and 773 K increased the proton conductivity at $h_{rel} > 20\%$, and surprisingly the proton conductive nature was maintained even after treatment at 893 K. This remarkable thermal stability may endow antimonic acid with a great technological advantage as proton conductor, since solid electrolyte membranes are often prepared or used at a high temperature. Figure 1 also shows that the relationships between conductivity and humidity vary with the treatment temperature. In order to know the reason for these changes, the crystal structure, composition, and ion exchange capacity for Na^+ were investigated for each sample by means of X-ray diffraction analysis, thermogravimetric analysis, and a potentiometric titration technique, respectively. The results are listed in Table 1. Pyrochlore structure was maintained after treatment at 513 K, while defect pyrochlore structure resulted from treatments above 593 K. A part of lattice oxygen was eliminated at 773 K, and stoichiometric Sb_6O_{13} phase was produced at 893 K. The water content was sensitive to the surrounding atmosphere. The amount of water remaining after evacuation at room temperature (strongly bonded water) decreased with a rise in the heat-treatment temperature (Column 2). This trend well coincided with that of C_{Na} (Column 4), indicating that the strongly bonded water is a source of protons. In wet atmospheres water was adsorbed additionally (Column 5), increasing the proton conductivity sensitively. Thus it is apparent that the variation of the conductivity vs. humidity relationship shown in Fig. 1 is associated with changes in fine structure of antimonic acid, though further study is needed to account for the exact nature of the relations. In conclusion, antimonic acid provides a unique proton conductor, its high proton conductive nature being resistive to high temperature treatments.

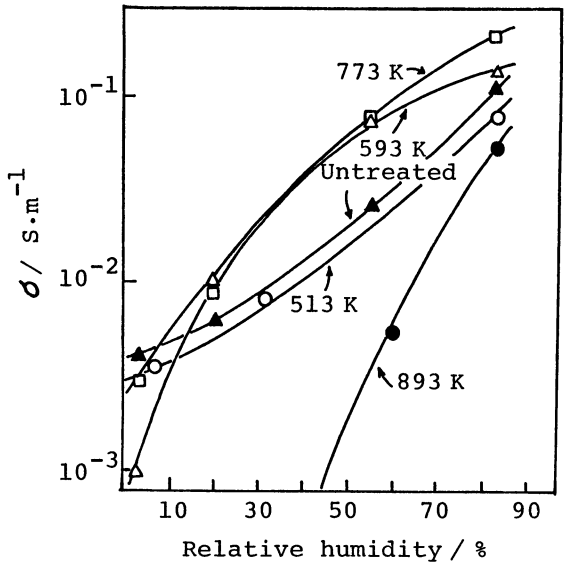

Fig.1 Relative humidity dependence of conductivity at 303 K of untreated and thermally treated antimonic acid samples.

Table 1 Various characteristics for the thermally treated antimonic acid samples

Temp. K	Composition*1 (evacuated)	C_{Na}*2 mmol·g^{-1}	C_{H_2O}*3 %
Untreated	$Sb_2O_5 \cdot 2H_2O$ (P)*4	4.0	14.0
513	$Sb_2O_5 \cdot 2H_2O$ (P)*4	4.0	14.0
593	$Sb_2O_5 \cdot 0.8H_2O$ (DP)*5	2.7	8.2
773	$Sb_2O_{4.6} \cdot 0.4H_2O$ (DP)*5	0.9	5.4
893	$Sb_6O_{13} \cdot 0.07H_2O$ (DP)*5	0.07	2.4

*1 After evacuation at room temperature.
*2 Ion exchange capacity for Na^+ per gram of the antimonic acid sample.
*3 Total water content by weight at a relative humidity of 83%.
*4 Pyrochlore structure.
*5 Defect pyrochlore structure.

References

1) N. Miura, Y. Ozawa, N. Yamazoe, and T. Seiyama, Chem. Lett., 1980, 1275.
2) O. Nakamura, T. Kodama, I. Ogino, and Y. Miyake, Chem. Lett., 1979, 17.
3) W. A. England, M. G. Cross, A. Hammett, P. J. Wiseman, and J. B. Goodenough, Solid State Ionics, 1, 231 (1981).
4) M. Abe, Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.), 70, 2226 (1967).

(Received August 9, 1982)