Proton transport properties of tin phosphate, chromotropic acid anchored onto tin phosphate and tin phenyl phosphonate

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Abstract. Tin (IV) phosphates of the class of tetravalent metal acid (TMA) salts have been synthesized by sol–gel method. The functionalized materials of tin (IV) phosphate (SnP) like chromotropic acid anchored tin phosphate (SnPCA) and tin phenyl phosphonate (SnPP) were also synthesized. These materials have been characterized for elemental analysis (ICP–AES), thermal analysis, X-ray analysis and FTIR spectroscopy. Chemical resistivity of these materials has been accessed in acidic, basic and organic solvent media. The proton present in the structural hydroxyl groups indicates good potential for TMA salts to exhibit solid-state proton conduction. The transport properties of these materials have been explored by measuring specific proton conductance at different temperatures. Based on the specific conduction data and Arrhenius plots, a suitable mechanism has been proposed.

Keywords. Proton transport properties; tin phosphate; tin phenyl phosphonate.

1. Introduction

Proton conductors are often considered to be electrolytes in which hydrogen is transported towards and evolved at the cathode during electrolysis. This would include electrolytes carrying positively charged protonic species such as H^+ and H_3O^+ and even NH_4^+.

Proton transport includes transport of protons (H^+) and any assembly that carries protons (OH^-, H_2O, H_3O^+, NH_4^+, HS^-, etc). The transport of protons (H^+) between relatively stationary host anions is termed the Grotthuss or free-proton mechanism. The size and absence of an electron cloud for the proton results in a strong interaction with the basic sites of its neighbouring molecules or anions. Therefore, its conductance must depend on the dynamics of its nearest neighbours. In the most trivial case it parasitically travels together with a molecule (vehicle mechanism) (Van Gool 1973).

Vehicle mechanisms are most frequently encountered in aqueous solution and other liquids/melts. Thus both aqueous and molten NaOH are OH^- ion conductors. H_2SO_4 (l) and H_2SO_4 (aq) are H^+ and H_3O^+ conductors depending on the water content. In solids, however, vehicle mechanisms are usually restricted to materials with open structures (channels, layers) to allow passage of the large ions and molecules. For instance, SiO_2 and many silicates allow diffusion of H_2O molecules and β-Al_2O_3 allows migration of H_3O^+ and NH_4^+ ions (Kreuer 1996; Norby 1999).

In crystalline hydrates, acids and hydroxides, conduction requires the formation of defects such as proton vacancies or interstitials. These can, in principle, be formed by thermal intrinsic disorder, nonstoichiometry or aliovalent doping. The latter is rarely pursued and instead the best conductors here have a finite number of protons distributed over a larger number of equivalent sites, typically occurring in high-temperature disordered phases, as in $CsHSO_4$.

The above classes of water-containing materials are vulnerable to decomposition (loss of water) at high temperature. The tolerance for high temperature increases as we reduce the water content. The liquid-like systems often lose too much of water even below 100 °C at ambient humidity, and most crystalline hydrates are dehydrated below 200 °C. Some solid acids are stable above 200 °C, and some hydroxides and oxyhydroxides are stable to several hundred centigrade.

Finally there are materials in which protons are not part of the nominal structure or stoichiometry, but are present as foreign species (defects) remaining from synthesis or in equilibrium with ambient hydrogen or water vapour. These materials thus withstand high-temperature treatments and dehydration as their structure is not affected. The introduction of protonic defects has become an important extension of studies of defect structure of oxides, and at present phosphates, sulfates, halides, sulfides, etc are also receiving an increased attention in this respect.

Inorganic ion exchangers of the type of zirconium phosphate behave as protonic conductors because of the presence of exchangeable surface H^+ sites. When the surface –OH groups of these compounds are hydrated, the protons can easily move on the surface, thus accounting for their conductivities which depend strongly on relative humidity, surface area and the degree of crystallinity. In anhydrous conditions, the distance among the adjacent surface –OH groups is too high to permit direct jumps between one site to another.

The conductivity in layered zirconium phosphates has been studied in detail by Alberti *et al* (1978a, 1979). They

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found that inspite of the very high concentration of acid groups in these materials, the bulk contribution to the conductivity was negligible. The main part of the measured conductivity is related to the surface P–OH groups and its value strongly depends on the surface area of the microcrystals (Alberti *et al* 1985).

Alberti *et al* (1978b) were able to show that the surface conducts protons 1000 times faster than the interior. The very low bulk conductivity at room temperature could be due to the lack of orientation and polarization of the P–OH groups present in the interlayer region of α-zirconium phosphate. On the other hand, P–OH groups present on the surface have much more freedom to rotate than the internal ones and that proton transport is assisted by water molecules forming a bridge between the acid groups (Alberti *et al* 1978b). The activation energy, E_a, for surface conduction was 0·17 eV whereas for conduction in the interior, E_a was found to be 0·65 eV. Thus materials with high surface area offer high values of conductivity. It has been found that amorphous materials have more surface area than that of crystalline materials (Clearfield and Berman 1981).

In order to improve the electrochemical properties of ZrP, many efforts have been made by Alberti *et al*. Intercalation has proven to be a remarkable tool for obtaining modified zirconium phosphate having conductivities much higher than that of the parent compound (Alberti *et al* 1985, 1989). These modified zirconium phosphates have conductivities much higher than that of the parent compound and reach values near to those of uranyl phosphate which is considered to be one of the best solid-state protonic conductors (Alberti *et al* 1989). These modified compounds are particularly interesting due to the possibility of obtaining thin and compact films and also a protonic conduction value which is very suitable for solid-state electrochemical devices. Indeed a very simple hydrogen sensor has been realized by covering suitable reference electrode (e.g. Ti Hx or Zr Hx) with a thin film of ZrP and then sputtering a thin film of Pt over the free faces of the ZrP films (Alberti and Polambari 1989).

Recently, Alberti *et al* (2001) synthesized modified titanium phosphonates with conductivities comparable to Nafion membrane. Chudasama *et al* in their studies with amorphous ion exchangers found that conductivity sometimes decreases with surface modifications (Heemanshu *et al* 2005).

In the present study, it was thought of interest to find the effect of surface modification on the conductivity of amorphous inorganic ion exchanger, tin phosphate (SnP). The conductivity of tin phosphate is compared with its derivatized forms like tin phenyl phosphonate (SnPP) and chromotropic acid anchored tin phosphate (SnPCA).

2. Experimental

SnP was prepared by mixing solutions of (0·1 M, 100 mL) tin (IV) chloride and (0·1 M, 100 mL) trisodium orthophosphate. The pH was adjusted to zero. The gel thus obtained was filtered, washed and dried. The dried material was converted to the hydrogen form completely by repeated treatment with 1 M HCl. SnPCA was prepared by equilibrating 1 g of acid treated SnP with an aqueous solution (25 ml, 0·05 M) of chromotropic acid (disodium salt) for 24 h with intermittent shaking at pH = 3, where the white colour of the inorganic ion exchanger changed to brown resembling organic resins. The excess of the organic reagent was decanted, the exchanger washed with conductivity water and dried at room temperature.

Tin phenyl phosphonate (SnPP) was prepared by adding a solution of Sn (IV) chloride to an aqueous solution of phenyl phosphonic acid (when an –OH group in the tetrahedral phosphate moiety of phosphoric acid is replaced by a phenyl group, phenyl phosphonic acid $C_6H_5 P (=O) (OH)_2$ is obtained) in 1:1 mol ratio with continuous stirring at zero pH. The white precipitate obtained was kept overnight, filtered, washed with conductivity water till free of chloride ions and dried at 40 °C. The materials obtained were sized by sieving to 30–60 mesh size and converted to the hydrogen form by immersion in 1 M HCl.

2.1 *Characterization*

Tin and phosphorous in SnP, SnPCA and SnPP were estimated by ICP–AES. FTIR spectra was recorded using Perkin–Elmer IR spectrophotometer. Thermal analysis was carried out using Perkin–Elmer thermal analyser. Carbon and hydrogen contents were determined by Coleman analyser model 33. Chemical resistivity in various media (acids, bases and organic solvents) was studied by taking 500 mg of the materials in 50 mL of the particular medium and allowing to stand for 24 h. The change in its colour, nature and weight was observed. The Na^+ exchange capacity (i.e.c) was determined by the column method. Further, the effect of heating on ion exchange capacity was studied by heating several 1 g portions of the exchangers for 2 h in the temperature range of 100–500 °C at intervals of 100 °C in a muffle furnace and determining the Na^+ exchange capacity by the column method at room temperature.

2.2 *Conductivity measurements*

In the present study, proton conductivities of the materials were measured using pellets of 10 mm diameter and 1·5–4·7 mm thickness at a relative humidity of ∼80%. Opposite sides of the pellets were coated with conducting silver paste to ensure good electrical contacts. Impedance measurements were taken in the temperature range 40–180 °C, at 20 °C intervals, using a solartron dataset impedance analyser (SI1260) over a frequency range 1 Hz–1 MHz at a signal level below 1 V, interfaced to a minicomputer for data collection.

3. Results and discussion

Elemental analysis performed by ICP–AES indicates the composition of SnP as 5:1. In addition to this, the elemental

analysis of SnPCA shows 1·12% C, 2·4% H and 0·44% S. For SnPP, the analysis data shows 20·659% Sn, 2·681% P, 11·95% C and 2·66% H. FTIR spectra of SnP, SnPCA and SnPP show bands in the region ~3430 cm^{-1} attributed to asymmetric and symmetric hydroxo –OH and aquo –OH stretches. The sharp medium band at 1620 cm^{-1} is attributed to aquo H–O–H bending. The bands around 1060 cm^{-1} region is due to symmetric and antisymmetric stretching of P–O bonds in –PO$_4$ group. The presence of bands around 560 cm^{-1} may be related to Sn–O bond vibrations.

FTIR spectrum of SnPCA shows additional bands at ~1372·53 cm^{-1} corresponding to the stretching frequency of the fused ring system. Bands at 1634·88 cm^{-1} and 1054·96 cm^{-1} are attributed to the stretching and bending frequencies of the fused ring system.

FTIR spectrum of SnPP also shows additional bands characteristic of the organic moiety. Band at 749·80 cm^{-1} is due to the out of plane bending of the C–H bonds. Bands at 1593·11, 1485·17 and 1438·87 cm^{-1} are due to C=C stretchings. Inplane bending bands occur in the region 1000–1200 cm^{-1}.

TG of SnP shows 21% weight loss up to 100 °C, corresponding to the loss of external water molecules after which a gradual loss in weight is observed till about 600 °C. This may be due to the condensation of structural hydroxyl groups.

TG of SnPCA shows 30% weight loss up to 200 °C. There is a gradual weight loss within the temperature range of 200–600 °C, corresponding to the decomposition of the organic moiety from the SnP matrix.

TG of SnPP shows 14% weight loss up to 150 °C corresponding to the loss of external water molecules. There is a gradual weight loss within the temperature range of 300–700 °C corresponding to the decomposition of the organic moiety and the condensation of structural hydroxyl groups.

The materials were found to be stable in mineral acids like HCl, HNO$_3$ and H$_2$SO$_4$ at all concentrations and were also found to be stable in bases such as NaOH and KOH up to 1 M concentrations. The exchangers were also stable in ethanol, benzene, acetic acid and diethyl ether.

The Na$^+$ exchange capacities of SnP, SnPCA and SnPP were found to be 3·0, 3·84 and 2·3 meq/g, respectively. In the case of SnP, results of the effect of heating on exchange capacity reveal that it decreases on heating. This may be due to the condensation of structural hydroxyl groups at higher temperatures. However, in the case of SnPCA and SnPP, the i.e.c. decreases on heating up to 300 °C and then again increases up to 500 °C. After 300 °C, the organic part starts decomposing, leading to the formation of active carbon, as evidenced by the change in colour of the sample to black at 500 °C. This is responsible for an increase in the i.e.c.

The presence of protons able to be exchanged and hence able to diffuse through the interspace make all these materials protonic conductors.

For the materials SnP, SnPCA and SnPP the conductivity decreases with increasing temperature thus suggesting the mechanism of transportation to be of the Grotthuss type.

SnP is a protonic conductor because of the presence of exchangeable surface H$^+$ sites. When the surface OH groups of these compounds are hydrated the protons can easily move on the surface thus accounting for their conductivities, which depend strongly on relative humidity, the surface area and the degree of crystallinity. Both Nogami *et al* (2000) and Yamada *et al* (2005) suggested that the P–OH forms strong hydrogen bonds with water, allowing the hydroxyl group to dissociate so that a proton can be transported through the material (Nogami *et al* 2000; Yamada *et al* 2005). In the case of phosphates, the Grotthuss transport mechanism suggests that charge transportation is controlled through H$_3$O$^+$ and H$_5$O$_2^+$ mediated charge transfer (Colomban and Novaka 1992; Yamada *et al* 2005).

At 40 °C, the specific conductivity of SnP is higher than that of hybrid varieties, i.e. 'σ' follows the order, SnP > SnPCA > SnPP (table 1). The E_a values at higher frequencies are found to be SnPP > SnP > SnPCP (table 2). Arrhenius plots at different frequencies are presented in figures 1(a–c). For all the three materials, linearity is observed in the temperature range 40–180 °C. Nyquist plots are presented in figures 2a–c, respectively.

In the case of SnPP, the bulky phenyl group comes in the matrix of SnP at the expense of a P–OH group. i.e. P–OH group is replaced by P–C$_6$H$_5$ group. Here there are no ionogenic protons in the organic moiety. So the contribution towards protonic conduction is nil from the organic group. But in the case of SnPCA, the bulky chromotropic acid is incorporated to the inorganic matrix. Here there are additional H$^+$ sites from the organic guest molecule. So the conductivity is higher than SnPP, but lesser than parent inorganic ion exchanger SnP. This could be due to poor interfacial contacts between the host and guest molecules. Also the trend in conductivities of these materials is in accordance with their surface areas. The specific surface area is maximum for SnP (236·51 m^2/g) whereas for SnPCA and SnPP it is 181·73 m^2/g and 51·47 m^2/g, respectively. Thus in the case of SnP the surface modifications decreases the conductivity. Such observations have been made earlier also in the case

Table 1. Specific conductivity values at 40 °C.

Ion exchange materials	Specific conductivity (Ω^{-1} cm^{-1})
SnP	2·1200 × 10^{-3}
SnPP	1·5223 × 10^{-7}
SnPCA	1·0500 × 10^{-3}

Table 2. Activation energies.

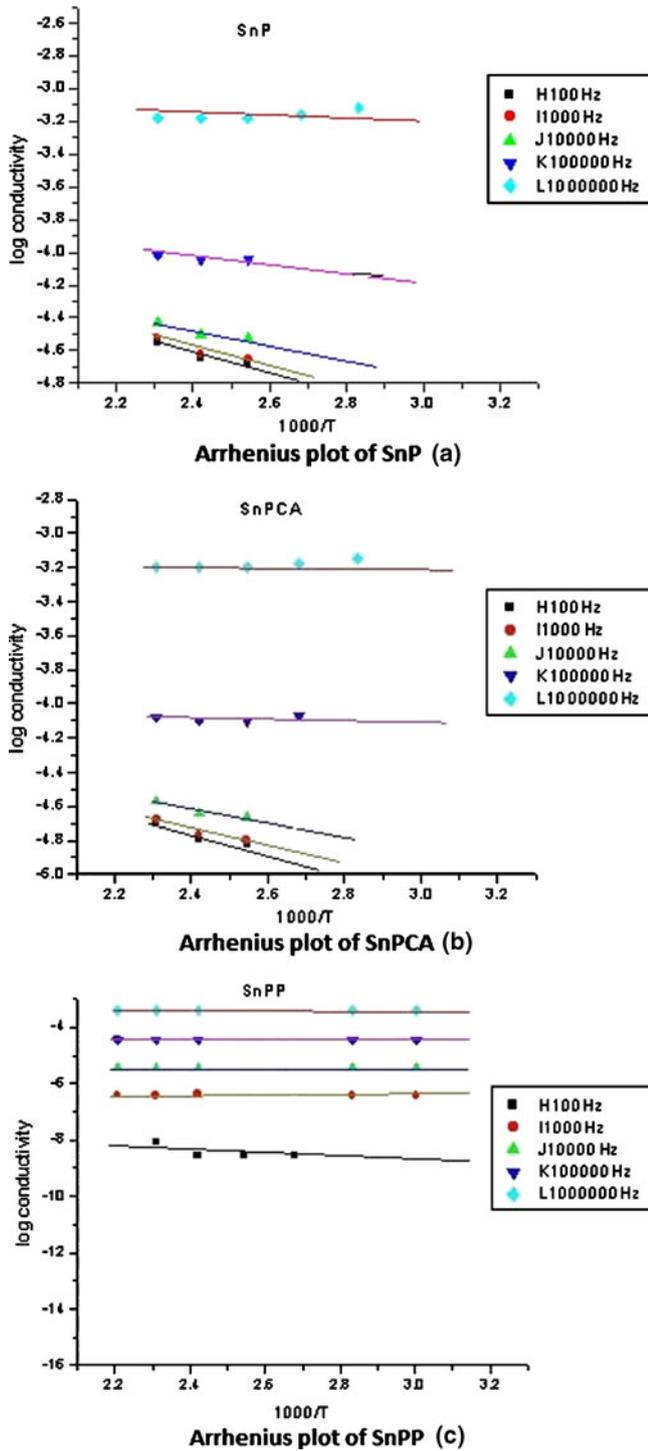| Ion exchange materials	Activation energy (eV)
SnP	0·0092
SnPP	0·0203
SnPCA	0·0033

Figure 1. Arrhenius plots of **(a)** SnP, **(b)** SnPCA and **(c)** SnPP.

of amorphous inorganic ion exchangers (Heemanshu *et al* 2005). The ion exchange particles are both bulky and surface conductive. In the case of SnPP, the P–OH group is replaced by the bulky phenyl group and the contribution towards proton conduction is nil from this organic group. The extremely low conductivity exhibited by sample SnPP may be due to the onset of Maxwell–Wagner effect model where the conductivity is mainly governed by the surface conductivity and
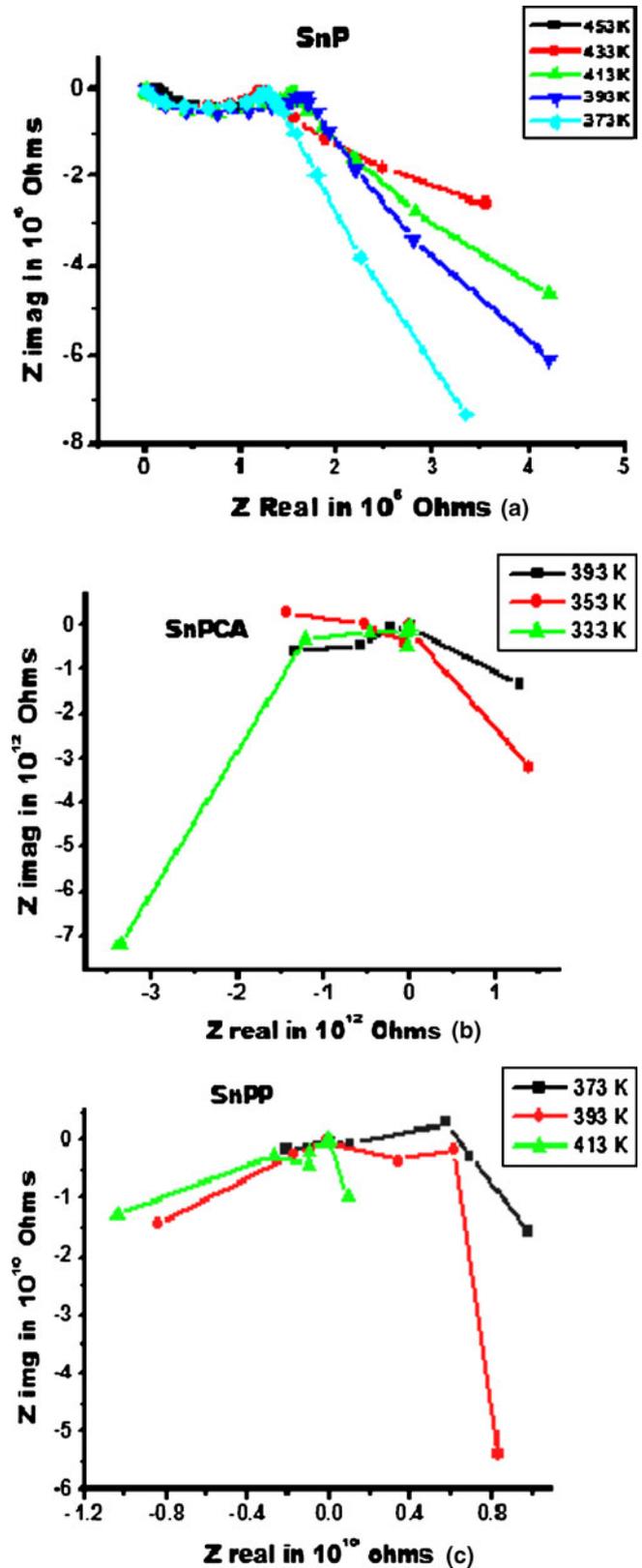

Figure 2. Nyquist plots of **(a)** SnP, **(b)** SnPCA and **(c)** SnPP.

which in turn has direct correlation with surface area which being smaller in comparison with other samples. The enhancement of dielectric effect is due to the interfacial

relaxation of polarization which occurs when charge carriers are trapped at the interface of heterogeneous systems.

4. Conclusions

Inorganic ion exchange materials are promising solid proton conductors at low temperature and they exhibit Grotthus type proton conduction mechanism.

The functionalized materials like SnPP with very low protonic conductivity of the order of $10^{-7}\Omega^{-1}$ cm^{-1} would be ideal for sensor applications where poor conductivity values are appreciated.

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