A comparative study of proton transport properties of metal (IV) phosphates

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Abstract.   M(IV) phosphates of the class of tetravalent metal acid (TMA) salts where M (IV) = Zr, Ti, Sn has been synthesized by the sol–gel method. These materials have been characterized for elemental analysis (ICP-AES), thermal analysis (TGA, DSC), X-ray analysis and FTIR spectroscopy. Chemical resistivity of these materials has been accessed in acidic, basic and organic solvent media. The protons present in the structural hydroxyl groups indicates good potential for TMA salts to exhibit solid-state proton conduction. The transport properties of these materials has been explored by measuring specific proton conductance at different temperatures in the range of 30–120°C at 10°C intervals, using a Solartron Dataset impedance analyzer (SI 1260) over a frequency range 1 Hz–10 MHz at a signal level below 1 V. Based on the specific conductance data and the Arrhenius plots, a suitable mechanism has been proposed and conductance performance of ZrP, SnP and TiP compared.

Keywords.   Proton conductors; proton transport properties; solid electrolytes; ionic conductors; metal (IV) phosphates.

1. Introduction

In recent years there has been intense research, aimed at discovering new proton conductors and determining their conduction mechanism, which is driven by the potential use of such compounds in fuel cells, sensors, water electrolysis units and other electrochemical devices. An entire class of materials has gained increasing interest as proton conductors: polymers, oxide ceramics, intercalation compounds etc. A brief overview of the past and present state on solid-state proton conductors has been reported.[1–3]. Most electrochemical devices based on solid-state proton conduction work only below 100°C and above 700°C.

Proton conductors are often considered to be electrolytes in which hydrogen is transported towards and evolved at the cathode during electrolysis. Proton transport includes transport of proton (H^+) and any assembly that carries protons (OH^-, H_2O, H_3O^+, NH_4^+ HS^- etc.).[4] The transport of protons (H^+) between relatively stationary host anions is termed the 'Grotthuss' or 'free-proton' mechanism. The Grotthuss

mechanism requires close proximity of water molecules which are held firmly but free to rotate. Transport by any other species is termed "Vehicle mechanism". Vehicle mechanism is most frequently encountered in aqueous solution and other liquids/melts. In solids, vehicle mechanism is usually restricted to materials with open structures (channels, layers) to allow passage of large ions and molecules. Compounds with smaller amounts of water would be expected to conduct by the vehicle mechanism in which a nucleophilic group such as H_2O or NH_3 acts as a proton carrier. The classification of proton conductors, according to the method of preparation, chemical composition, structural dimensionality, mechanism of conduction etc., has been summarized in a comprehensive book on proton conductors.[5]

Inorganic ion exchangers of the class of tetravalent metal acid (TMA) salts exhibit the general formula M(IV) $(HXO_4)_2 \cdot nH_2O$ where M (IV) = Zr, Ti, Sn, Ce, Th, etc. and X = P, Mo, W, As, Sb, etc. The number of water molecules depends on the method of preparation and the drying conditions. TMA salts possess structural hydroxyl protons that are responsible for their ion-exchange behaviour. The number of protons present in the structural hydroxyl groups

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indicate the potential of TMA salts to exhibit solid-state proton conduction. When these –OH groups are hydrated, the protons can move easily on the surface, thus accounting for their conductivities, which depend strongly on relative humidity, surface area and degree of crystallinity.[6] Alberti and coworkers have shown that the surface conducts protons a thousand times faster than bulk protons.[7] M(IV) phosphates of the class of TMA salts hold great promise as proton-conducting materials possessing high conductivity and thermal stability at medium temperatures.[1]

The mechanism of diffusion and proton transport in crystalline zirconium phosphate and titanium phosphate has been studied in detail by various workers.[7–16] An early investigation on zirconium phosphate with varying degrees of crystallinity shows that the conductivity decreases considerably with increasing degree of crystallinity.[7,17,18]

From our laboratory, we have reported transport properties in amorphous zirconium phosphomolybdate and its single salt counterparts, zirconium molybdate and zirconium phosphate[19] and of M(IV) tungstates,[20] where M(IV) = Sn, Ti, Zr. Stenina and coworkers have reported the conduction behaviour of tin phosphate.[21]

Literature survey reveals that most of the proton transport properties carried out in case of zirconium phosphate and titanium phosphate have been on crystalline phases and not many reports exist in the case of tin phosphate. We therefore considered it worth while to study the proton transport properties of amorphous M(IV) phosphates, where M(IV) = Zr, Sn and Ti abbreviated as ZrP, SnP and TiP respectively, and compare their proton conduction behaviour.

In the present endeavour, amorphous ZrP, SnP and TiP have been synthesised by a modified sol–gel method. These materials have been characterized for elemental analysis (ICP-AES), thermal analysis (TGA, DSC), X-ray analysis and FTIR spectroscopy. Chemical resistivity of these materials has been accessed in acidic, basic and organic solvent media. The transport properties of these materials has been explored by measuring specific proton conductance at different temperatures in the range 30–120°C at 10°C intervals, using a Solartron Dataset impedance analyser (SI 1260) over the frequency range 1 Hz–10 MHz at a signal level below 1V. Based on the specific conductance data and Arrhenius plots, a suitable mechanism has been proposed and the conductance performance of ZrP, SnP and TiP compared.

2. Experimental

2.1 *Preparation of M(IV) phosphates (ZrP, SnP, TiP)*

M(IV) phosphates have been prepared by mixing aqueous solutions of $ZrOCl_2 \cdot 8H_2O$ or $SnCl_4$ or $TiCl_4$ (0·1M, 100 mL) and sodium dihydrogen phosphate (0·2M,100 mL) in the pH range 1–2, dropwise and with continuous stirring, at 70°C. The gelatinous precipitates obtained was digested for one hour at 70°C, filtered, washed with conductivity water till complete removal of chloride ions, followed by drying at room temperature. The material was sized by sieving [(30–60 mesh) ASTM] and finally converted to acid form by treating 5 g of the material with 50 mL of 1 $MHNO_3$ for 30 min. with occasional shaking. The sample was then separated from the acid by decantation and treated with conductivity water for removal of adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature. This material was used for all studies.

2.2 *Instrumentation*

The samples were analysed for zirconium, titanium, tin and phosphorous content by ICP-AES. X-ray diffractograms ($2\theta = 5$–80°) were obtained on an X-ray diffractometer (Rigaku Dmax 2200) with Cu–Kα radiation and nickel filter. FTIR spectra was recorded using KBr wafer on a Bomem MB series. Thermal analysis (TGA/DSC) was carried out on a Shimadzu thermal analyser at a heating rate of 10°C/min. Chemical resistivity in various media (acids, bases and organic solvents) was studied by taking 500 mg of the particular M(IV) phosphate 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 (IEC) was determined by the column method.[22] 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 to 500°C at intervals of 100°C in a muffle furnace and determining the Na^+ exchange capacity by the column method[22] at room temperature.

2.3 *Conductivity measurements*

Proton conductivities of the materials were measured using pellets of 10 mm diameter and 1.5–2 mm

thickness. Opposite sides of the pellets were coated with conducting silver paste to ensure good electrical contacts. Specific conductance was measured in the temperature range 30–120°C, at 10°C intervals, using a Solartron Dataset impedance analyzer (SI 1260) over a frequency range 1 Hz–10 MHz at a signal level below 1 V, interfaced to a minicomputer for data collection. In all cases, since the impedance plots of the materials consist of single depressed semicircles, the pellet conductivity was calculated by arc extrapolation to the real axis, taking into account the geometrical sizes of the pellets.

3. Results and discussion

3.1 *Characterization*

ZrP, SnP and TiP were obtained as white hard granules. Elemental analysis performed by ICP-AES shows the ratio of M:P in ZrP, SnP and TiP to be 1 : 2.

ZrP, SnP and TiP belong to the class of TMA salts. Except for the IEC values, the thermal behaviour, FTIR spectra etc. show similar behaviour. For

illustrations, the plots (thermal, FTIR, X-ray) for ZrP have been presented in this paper.

The absence of any sharp peaks in the X-ray diffractograms for ZrP (figure 1), SnP and TiP indicates the amorphous nature of the materials.

The FTIR spectra of ZrP (figure 2) exhibits a broad band in the region ~ 3400 cm^{-1} which is attributed to asymmetric and symmetric –OH stretches. A sharp medium band at 1635 cm^{-1} is attributed to aquo (H–O–H) bending. A band in the region ~ 1035 cm^{-1} is attributed to the presence of P=O stretching. A medium intensity band at 1400 cm^{-1} is attributed to the presence of δ(POH).[23] (Similar bands are obtained in case of SnP and TiP.) These bands indicate the presence of structural hydroxyl groups/protonic sites in the material. This fact is further evident from the IEC values that have been evaluated.

The Na$^+$ exchange capacity of ZrP, SnP and TiP have been evaluated at room temperature and observed to be 2·77, 1·90 and 3·09 meq g^{-1} respectively. The effect of calcination on IEC was studied in the temperature range of 100 to 500°C at intervals of 100°C and the results are presented in table 1. The initial increase in the IEC value at 100°C could be attributed to loss of moisture adherent to it, thereby increasing the active exchanger content for the same weight of material taken for IEC determination. The loss of IEC is very high beyond 300°C and this could be attributed to the condensation of structural hydroxyl groups.
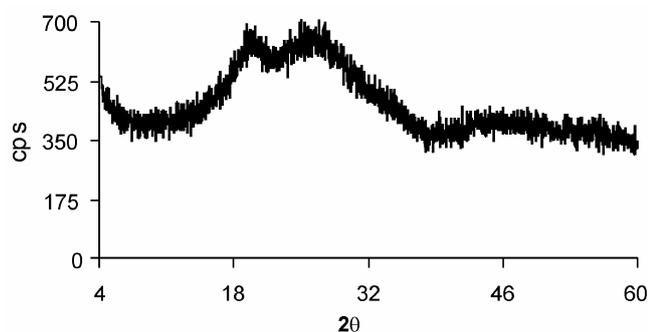
Figure 1. XRD pattern for ZrP.
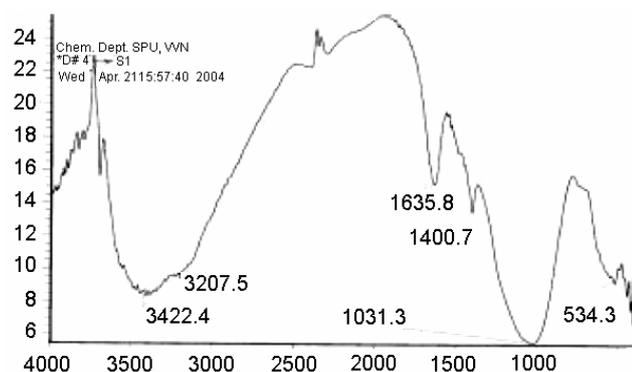
Figure 2. FTIR spectra ZrP.

Table 1. Effect of heating on ion exchange capacity of ZrP, SnP and TiP.

Material	Temperature (°C)					
	RT	100	200	300	400	500
ZrP	2·77	2·82	2·55	2·39	1·69	1·46
SnP	1·90	1·92	1·61	1·57	1·29	1·18
TiP	3·09	3·60	3·40	1·98	1·32	1·02
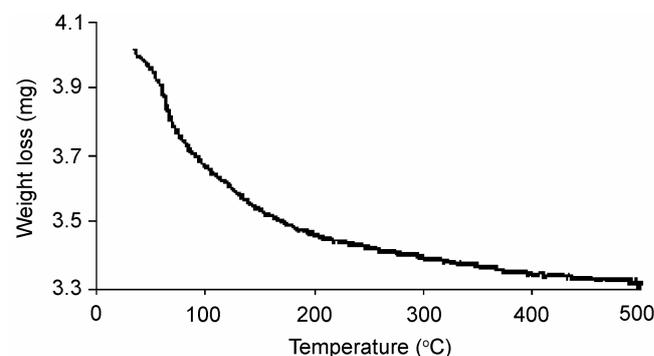
Figure 3. TGA plot for ZrP.

Table 2. Chemical resistivity of ZrP, SnP and TiP.

	Acid		Base			
Material	H_2SO_4	HNO_3	HCl	NaOH	KOH	Organic solvents*
ZP	36N	16N	10N	5N	5N	Stable
SnP	36N	16N	10N	5N	5N	Stable
TiP	36N	16N	10N	5N	5N	Stable

*Alcohol, benzene, acetone
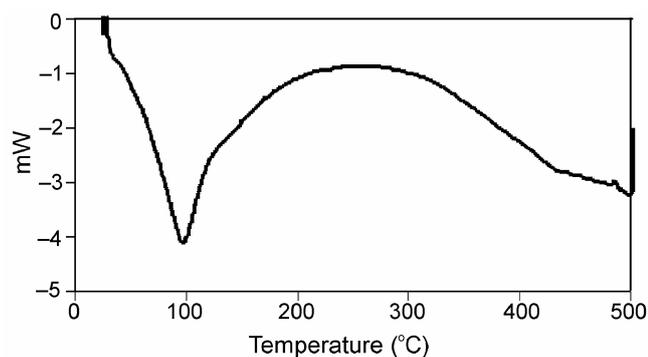
Figure 4. DSC curve for ZrP.

TGA (figure 3) indicates two weight-loss regions. The first weight-loss region ($\approx 13\%$ up to 180°C) in case of ZrP ($\approx 10\%$ up to 160°C) in case of SnP ($\approx 26\%$ up to 155°C) in case of TiP is attributed to loss of moisture/hydrated water. The second weight loss in the range 250–500°C for all the M(IV) phosphates is attributed to condensation of structural hydroxyl groups. The material gets converted to the pyrophosphate at temperatures greater than 700°C and the oxide at very high temperatures. The DSC curve (figure 4) exhibits an endothermic peak at ≈ 100°C for ZrP, ≈ 127°C for SnP, and ≈ 135°C for TiP, attributed to loss of moisture/hydrated water. An endothermic process which starts at ≈ 300°C can be attributed to the condensation of structural hydroxyl groups. These observations are further supported by the fact that IEC decreases on calcination, as discussed above.

Based on the elemental analysis (ICP–AES) and thermal analysis (TGA) data ZrP, SnP and TiP have been formulated as $Zr(HPO_4)_2 \cdot 2 \cdot 5H_2O$, $Sn(HPO_4)_2 \cdot 2H_2O$ and $Ti(HPO_4)_2 \cdot 5H_2O$ respectively, using the Alberti and Torracca formula.[24]

Chemical resistivities of ZrP, SnP and TiP in acids, bases and organic solvent media (ethanol, benzene, acetone, acetic acid, etc.) have been studied. The results presented in table 2 show maximum tolerable limits in the particular media, and indicate good stability of ZrP, SnP and TiP in acidic and organic solvent media but not as good in basic media.
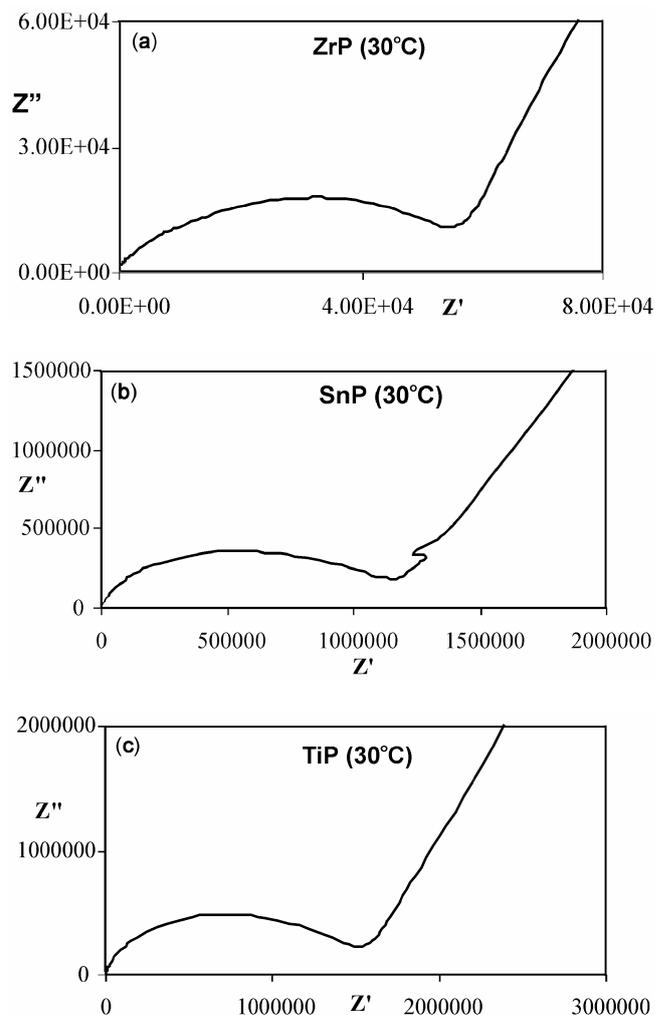

Figure 5. Complex impedance plot at 30°C for (**a**) ZrP, (**b**) SnP and (**c**) TiP.

3.2 *Impedance measurements*

The results of specific conductance for ZrP, SnP and TiP have been presented in table 3. The complex impedance plots (30°C) have been presented in figure 5.

For all the three materials, it is observed that specific conductivity decreases with increasing tem-

perature (see table 3). This is attributed to the loss of water of hydration as well as condensation of structural hydroxyl groups with increasing temperature. This fact is also supported by study of the effects of heating on ion exchange capacity as discussed above. This suggests the mechanism of transportation to be of the Grotthuss type[25] where the conductivity depends on the ability of the water located on the surface to rotate and participate. Further, the results are also in agreement with the suggestion that protons are not able to diffuse along an anhydrous surface, where the spaces between –OH groups are very large[26]. Besides, the fact that the loss of protons resulting from hydroxyl condensation causes considerable decrease in conductivity, also indicates that the conduction is protonic. These factors reveal the importance of water in the conduction mechanism.

In the present study, since the anion HPO_4^{2-} is common to all the solids studied, the proton conductivity of the various phosphates should bear a correlation with the acidity of the cations, viz. Zr^{4+}, Sn^{4+} and Ti^{4+}. Acidity of a cation is related to ion size and charge. The ionic radius for Ti^{4+} is 0·745 Å, Zr^{4+} is 0·86 Å and Sn^{4+} is 0·83 Å.[27] The observed conductance depends on several factors described earlier in the text. The order of specific conductances at 30°C (table 3) is found to be – ZrP ($4·2 \times 10^{-6}$ S cm^{-1}) > SnP ($7·6 \times 10^{-7}$ S cm^{-1}) > TiP ($1·3 \times 10^{-7}$ S cm^{-1}). The specific conductivity of ZrP in the present study is comparable to values reported for α–ZrP ($3·2 \times 10^{-6}$ S cm^{-1})[28] and for polymer electrolyte blends.[29–31] The values are however lower by two orders of magni-

tude compared to modified forms like pellicular ZrP ($1·1 \times 10^{-4}$ S cm^{-1}).[32]

Compared to the specific conductivity of ZrP, the values of SnP and TiP are about one order of magnitude lower. The work carried out by Szirtes and co-workers shows similar behaviour, where specific conductivity of ZrP > TiP and one order of magnitude higher.[16] In the present study the specific conductivity of SnP ($7·6 \times 10^{-7}$ S cm^{-1}) is about two orders of magnitude lower compared to the values reported by Stenina and coworkers[21] ($5·4 \times 10^{-5}$ S cm^{-1}). The studies have however been carried out under the influence of humidity, and the fact that a decrease in relative humidity results in decreased conductivity, establishes this as well. Lower conductance value in case of SnP is probably due to anhydrous conditions in the present study.

Arrhenius plots have been presented in figure 6. For all the three materials, linearity is observed in the

Table 3. Specific conductivity (S cm^{-1}) of ZrP, SnP and TiP.

Temperature (°C)	Specific conductivity (σ) S cm^{-1}		
	ZrP ($\times 10^{-6}$)*	SnP ($\times 10^{-6}$)	TiP ($\times 10^{-6}$)
30	4·2	7·6	1·3
40	3·8	7·2	1·9
50	3·5	6·8	2·4
60	3·1	6·4	3·5
70	2·8	5·1	4·8
80	2·8	5·5	5·3
90	2·6	4·8	4·4
100	2·3	3·2	3·2
110	2·1	1·5	2·1
120	1·9	0·13	0·95
E_a (kcal/mol)	1·00	13·80	5·80

*Values have to be multiplied by the factor in parentheses
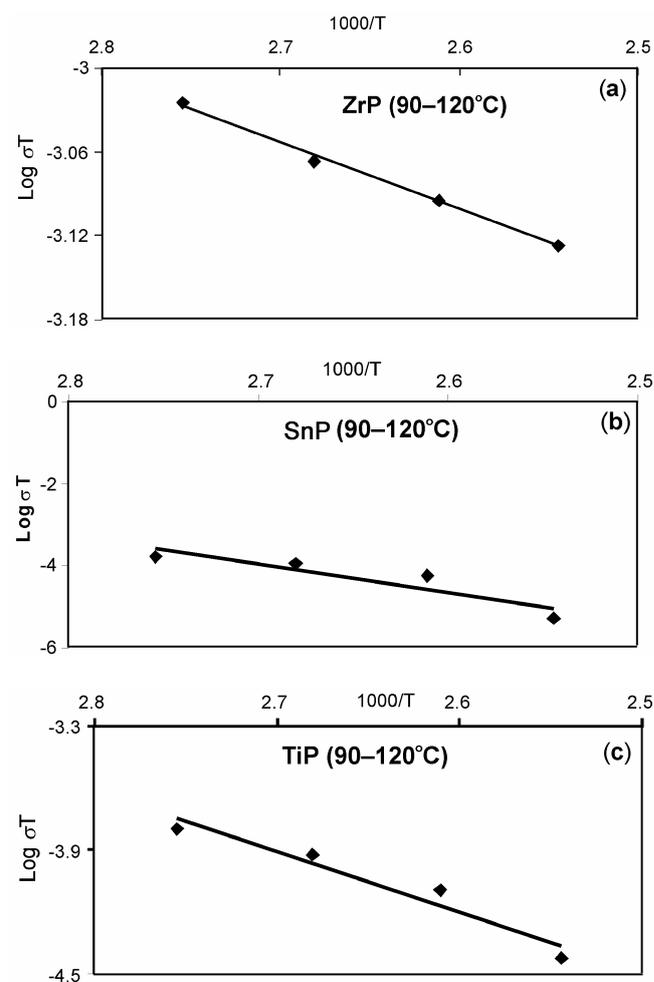
Figure 6. Arrhenius plot in the range 90–120°C for (**a**) ZrP, (**b**) SnP and (**c**) TiP.

temperature range (90–120°C). The energy of activation (E_a) has been calculated and the order of E_a is found to be SnP (13·8 kcal/mol) > TiP (5·8 kcal/mol) > ZrP (1·0 kcal/mol). However, the order of specific conductivity at 30°C is ZrP > SnP > TiP. The lower value of E_a and the high conductivity behaviour fit well in case of ZrP, showing the ease of conduction. The specific conductivity in case of TiP and SnP is of the same order ($\sim 10^{-7}$ S cm^{-1}). In this case, no correlation can be drawn between E_a and specific conductivity values observed. Stenina and coworkers, have studied the proton transport behaviour of Sn(HPO$_4$)$_2$·H$_2$O and have observed a lower conductivity and higher E_a compared to ZrP. They have attributed this behaviour to the strong H-bonds in acid tin phosphate resulting in a higher energy requirements for proton jumps from one site to another.[21] Similar explanation can also be extended in case of SnP in the present study.

4. Conclusion

In the present study, the proton transport properties of amorphous M(IV) phosphates exhibit lower conductance compared to reported crystalline phases. A study of transport properties under humid conditions would throw more light on the present investigation.

Acknowledgements

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