A comparative study of the proton transport properties of metal (IV) tungstates

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Abstract. Tetravalent metal acid (TMA) salts are cation exchangers due to the presence of structural hydroxyl groups. The presence of protons makes the TMA salt, a potential candidate for solid state protonic conduction. In the present endeavour, amorphous inorganic ion exchangers of the class of TMA salts, tin tungstate (SnW), titanium tungstate (TiW) and zirconium tungstate (ZrW) have been synthesized and characterized for elemental analysis, thermal analysis (TGA, DSC), FTIR spectroscopy and X-ray analysis. Chemical resistivity of these materials have been assessed in various acidic, basic and organic media. Ion exchange capacity has been determined and effect of heating on ion exchange capacity has been studied. The proton conduction behaviour of these materials has been studied by measuring specific conductance (*s*) at different temperatures in the range 30–175°C using HP 4192 A impedance analyzer. The specific conductance values for the three materials have been compared.

Keywords. Tetravalent metal acid salts; inorganic ion exchangers; proton conduction; metal (IV) tungstates; transport properties.

1. Introduction

In recent years, there has been intense research aimed at discovering new proton conductors and the mechanism of conduction in solids. Materials with high and pure protonic conductivity are candidates for electrolytes in sensors, batteries, fuel cells, electrolysers, etc. An entire class of materials has gained increasing interest as proton conductors: Polymers, oxide ceramics, intercalation compounds etc. Recently, a brief overview of the past and present state of solid state protonic conductors has been reported.[1,2]

Protonic conductors are often considered to be electrolytes in which hydrogen is transported towards and evolved at the cathode during electrolysis. Protonic 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 'Grothus' or 'free-proton mechanism'. Transport by any of other species is termed as a 'vehicle mechanism'.[3] In solids, vehicle mechanisms are usually restricted to materials with open structures (channels, layers) to allow passage of the large ions and molecules, while the Grothus mechanism requires close proximity of water molecules

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which are held firmly but are able to rotate. The classification of proton conductors according to the preparation method, chemical composition, structural dimensionality, mechanism of conduction etc. have been summarized in a comprehensive book on proton conductors.[4]

Inorganic ion exchangers of the class of TMA salts have been extensively studied in the field of separation science and catalysis. However, attempts have also been made to study the transport properties of these materials.[5,6] The mechanism of diffusion and ionic transport in crystalline *a*-zirconium phosphate has been studied in detail.[6] TMA salts have the general formula $M(IV) (HXO_4)_2.nH_2O$ where $M(IV) =$ Zr, Ti, Th, Ce, Sn, etc. and X = P, Mo, W, As, Sb, etc. The number of water molecules depend upon the method of preparation, drying conditions etc. They possess structural hydroxyl protons, which are responsible for their ion exchange behaviour. When these –OH groups 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.[7] From our laboratory we have reported protonic conduction behaviour of amorphous zirconium phosphomolybdate and its single salt counter parts, zirconium phosphate and zirconium molybdate.[8] Literature survey reveals that no work has been done on the proton conduction behaviour of tungstates of tin, titanium and zirconium.

In the light of the recent advances in the field of protonic conduction, the present study includes synthesis, characterization and study of transport properties of metal (IV) tungstates, SnW, TiW and ZrW. The materials have been characterized for elemental analysis, thermal analysis (TGA, DSC), FTIR spectroscopy, X-ray analysis and surface area measurements (BET method). Chemical stability of these materials have been assessed in various acidic, basic and organic media. Ion exchange capacity has been determined and effect of heating on ion exchange capacity studied. Further, protonic conductivities in these materials have been measured at various temperatures and the specific conductance values for these materials compared.

2. Experimental

2.1 *Preparation of the materials (SnW, TiW and ZrW)*

The materials SnW, TiW and ZrW were prepared by adding aqueous solution of sodium tungstate (0·2 M, 100 ml) to aqueous solution of metal salts in chloride form (0·1 M, 100 ml) dropwise and with continuous stirring. The pH of the resulting solution along with the gel obtained was maintained at ~2 pH and allowed to stand for at least 24 h, filtered, washed with conductivity water till free of chloride ions and dried at room temperature. The dried materials were brought to the desired particle size (60–100 mesh) and sorted by sieving. The materials were finally converted to the acid form by immersing in 1 M HNO_3, the acid being intermittently replaced, washed with conductivity water till free from acid and again dried at room temperature.

2.2 *Characterization*

The materials have been analysed for tin, titanium, zirconium and tungsten. Tin, titanium and zirconium were determined gravimetrically as oxides by the cupferron method[9] whereas tungsten was determined as barium tungstate.[10] Thermograms (TGA) were recorded on a Shimadzu DT-30 thermal analyser at a heating rate of 10°C min^{-1}. DSC of

the samples were performed on a Melter TA 4000 system at a heating rate of 20°C min^{-1}. FTIR spectra were recorded on a Bomen MB 104 series equipped with Epson Hi 80 printer/plotter. X-ray analyses of samples were carried out on a Rigaku D$_{max}$-30 using Cu-K*a* radiation with a nickel filter. Chemical resistivity of the materials were assessed by soaking the exchangers in several mineral acids, bases and organic solvents. Ion exchange capacities (i.e.c.) of the materials were determined by the column method[11] by taking 1 g of the exchanger in H$^+$ form in a glass column and eluting with Na$^+$ ions. The hydrogen ions thus eluted were determined titrimetrically against standard NaOH.

2.3 *Conductivity measurements*

The protonic conductivities of the materials were measured using pellets of 14 mm diameter and 1·5–2 mm thickness. The opposite sides of the pellets were coated with conducting silver paste to ensure good electrical contact. Impedance measurements were taken using HP 4192 A impedance analyser over a frequency range of 5 Hz to 13 MHz at a signal level below 1 V, interfaced to a minicomputer for data collection. The measurements were made in the temperature range 30–175°C. In all cases, since the impedance plots of the materials consist of single depressed semi-circles, the pellet conductivity was calculated by arc extrapolation to the X-axis, taking into account the geometric size of the pellets.

3. Results and discussion

All the tungstates were hard and white except TiW which is yellow. The chemical resistivity of the materials SnW, TiW and ZrW have been presented in table 1. As an illustration, for all the characterizations, the results for SnW have been shown, as all three tungstates show similar behaviour.

Chemical analyses of all three materials SnW, TiW and ZrW indicate the metal (IV) to tungstate ratio to be 1 : 2.

Thermograms of SnW (figure 1), TiW and ZrW indicate 13, 14 and 15% weight loss within the temperature range of 100–180°C corresponding to the loss of water molecules, after which a gradual weight loss is observed till 600°C. This may be due to the condensation of structural hydroxyl groups. DSC (figure 2) of the tungstates shows only one exothermic peak at ~ 132°C which is attributed to the presence of water. There is no endothermic peak up to 500°C, which indicates that there is no phase change.

Table 1. Chemical resistivity of SnW, TiW and ZrW in various media.

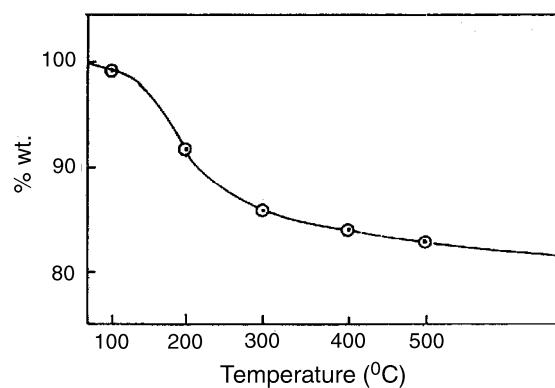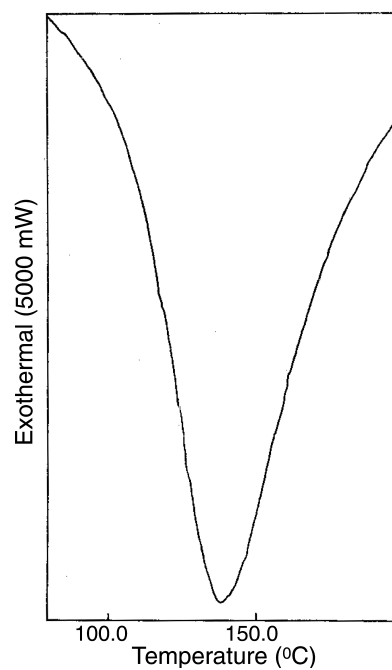| Medium	SnW	TiW	ZrW
Acids			
H_2SO_4	36 N	36 N	3 N
HCl	1 N	11·3 N	3 N
HNO_3	14 N	14 N	3 N
Bases			
NaOH	0·5 M	0·1 M	1 M
KOH	0·5 M	0·1 M	1 M
Organic solvents	All materials were found to be stable		

Figure 1.   TGA of SnW.

Figure 2.   DSC of SnW.

The Alberti Torrocca formula[12] has been used to determine the number of water molecules in SnW, TiW and ZrW. From this data, along with gravimetric determination of M(IV) and tungsten (as their oxides) we could probably formulate the three materials SnW, TiW and ZrW as $Sn^{IV}(W^{VI}O_2(OH)_2).5H_2O$; $Ti^{IV}(W^{VI}O_2(OH)_2).6H_2O$ and $Zr^{IV}(W^{VI}O_2(OH)_2).8H_2O$.

FTIR spectra shows a broad band in the region ~3400 cm^{-1} attributed to asymmetric and symmetric hydroxo -OH and aquo -OH stretches. A sharp medium band at   ~1620 cm^{-1} is attributed to aquo (H–O–H) bending.

XRD of the as prepared materials and materials calcined at 400°C, do not exhibit any sharp peaks, indicative of non-crystalline nature of the materials.

The Na^+ exchange capacity for SnW, TiW, and ZrW was found to be 1·52, 1·95 and 1·32 $meq.g^{-1}$ respectively.

The effects of heating on ion exchange capacity, represented in table 2 reveal that, in general, ion exchange capacity decreases on heating. This may be due to the condensation of structural hydroxyl groups at higher temperatures. This fact is also evident from the FTIR spectra of the heated samples (figure 3). It is seen that the intensity of the peaks at ~3400 cm^{-1} and 1620 cm^{-1}, representative of the –OH group, and external water molecules respectively diminishes as heating temperature increases.

The results of specific conductance for SnW, TiW, and ZrW have been presented in table 3. The complex impedance plots for all tungstates at 30°C have been presented (figure 4).

For all materials, it is observed that, specific conductivity decreases with increasing temperature (table 3). This is attributed to the loss of water of hydration as well as the condensation of structural hydroxyl groups with increasing temperature. This fact is also

Table 2. Effect of heating on ion exchange capacity of SnW, TiW and ZrW.

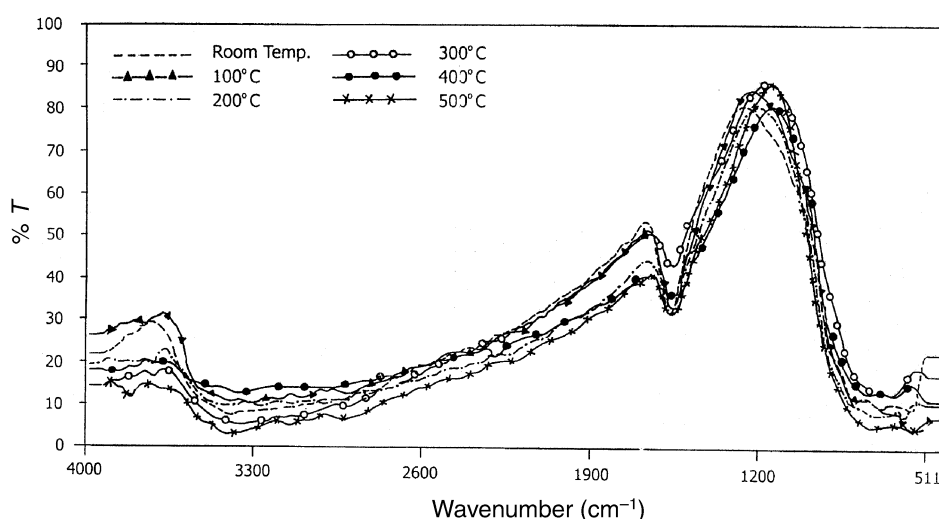| Temp. (°C)	Colour			Ion exchange capacity ($meq.g^{-1}$)		
	SnW	TiW	ZrW	SnW	TiW	ZrW
RT	White	Yellowish	White	1·52	1·95	1·32
100	Yellowish	Yellowish	Yellowish	1·08	1·90	0·49
200	Light brown	Yellowish	Light brown	0·82	1·28	0·24
300	Brown	Dull green	Brown	0·62	0·72	0·22
400	Brown	Dull green	White	0·50	0·26	0·16
500	Brown	Dull green	White	0·39	0·21	0·10

Figure 3. FTIR spectra of SnW and SnW heated at various temperatures.
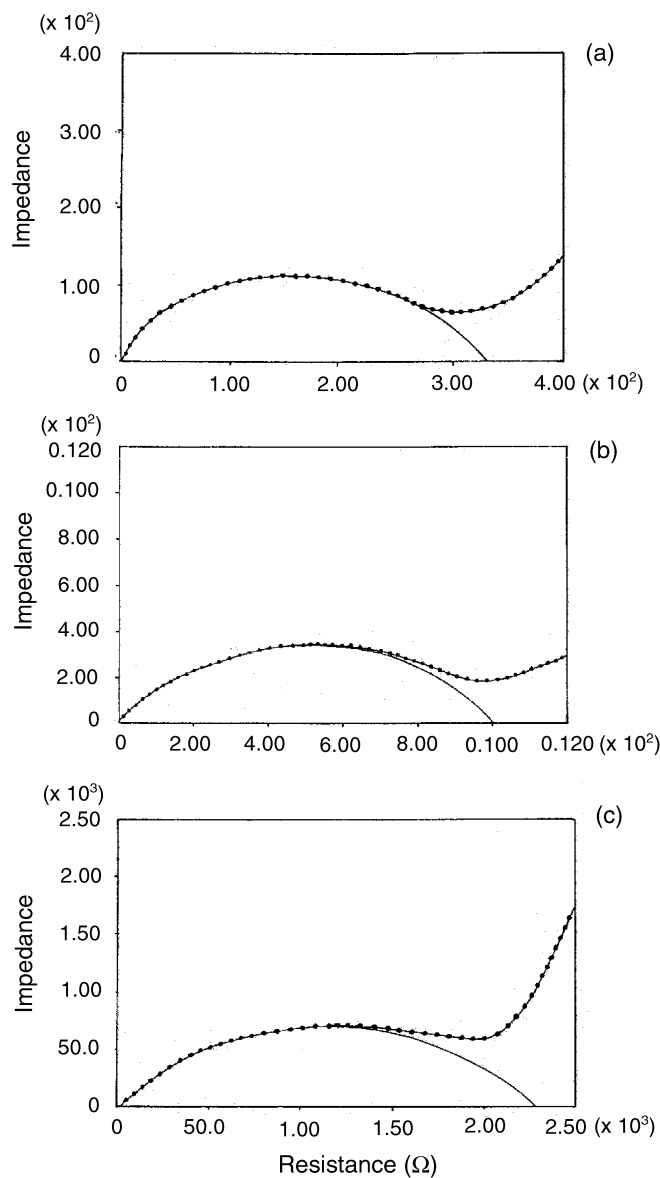
Figure 4.   Complex impedance plots for (**a**) SnW, (**b**) TiW and (**c**) ZrW at 30°C.

supported by the study of effect of heating on ion exchange capacity and FTIR spectra of the heated samples (figure 3), as discussed above. This suggests the mechanism of transportation as Grotthus type[13] 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 spacing of the –OH groups is too high.[14] Besides, the fact that the loss of protons resulting from the hydroxyl condensation causes a considerable decrease in conductivity, indicates that the conduction is protonic also.

Table 3. Variation of specific conductance (s) with temperature.

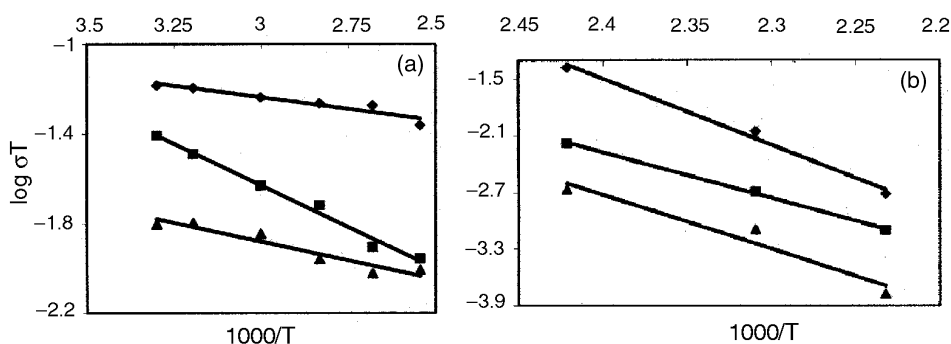| Temp. (°C)	s (Ω cm)$^{-1}$		
	SnW ($\times 10^{-4}$)	TiW ($\times 10^{-5}$)	ZrW ($\times 10^{-5}$)
30	2·166	12·99	5·220
40	2·043	10·39	5·110
60	1·744	7·026	4·294
80	1·554	5·415	3·121
100	1·430	3·330	2·550
120	1·117	2·825	2·500
140	1·021	1·604	0·5227
160	0·2040	0·4726	0·1878
175	0·04300	0·1768	0·03699

Figure 5. Arrhenius plot in the temperature range 30–120°C (**a**) and (**b**) 140–175°C. (◆ SnW, ■ TiW, ▲ ZrW).

Table 3 reveals the order of specific conductivity (s) at 30°C to be SnW ≥ TiW > ZrW. This trend is also in keeping with the ion exchange capacities of the tungstates that reflects on the proton conduction capacity. Arrhenius plots have been presented in (figure 5). For all the three materials linearity is observed in the temperature range (30°C–120°C) and (140°C–175°C). The energy of activation has been calculated and found to be 0·41 (SnW), 1·47 (TiW) and 0·66 (ZrW) in the temperature range 30°C–120°C, whereas it is found to be 13·92 (SnW), 9·65 (TiW) and 11·41 (ZrW) in the temperature range (140°C–175°C). Further, specific conductivity values at 30°C for SnW and TiW are much higher than that of a-ZrP[15] ($3.2 \times 10^{-6}\ \Omega^{-1}$ cm^{-1}) but are comparable to its modified forms like pellicular ZrP ($1.1 \times 10^{-4}\ \Omega^{-1}$ cm^{-1})[16] and polyhydrated ZrP[17] ($2.7 \times 10^{-6}\ \Omega^{-1}$ cm^{-1}) where the method of preparation is also rather difficult. The values of specific conductivity (s) for SnW and TiW are also comparable to that of amorphous polymer electrolyte blends.[18]

4. Conclusion

The present work is an attempt to establish the use of SnW, TiW and ZrW as proton conductors. However, further studies have to be carried out to establish the various

factors contributing to protonic conductivity such as role of the tetravalent metal M(IV) and the anion moiety e.g. phosphates, arsenates, molybdates etc. before making any final conclusions. Research in this line is being carried out in our laboratory.

Acknowledgements

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