A comparative study of proton transport properties of metal (IV) tungstates and their organic derivatives

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Abstract. New hybrid inorgano–organic materials were synthesized by anchoring organic moieties, ortho chlorophenol and para chlorophenol onto metal (IV) tungstates viz. tin tungstate (SnW), titanium tungstate (TiW) and zirconium tungstate (ZW) to give SnWoCP, SnWpCP, TiWoCP, TiWpCP, ZWoCP and ZWpCP, respectively. The materials were characterized for elemental analysis, thermal analysis (TGA, DSC), X-ray analysis and FTIR spectroscopy. Chemical resistivity of these materials were assessed in several acidic, basic and organic media. Further, the study of transport properties of these materials has been explored by measuring proton conductivity at different temperatures in the range 30–175°C using HP4192A impedance analyser over a frequency range 5 Hz–13 MHz at a signal level below 1 V. Based on the specific conductance data and Arrhenius plots, a suitable mechanism was proposed and conductance performance of derivatized and non-derivatized materials compared.

Keywords. Proton conductors; proton transport properties; solid electrolytes; ionic conductors; proton conduction in metal (IV) tungstates; proton conduction in derivatized metal (IV) tungstates.

1. Introduction

There is currently high interest in engineering mixed materials (organic/inorganic), where features of the organic and inorganic components complement each other leading to the formation of new solid-state structures and materials with new composite properties. Some examples of recent interest are inorganic solids with organic intercalates (Casciola *et al* 1989, 1993, 1994; Averill and Bringley 1990; Jones *et al* 1993), zeolites and open framework host materials with organic guests (Ozin 1992) and thin film heterostructures built up from alternating layers of organic polyelectrolytes and colloidal inorganic polyanions (Keller *et al* 1994; Kleinfeld and Ferguson 1994). New inorganic lattice structures are formed, resulting from cooperative interactions between the organic and inorganic components. In all cases, there is promise of developing new materials with properties not seen in purely organic or purely inorganic solids. Hybrid inorgano–organic compounds are novel multifunctional materials that offer a wide range of interesting properties. In this area, organic derivatives of inorganic ion exchangers of the class of tetravalent metal acid (TMA) salts are of particular interest. TMA salts have the general formula, $M(IV)(HXO_4)_2 \cdot nH_2O$, where $M(IV) = Zr, Ti, Ce, Th, Sn$ etc and $X = P, Mo, W, As, Sb$ etc. The protons of the structural hydroxyl groups in these materials can be exchanged for several cations and thus they act as cation

exchangers. They behave as protonic conductors due to the presence of surface hydroxyl protons that can easily move on the surface, accounting for their conductivities, which depend strongly on relative humidity, surface area and degree of crystallinity (Clearfield and Berman 1981).

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 proton (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 ‘Grotthus’ or ‘Free-proton’ mechanism. Transport by any other species is termed as a ‘Vehicle’ mechanism. 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 Grotthus mechanism requires close proximity of water molecules, which is firmly held but able to rotate. Compounds with less amount of water would be expected to conduct by vehicle mechanism in which a nucleophilic group such as H_2O or NH_3 acts as a carrier of proton.

Anchoring of organic molecules bearing ionogenic groups such as $-OH$, $-CO_2H$, $-SO_3H$, etc onto TMA salts are reported (Alberti *et al* 1985). Protons in these materials can also be replaced by several cations. Such materials are termed as inorgano–organic ion exchangers or hybrid materials or derivatized TMA salts.

Organic derivatives of α -zirconium phosphate was first prepared by Alberti and coworkers and are represented

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by the general formula, $\alpha\text{-Zr}(\text{O}_3\text{PR})_2\text{S}$, where R is an organic group and S an intercalated molecule when present. α -Zirconium carboxy alkylphosphonates (Alberti *et al* 1991) and α -zirconium alkyl sulphophenylphosphonates (Alberti *et al* 1992a,b) have been investigated for their proton conduction properties. Proton conduction in layered metal (IV) phosphonates was studied by Alberti and Casciola (1997). Other workers have also reported on the proton conduction behaviour of intercalated TMA salts (Costantino *et al* 1992; Casciola *et al* 1995; Stein *et al* 1996; Jaimez *et al* 1997; Szistet *et al* 1997; Yaroslavtsev *et al* 1997; Zima *et al* 1998). From our laboratory, we have reported proton conduction behaviour in amorphous zirconium phosphomolybdate and its single salt counterparts, zirconium molybdate and zirconium phosphate (Beena and Chudasama 1996) as well as organic derivatives of zirconium molybdate (ortho chlorophenol and para chlorophenol anchored onto it) (Pandit *et al* 1998). Proton transport properties of M(IV) tungstates have also been reported by us (Parikh and Chudasama 2003), where $\text{M(IV)} = \text{Sn, Ti, Zr}$.

In the present endeavour, amorphous tungstates of tetravalent tin, titanium and zirconium abbreviated as SnW, TiW and ZW, have been synthesized. Further, their organic derivatives have been synthesized by anchoring ortho chlorophenol and para chlorophenol onto them abbreviated as SnWoCP, SnWpCP, TiWoCP, TiWpCP, ZWoCP and ZWpCP, respectively. The materials have been 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 of these materials have been determined and effect of heating on ion exchange capacity studied. Earlier, ZWoCP and ZWpCP were synthesized, characterized and their ion exchange behaviour studied by us (Pandit and Chudasama 2001). Further we report the transport properties of derivatized materials as mentioned above using HP4192A Impedance Analyser, over a frequency range of 5 Hz–13 MHz at a signal level below 1 V in the temperature range 30–175°C. Specific conductance has been determined and the values compared with non derivatized samples.

2. Experimental

2.1 Preparation of inorgano-organic materials (SnWoCP, SnWpCP, TiWoCP, TiWpCP, ZWoCP and ZWpCP)

All three materials, SnW, TiW and ZW, were prepared as per the method described earlier (Parikh and Chudasama 2003). The anchoring of ortho chlorophenol and para chlorophenol onto SnW, TiW and ZW was carried out by treating 1 g of the acid treated TMA salt SnW, TiW or ZW with 20 ml of pure distilled chlorophenol and heated to reflux for ~ 2 h. The excess organic reagent was de-

canted. The material was then washed several times with alcohol so as to remove any trace of adhering chlorophenol from the surface. The sample thus obtained was dried at room temperature.

2.2 Instrumentation

The samples were analysed for tin, titanium and zirconium gravimetrically as their oxides by cupferron method (Elv-ing and Olson 1955). Tungsten was determined gravimetrically as barium tungstate (Vogel 1978). Thermogravimetric analysis of the samples was performed on a Shimadzu DT-30 thermal analyser at a heating rate of 10°C/min. DSC of the samples were performed on Mettler TA 4000 system at a heating rate of 20°C/min. FTIR spectra of the samples were performed using KBr wafer on a Bomem MB series with Epson Hi 80 printer/plotter. X-ray diffractogram ($2\theta = 5\text{--}90^\circ$) was obtained on X-ray diffractometer (Rigaku Dmax-30) with Cu-K_α radiation and nickel filter. Chemical stability/resistivity of the synthesized materials was assessed in different acids like HCl, H_2SO_4 , HNO_3 , bases like NaOH and KOH, organic solvents like ethyl alcohol, diethyl ether, acetic acid etc. The Na^+ ion exchange capacity (IEC) was determined as usual by the column method (Nabi and Rao 1981). Further, the effect of heating on ion exchange capacity was also studied by heating several 1 g portions of the exchangers for 2 h at various temperatures in a muffle furnace and determining the Na^+ exchange capacity by the column method at room temperature.

2.3 Conductivity measurements

The proton conductivity of the materials was measured using pellets of 14 mm diameter and 1.5–2 mm thickness with relative humidity of ~ 80%. The opposite sides of the pellets were coated with conducting silver paste to ensure good electrical contacts. Impedance was measured in the temperature range 30–175°C using HP4192A Impedance Analyser, over a frequency range of 5 Hz–13 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 semicircle, 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

SnW and ZW were obtained as white hard granules, whereas TiW was obtained as yellow granules. The derivatization of the organic moieties, ortho chlorophenol and para chlorophenol, is indicated visually by the change in colour of the inorganic matrix. SnWoCP, SnWpCP,

The FTIR spectra of ZW (figure 5) shows broad bands in the region $\sim 3400\text{ cm}^{-1}$ 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)

Derivatization in case of layered TMA salts occurs through intercalation whereas in non-layered materials, organic molecules get either sorbed or anchored onto the surface or get encapsulated within the pores of the inorganic matrix. So far as the nature of bonding of the organic moiety with the inorganic matrix is concerned, it could be either weak van der Waals forces, encapsulation, hydrogen bonding, covalent bonding or a strong ionic interaction, resulting into the localization of the attractive forces (Singh *et al* 1985; Khan and Singh 1987; Varshney *et al* 1993). Several groups have commented on the nature of interaction of the organic guests with the inorganic matrix. In case of layered TMA salts, the organic moieties interact with the inorganic matrix through van der Waals forces or hydrogen bonding as revealed by the IR and TGA data (Alberti *et al* 1979; Dines and Digiacomio 1981). Interaction of amino acids such as L-asparagine and L-alanine with crystalline TMA salt, zirconium phosphate, has been suggested to occur through an ion exchange reaction (Kijima *et al* 1981). The adsorption of organic molecules such as phosphamidon and carbofuran occurs through the localization of the attractive forces, between the surface protons of the inorganic matrix and the -CO and -PO groups of the organic molecules (Singh *et al* 1985; Khan and Singh 1987; Varshney *et al* 1993). Anchoring of organic molecules such as sodium salts of chromotropic acid (1,8-dihydroxynaphthelene-3,6-disulphonic acid) and tiron (1,2-dihydroxybenzene-3,5-disulphonic acid) have been investigated

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ted in our laboratory (Pandit and Chudasama 1996, 1998). These salts possessing $-\text{OH}$ as well as SO_3Na groups are attached by ion exchange.

In the present study, a band at 1050 cm^{-1} attributed to the presence of the aryl chloride group (in neat *o*CP/*p*CP)

however, disappears in the different FTIR spectrum of MWOCP–MW and MWpCP–MW ($M = \text{Sn}, \text{Ti}, \text{Zr}$). The interaction could be proposed to occur through the $-\text{OH}$ of the inorganic matrix and the $-\text{Cl}$ of the chlorophenols, with the elimination of an HCl molecule (Pandit and Chudasama 2001).

The X-ray diffractograms of the materials do not show any sharp bands, indicating the materials to be amorphous in nature (figure 7).

The Na^+ exchange capacity of SnW, TiW and ZW were found to be 1.52 , 1.95 and $1.32\text{ meq}\cdot\text{g}^{-1}$, respectively whereas Na^+ exchange capacity of derivatized materials SnWoCP, SnWpCP, TiWoCP, TiWpCP, ZWoCP and ZWpCP were found to be 2.64 , 2.70 , 3.03 , 3.33 , 1.37 and $1.46\text{ meq}\cdot\text{g}^{-1}$, respectively. The derivatized materials indicate an increase in IEC values as compared to that of nonderivatized materials. Also IEC of para derivatives is greater than ortho derivatives. The increase in IEC values is attributed to the presence of additional H^+ sites of the ionogenic $-\text{OH}$ present in the organic moiety. However, the enhancement in the values of IEC is not large. This may be probably due to the fact that the amount of chlorophenol anchored is less. The lesser value of IEC for ortho derivatives as compared to para derivatives may be due to the steric hindrance felt by the exchanging ion in case of ortho derivatives as compared to the para derivatives.

The results of the effect of heating on IEC values represented in table 2, reveals that in general IEC decreases

Figure 1. TGA plot for zirconium tungstate (ZW).

Figure 2. TGA plot for anchored material (ZWoCP).

Figure 3. DSC curve for zirconium tungstate (ZW).

Figure 4. DSC curve for anchored material (ZWoCP).

Figure 5. FTIR spectra of zirconium tungstate (ZW).

on heating. This may be due to the condensation of structural hydroxyl groups at higher temperature. This fact is also evident from the FTIR spectra of the heated samples of ZW (figure 8). It is seen that the intensity of the peaks at $\sim 3400\text{ cm}^{-1}$ and 1620 cm^{-1} representative of the $-\text{OH}$ group and external water molecules, respectively diminishes as heating temperature increases. However, in case of derivatized materials (table 3, figure 9), IEC initially decreases and exhibits a change in behaviour at temperatures between 200°C and 300°C . In case of ortho derivatives, IEC decreases up to 200°C and then

increases for the samples heated at 300°C . Again for the samples heated at 400°C and 500°C , IEC decreases. This may be due to the fact that, on heating in the range of $200\text{--}300^\circ\text{C}$, the organic moiety decomposes, leading to the formation of active carbon as evidenced by the change in colour of the heated samples, which is responsible for an increase in IEC that is later lost as CO_2 , as the temperature of heating increases. Similarly, in case of para derivatives, IEC values decrease on heating up to 200°C and then increase at 300°C . Again at temperatures 400°C and 500°C , the IEC value decreases. This study is supported by the FTIR spectra of the normal and heated samples. The intensities of the bands in the $\sim 3400\text{ cm}^{-1}$ region, between $1500\text{--}1400\text{ cm}^{-1}$, $1250\text{--}1150\text{ cm}^{-1}$ and $1060\text{--}1010\text{ cm}^{-1}$ diminishes as the temperature of heating increases.

Figure 6. FTIR spectra of anchored material (ZWoCP).

3.2 Impedance measurements

The results of specific conductance for nonderivatized (SnW, TiW, ZW) and derivatized materials (SnWoCP, SnWpCP, TiWoCP, TiWpCP, ZWoCP and ZWpCP) have been presented in table 4. The complex impedance plots of ZW, ZWoCP and ZWpCP at 30°C have been presented in figure 10.

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

Temperature ($^\circ\text{C}$)	Colour			Ion exchange capacity		
	SnW	TiW	ZW	SnW	TiW	ZW
Room temp.	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

Table 3. Effect of heating on ion exchange capacity of derivatized TMA salts.

Temperature ($^\circ\text{C}$)	Colour						Ion exchange capacity ($\text{meq}\cdot\text{g}^{-1}$)					
	SnWoCP	SnWpCP	TiWoCP	TiWpCP	ZWoCP	ZWpCP	SnWoCP	SnWpCP	TiWoCP	TiWpCP	ZWoCP	ZWpCP
Room temp.	Light yellow	Light brown	Cream	Light brown	Light yellow	Dark yellow	2.64	2.70	3.03	3.33	1.37	1.46
100	Light yellow	Light brown	Cream	Light brown	Light yellow	Dark yellow	2.58	2.61	2.83	3.31	1.27	1.41
200	Brown	Dark brown	Cream	Brown	Dark brown	Black	1.95	2.50	2.79	3.25	0.60	1.01
300	Brown	Dark brown	Light brown	Greenish yellow	Black	Black	2.08	2.64	3.01	3.26	0.69	1.10
400	Brown	Brown	Greenish yellow	Greenish yellow	Grey	Grey	1.69	2.62	2.16	2.48	0.18	0.34
500	Brown	Brown	Greenish yellow	Greenish yellow	Grey	Grey	1.58	2.32	0.50	1.18	0.08	0.10

Table 4. Specific conductivity ($\Omega^{-1} \text{ cm}^{-1}$) for nonderivatized and derivatized TMA salts.

Temp. ($^{\circ}\text{C}$)	SnW	SnWoCP	SnWpCP	TiW	TiWoCP	TiWpCP	ZW	ZWoCP	ZWpCP
30	2.16×10^{-4}	3.44×10^{-6}	4.92×10^{-6}	1.29×10^{-4}	5.84×10^{-8}	1.10×10^{-4}	5.22×10^{-5}	1.63×10^{-6}	1.44×10^{-5}
40	2.04×10^{-4}	3.22×10^{-6}	4.58×10^{-6}	1.03×10^{-4}	5.01×10^{-8}	1.01×10^{-4}	5.11×10^{-5}	1.57×10^{-6}	1.39×10^{-5}
60	1.74×10^{-4}	3.02×10^{-6}	4.28×10^{-6}	7.02×10^{-5}	2.42×10^{-8}	6.01×10^{-5}	4.29×10^{-5}	1.22×10^{-6}	1.36×10^{-5}
80	1.55×10^{-4}	2.77×10^{-6}	3.90×10^{-6}	5.41×10^{-5}	2.19×10^{-8}	4.56×10^{-5}	3.12×10^{-5}	1.18×10^{-6}	1.27×10^{-5}
100	1.43×10^{-4}	1.53×10^{-6}	2.60×10^{-6}	3.33×10^{-5}	1.67×10^{-8}	4.00×10^{-5}	2.55×10^{-5}	1.09×10^{-6}	1.19×10^{-5}
120	1.11×10^{-4}	1.03×10^{-6}	1.39×10^{-6}	2.82×10^{-5}	1.15×10^{-8}	1.78×10^{-5}	2.50×10^{-5}	8.28×10^{-7}	1.01×10^{-5}
140	1.02×10^{-4}	1.09×10^{-7}	1.57×10^{-7}	1.60×10^{-5}	1.04×10^{-8}	2.45×10^{-6}	5.22×10^{-6}	2.26×10^{-7}	2.07×10^{-6}
160	2.04×10^{-5}	6.24×10^{-7}	1.20×10^{-7}	4.72×10^{-6}	8.88×10^{-9}	6.15×10^{-7}	1.87×10^{-6}	1.04×10^{-7}	6.30×10^{-7}
175	4.30×10^{-6}	4.34×10^{-7}	8.63×10^{-8}	1.76×10^{-6}	8.25×10^{-9}	2.64×10^{-7}	3.69×10^{-7}	7.10×10^{-8}	2.02×10^{-7}
E_{act} (kcal/mole)	0.41	1.00	0.96	1.47	0.76	0.72	0.66	0.37	0.62

Figure 7. XRD pattern for zirconium tungstate (ZW). **Figure 9.** FTIR spectra of anchored material (ZWoCP) from room temperature to 500°C. **Figure 8.** FTIR spectra of zirconium tungstate (ZW) from room temperature to 500°C.

For all the nine materials, it is observed that specific conductivity decreases with increasing temperature (table 4). 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 supported by the study of effect of heating on IEC, that IEC decreases as the temperature of heating increases (also evident from the FTIR spectra of heated samples) (figures 8, 9).

This suggests the mechanism of transportation to be of a Grotthus type (Clearfield 1988) 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 $-\text{OH}$ groups is too high (Alberti *et al* 1989). 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.

Arrhenius plots have been presented in figure 11. For all materials, linearity was observed in the temperature range 30–120°C. The energy of activation has been calculated and found to be (in Kcal/mole) 0.41 (SnW), 1.00 (SnWoCP), 0.96 (SnWpCP), 1.47 (TiW), 0.76 (TiWoCP), 0.72 (TiWpCP), 0.66 (ZW), 0.36 (ZWoCP) and 0.62 (ZWpCP). From table 5, it is observed that values of specific conductivity (s) at 30°C for all three tungstates exhibit the order $\text{SnW} > \text{TiW} > \text{ZW}$. Further, specific conductivity values at 30°C for SnW and TiW is much higher than that of $\alpha\text{-ZrP}$ ($3.2 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$) (Casciola and Bianchi 1985), but comparable to that of its modified forms like pellicular ZrP ($1.1 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$) (Casciola and Costantino 1986). The values are also comparable to that of polymer electrolyte blends (Paulmer and Kulkarni 1992). In general, it is observed that specific conductivity of derivatized materials is less than that of nonderivatized materials. This can be explained on the basis of the fact that since the inorganic host SnW, TiW and ZW are

amorphous and nonlayered (Srivastava *et al* 1980), the organic guests get anchored on the surface of the inorganic matrix. Thus contribution due to internal protonic conduction is not possible as has been observed earlier (Casciola *et al* 1990). Further, as reported by Alberti *et al* (1978), in spite of the very high concentration of acid groups in layered materials, the bulk contribution to the conductivity is negligible because the main part of the measured conductivity is related to the surface. The very low bulk conductivity at room temperature could be due to lack of orientation and polarization of the W–OH groups present in the materials. However, the observed

conductivity is attributed to W–OH groups present on the surface, which have freedom to rotate, as well as by the water molecules that are present (Casciola *et al* 1983).

Amongst the derivatized materials, specific conductivity values for ortho derivatives are less as compared to that of para derivatives. This could be attributed to their orientation on the matrix. In case of para chlorophenol

Figure 10. Complex impedance plots for **a.** zirconium tungstate (ZW), **b.** anchored material (ZWoCP) and **c.** anchored material (ZWpCP).

Figure 11. Arrhenius plots for **a.** metal (IV) tungstates, **b.** tin tungstate (SnW) and anchored materials (SnWoCp & SnWpCP), **c.** titanium tungstate (TiW) and anchored materials (TiWoCP & TiWpCP) and **d.** zirconium tungstate (ZW) and anchored materials (ZWoCP & ZWpCP) in the range 30–120°C.

both orientation as well as the electron withdrawing nature of phenyl ring facilitates proton release for conduction.

4. Conclusion

The work reported in this paper is a humble attempt to establish the use of SnW, TiW and ZW as well as their organic derivatives as proton conductors. However, further studies are being carried out in our laboratory to establish the various factors contributing to protonic conduction such as role of tetravalent metal, M(IV), and the anion e.g. phosphates, arsenates, molybdates, tungstates etc before making any final conclusions.

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