Synthesis, characterization and proton transport property of crystalline - zirconium titanium phosphate, a tetravalent bimetallic acid salt

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An advanced inorganic material of the class of tetravalent bimetallic acid (TBMA) salt - zirconium titanium phosphate (ZTP) has been synthesized by sol gel route. ZTP has been characterized for elemental analysis by ICP-AES, FTIR, TGA and X-ray diffraction studies. Ion exchange capacity (IEC) of material was determined and effect of calcination (373-773 K) on IEC studied. Chemical resistivity of material was assessed in acids, bases and organic solvents. Protons present in structural hydroxyl groups in ZTP indicate good potential to exhibit solid-state proton conduction. Proton transport property of ZTP was explored by measuring specific conductance at different temperatures (303-423 K) at 10 K intervals, over a frequency range (1-32 MHz) at a signal level below 1 V. Proton transport properties of zirconium phosphate and titanium phosphate, synthesized and characterized under identical conditions, have been investigated for comparative studies. In all cases, conductivity decreases with increasing temperature. ZTP exhibit enhanced conductance and mechanism of transportation is proposed to be Grotthuss type.

Keywords: Proton conductor, Proton transport property, Solid electrolyte, Tetravalent bimetallic acid salt, Zirconium titanium phosphate

Introduction
Proton conductors (PCs), which are used in fuel cells, sensors, water electrolysis units and other electrochemical devices, are often considered to be electrolytes, in which hydrogen is transported towards and evolved at cathode during electrolysis\(^1,2\). Proton exchange membrane fuel cells (PEMFC) is limited by its inability to operate at high temperatures\(^3\) (>373 K). Classification of PCs according to preparation method, chemical composition, structural dimensionality, mechanism of conduction etc has been summarized\(^4\). Based on temperature, PCs are classified as, near ambient temperature (< 373 K), medium temperature (373-463 K) and high temperature (> 463 K). Medium temperature PCs are of particular interest, however, not much work has been explored as compared to PCs at elevated temperatures\(^5,6\).

Inorganic ion exchangers of the class of tetravalent metal acid (TMA) salts [general formula, \(\text{M(IV)}(\text{HXO}_4)_2 \cdot n\text{H}_2\text{O}\) where \(\text{M(IV)} = \text{Zr, Ti, Sn, Ce, Th etc and X = P, Mo, W, As, Sb etc.}\)] possess structural hydroxyl protons; \(\text{H}^+\) of –OH being exchangeable sites. A number of cations can be exchanged with \(\text{H}^+\), due to which material possesses cation exchange properties. Protons present in structural hydroxyl groups indicate good potential for these materials to exhibit solid-state proton conduction. When –OH groups are hydrated, protons can move easily on the surface, thus accounting for their conductivities, which depend strongly on relative humidity, surface area and degree of crystallinity\(^8\). TMA salts have exhibited interesting conducting properties\(^9-11\) and hold great promise as PCs possessing high conductivity, chemical resistivity and thermal stability at medium temperatures\(^1\). Layered zirconium based PCs have been extensively investigated for fuel cell applications\(^12\). Surface conducts protons four orders of magnitude greater than bulk protons\(^13\). Mechanism of diffusion and proton transport in crystalline zirconium phosphate (ZP), titanium phosphate (TP), tin phosphate, tantalum phosphate, uranyl phosphate have been studied\(^14-18\). Proton transport properties of amorphous M(IV) tungstates\(^19\) and phosphates\(^20\), where M(IV) = Zr, Sn, Ti, have been reported.

Mixed materials of the class of TMA salts (compounds containing two different cations and a given anion or two...
different anions and a cation) have been widely investigated as ion exchangers and exhibit improved ion exchange properties in comparison to their single salt counterparts\textsuperscript{21,22}. Mixed material containing two anions and a cation, zirconium phosphomolybdate, has been synthesized, characterized and their proton conduction properties compared with single salt counter parts, zirconium phosphate and zirconium molybdate\textsuperscript{23}. Zirconium phosphomolybdate exhibits higher conductivity compared to single salt counter parts. Amorphous zirconium titanium phosphate, a tetravalent bimetallic acid (TBMA) salt, has been synthesized, characterized and its ion exchange characteristics have been reported\textsuperscript{24-26}.

In present study, crystalline zirconium titanium phosphate (ZTP), an advanced inorganic material of the class of TBMA salt, has been synthesized by sol gel route and characterized. Proton transport property of ZTP has been explored by measuring specific conductance at different temperatures (303-423 K) at 10 K intervals, over a frequency range (1-32 MHz) at a signal level below 1 V. Proton transport properties of zirconium phosphate (ZP) and titanium phosphate (TP), synthesized and characterized under identical conditions, have been investigated for comparative studies. Conductivity performance of ZTP, ZP and TP is discussed based on conductivity data and activation energy and a suitable mechanism has been proposed.

### Materials and Methods

Zirconium oxychloride (ZrOCl\textsubscript{2}.8H\textsubscript{2}O) was procured from Loba Chem. Titanium tetrachloride (TiCl\textsubscript{4}) was obtained from Spectrochem India Pvt. Ltd. Sodium dihydrogen phosphate (NaH\textsubscript{2}PO\textsubscript{4}.2H\textsubscript{2}O) was obtained from E. Merck, India. HNO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} used were of AR grade. Double-distilled water was used for all the studies.

#### Synthesis of ZTP

In a solution containing 0.1 M ZrOCl\textsubscript{2}.8H\textsubscript{2}O and 0.1 M TiCl\textsubscript{4} in 10 % w/v H\textsubscript{2}SO\textsubscript{4} (100 ml), 0.2 M NaH\textsubscript{2}PO\textsubscript{4}.2H\textsubscript{2}O (200 ml) was added drop wise (flow-rate, 1 ml.min\textsuperscript{-1}) with continuous stirring at room temperature. After complete precipitation, gel was stirred for another 5 h. Precipitate was kept in contact with mother liquor overnight, filtered, washed with double distilled water to remove adhering ions (chloride and sulfate). Gel obtained was refluxed with phosphoric acid for 100 h, filtered, washed, dried at room temperature, and then used.

#### Synthesis of ZP and TP

In a solution of ZrOCl\textsubscript{2}.8H\textsubscript{2}O (0.1 M, 100 ml) or TiCl\textsubscript{4} (0.1 M, 100 ml) in 10 % w/v H\textsubscript{2}SO\textsubscript{4}, 0.2 M NaH\textsubscript{2}PO\textsubscript{4}.2H\textsubscript{2}O (200 ml) was added drop wise (flow-rate, 1 ml.min\textsuperscript{-1}) with continuous stirring at room temperature. Rest of the process was same as for ZTP.

#### Ion exchange Capacity (IEC) and Calcination Studies

Na\textsuperscript{+} ion exchange capacity (IEC) for ZP, TP and ZTP were determined by column method\textsuperscript{27}. Effect of heating on IEC was studied by heating several portions (1 g each) of material for 2 h at 373, 473, 573, 673 and 773 K in a muffle furnace and determining Na\textsuperscript{+} exchange capacity by column method\textsuperscript{27} at room temperature.

#### Chemical Stability

Chemical stability of material in various media [acids (HCl, H\textsubscript{2}SO\textsubscript{4}, HNO\textsubscript{3}), bases (NaOH and KOH) and organic solvents (ethanol, benzene, acetone and acetic acid)] was studied by taking synthesized material (500 mg each) in particular medium (50 ml) and allowed to stand for 24 h. Change in colour, nature and weight was observed.

#### Instrumentation

Samples were analyzed for zirconium, titanium and phosphorous content using Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES), Labtam, 8440 Plasmalab. X-ray diffractometer (2\theta = 5-80\degree) was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-K\alpha X-ray source of wavelength 1.5418 Å and nickel filter. FTIR spectra were recorded using KBr wafer on a Perkin Elmer Paragon 1000 spectrophotometer. TGA was carried out on a Shimadzu DT 30 thermal analyzer at a heating rate of 10 K.min\textsuperscript{-1}. Solartron Impedance Analyzer (SI 1260) was used for specific conductance measurement.

#### Conductivity Measurements

Proton conductivity of materials was measured using pellets (diam, 10 mm; thickness, 1.5 - 2.0 mm) prepared by pressing material (300 mg) at 40 KN/cm\textsuperscript{2}. Two opposite flat surfaces of pellets were coated with conducting silver paste to ensure good electrical contacts. Complex impedance was measured in between 303-423 K, at 10 K intervals, using Solartron Impedance Analyzer (SI 1260) over a frequency range 1-32 MHz at a signal level below 1 V.

In a solution containing 0.1 M ZrOCl\textsubscript{2}.8H\textsubscript{2}O and 0.1 M TiCl\textsubscript{4} in 10 % w/v H\textsubscript{2}SO\textsubscript{4} (100 ml), 0.2 M NaH\textsubscript{2}PO\textsubscript{4}.2H\textsubscript{2}O (200 ml) was added drop wise (flow-rate, 1 ml.min\textsuperscript{-1}) with continuous stirring at room temperature. After complete precipitation, gel was stirred for another 5 h. Precipitate was kept in contact with mother liquor overnight, filtered, washed with double distilled water to remove adhering ions (chloride and sulfate). Gel obtained was refluxed with phosphoric acid for 100 h, filtered, washed, dried at room temperature, and then used.
level below 1 V, interfaced to a computer for data collection. In all cases, since impedance plots of materials consist of single depressed semicircle, pellet conductivity was calculated by arc extrapolation to real axis, taking into account geometrical sizes of pellets.

**Results and Discussion**

**Characterization**

Synthesized materials (ZP, TP and ZTP) were obtained as white powder. Elemental analysis performed by ICP-AES shows the ratio of M: P in ZP and TP is 1: 2, while in case of ZTP, ratio of Zr : Ti : P is 1 : 1 : 2. All materials exhibit good chemical stability in acid media (maximum tolerable limits being 36 M H$_2$SO$_4$ (ZP & ZTP) and 18 M H$_2$SO$_4$ (TP), 16 M HNO$_3$ (ZP, TP and ZTP), 10 M HCl (ZP) and 11.3 M HCl (TP & ZTP)] and in organic solvents (ethanol, benzene, acetone and acetic acid), but a lower stability in alkaline media (maximum tolerable limits being 5 M NaOH and 5 M KOH for ZP and ZTP and 2 M NaOH and 2 M KOH for TP). Sharp peaks observed in X-ray diffractograms of ZP (Fig. 1a), TP (Fig. 1b) and ZTP (Fig. 1c), confirm crystalline nature of materials. Crystalline phases of ZP and TP were confirmed from JCPDS card no. 33-1482 and 44-0382 respectively.

FTIR spectra of ZP (Fig. 2a), TP (Fig. 2b) and ZTP (Fig. 2c) exhibit a broad band (3400 cm$^{-1}$) attributed to asymmetric and symmetric –OH stretches. A sharp
medium band (1620 cm\(^{-1}\)) is attributed to aquo (H–O–H) bending. A band (1035 cm\(^{-1}\)) is attributed to the presence of P=O stretching. A medium intensity band (1400 cm\(^{-1}\)) is attributed to \(\text{P(OH)}\)\(^2\) presence. These bands indicate presence of structural hydroxyl groups/protonic sites in the material.

\(\text{Na}^+\) exchange capacity have been evaluated at room temperature and observed to be: ZP, 2.02; TP, 2.08; and ZTP, 2.90 meq.g\(^{-1}\). IEC on calcination at 373, 473, 573, 673, 773 K were found to be (respectively): ZP, 2.06, 1.86, 1.74, 1.23 and 1.06; TP, 2.12, 1.93, 1.81, 1.27 and 1.09; and ZTP, 2.80, 2.62, 2.30, 1.97 and 1.61 meq.g\(^{-1}\).

Decrease in IEC with increasing temperature is attributed to condensation of structural hydroxyl groups, and also evident from FTIR spectra of calcined samples, where intensity of peaks at 3400 cm\(^{-1}\) and 1620 cm\(^{-1}\) (representative of \(\text{–OH}\) group) diminishes as heating temperature increases.

TGA indicates two weight loss regions. First weight loss region up to 453 K [ZP, 4% (Fig. 3a); TP, 3% (Fig. 3b); and ZTP, 5% (Fig. 3c)] is attributed to loss of moisture/hydrated water. Second weight loss between 523–773 K for all materials is attributed to condensation of structural \(\text{–OH}\) groups. These observations are further

![Fig. 3—Thermograms of: (a) ZP; (b) TP; and (c) ZTP](image1)

![Fig. 4—Complex impedance plots for: (a) ZP; (b) TP; and (c) ZTP at 303 K](image2)
Impedance Measurements

In complex impedance plots for ZP (Fig. 4a), TP (Fig. 4b) and ZTP (Fig. 4c) at 303 K, impedance spectrum consists of a single depressed semicircle. Sample resistance \((R)\) was measured by extrapolation of high frequency arc crossing to \(Z\) (real) axis. Proton conductivity was measured using Eq., \(\sigma = \frac{l}{RA}\), where \(l\) is sample thickness (cm) and \(\sigma\) is electrode area (cm\(^2\)). Arrhenius plots \((\log \sigma T vs 1/T)\) are presented for ZP (Fig. 5a), TP (Fig. 5b) and ZTP (Fig. 5c). Activation energy \((E_a)\) for each sample was calculated using Arrhenius equation \([\sigma = \sigma_0 exp (-E_a / kT)]\), where \(k\) is Boltzmann’s constant and \(T\) is temperature.

Proton transport includes, transport of proton \((H^+)\) and any assembly that carries protons \((OH, H_2O, H_3O^+, NH_4^+\) etc). Transport of protons \((H^+)\) between relatively stationary host anions is termed ‘Grotthuss’ or ‘free-proton’ mechanism\(^{30}\), which requires close proximity of water molecules, that are firmly held but able to rotate. \(E_a\) is thus low, since it depends entirely on reorientation step\(^{31}\). Transport by any other species is termed as “vehicle mechanism”. Here, polyatomic ion \((H_3O^+, OH^- or NH_4^+)\) migrates as entities through bulk materials. Thus, \(E_a\) is expected to be high. Vehicle mechanism is most frequently encountered in aqueous solution and other liquid/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 less amount of water would be expected to conduct by vehicle mechanism, in which a nucleophilic group \((H_2O or NH_3)\) acts as a proton carrier.

From specific conductance \((\sigma)\) and \(E_a\) for ZP, TP and ZTP (Table 1), it is observed that \(\sigma\) decreases with increasing temperature. Similar trend was observed in TMA salts, and attributed to the loss of water of hydration as well as condensation of structural –OH groups with increasing temperature\(^{19,20,23}\). This fact is also supported by the study of heating effect on IEC, suggesting mechanism of transportation to be Grotthuss type\(^9\), where conductivity depends on water ability located on the surface to rotate and participate. Further, results are also in agreement with the suggestion that protons are not able to diffuse along an anhydrous surface, where spacing of –OH groups is too high\(^{32}\). Besides, loss of protons resulting from –OH condensation causes a considerable decrease in conductivity, indicates that conduction is protonic also.

supported by the fact that IEC decreases as calcination temperature decrease.

Based on ICP-AES and TGA data, materials were formulated as ZP \([Zr(HPO_4)_{2.0.5H_2O}\), TP \([Ti(HPO_4)_{2.0.5H_2O}\) and ZTP \([\dot{Zr}_{0.51}Ti_{0.49} (H_2PO_4).0.5H_2O]\) using reported\(^{29}\) formula.
Table 1—Specific conductance of crystalline phases of ZP, TP and ZTP at various temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \sigma_{ZP} ) (S cm(^{-1} ))</th>
<th>( \sigma_{TP} ) (S cm(^{-1} ))</th>
<th>( \sigma_{ZTP} ) (S cm(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>6.56 X 10(^6)</td>
<td>9.09 X 10(^6)</td>
<td>2.72 X 10(^5)</td>
</tr>
<tr>
<td>313</td>
<td>5.07 X 10(^6)</td>
<td>7.52 X 10(^6)</td>
<td>2.13 X 10(^5)</td>
</tr>
<tr>
<td>323</td>
<td>2.33 X 10(^6)</td>
<td>4.46 X 10(^6)</td>
<td>1.77 X 10(^5)</td>
</tr>
<tr>
<td>333</td>
<td>1.33 X 10(^6)</td>
<td>3.50 X 10(^6)</td>
<td>1.59 X 10(^5)</td>
</tr>
<tr>
<td>343</td>
<td>9.63 X 10(^7)</td>
<td>3.03 X 10(^6)</td>
<td>1.50 X 10(^5)</td>
</tr>
<tr>
<td>353</td>
<td>9.25 X 10(^7)</td>
<td>2.87 X 10(^6)</td>
<td>1.49 X 10(^5)</td>
</tr>
<tr>
<td>363</td>
<td>9.23 X 10(^7)</td>
<td>2.73 X 10(^6)</td>
<td>1.43 X 10(^5)</td>
</tr>
<tr>
<td>373</td>
<td>8.88 X 10(^7)</td>
<td>2.59 X 10(^6)</td>
<td>1.39 X 10(^5)</td>
</tr>
<tr>
<td>383</td>
<td>8.54 X 10(^7)</td>
<td>2.45 X 10(^6)</td>
<td>1.35 X 10(^5)</td>
</tr>
<tr>
<td>393</td>
<td>8.17 X 10(^7)</td>
<td>2.29 X 10(^6)</td>
<td>1.31 X 10(^5)</td>
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<tr>
<td>403</td>
<td>7.36 X 10(^7)</td>
<td>2.14 X 10(^6)</td>
<td>1.25 X 10(^5)</td>
</tr>
<tr>
<td>413</td>
<td>6.61 X 10(^7)</td>
<td>2.07 X 10(^6)</td>
<td>1.19 X 10(^5)</td>
</tr>
<tr>
<td>423</td>
<td>6.03 X 10(^7)</td>
<td>2.04 X 10(^6)</td>
<td>1.12 X 10(^5)</td>
</tr>
</tbody>
</table>

Order of \( \sigma \) at 303 K is: \( \sigma_{ZTP} \) (2.72 X 10\(^5\) S cm\(^{-1} \)) > \( \sigma_{TP} \) (9.09 X 10\(^6\) S cm\(^{-1} \)) > \( \sigma_{ZP} \) (6.56 X 10\(^6\) S cm\(^{-1} \)). This trend is also in keeping with IEC values: ZTP (2.90 meq.g\(^{-1} \)) > TP (2.08 meq.g\(^{-1} \)) > ZP (2.02 meq.g\(^{-1} \)). Higher IEC values indicate more exchangeable protons (H\(^+\) of structural –OH group in present case) and hence more available conducting protons. In present study, \( \sigma_{ZP} \) and \( \sigma_{TP} \) are comparable to reported\(^4\) values. Higher value of \( \sigma_{TP} \) than \( \sigma_{ZP} \) could be explained due to acidity of cation, which is related to ion size (ionic radii for Ti\(^{4+}\) is 0.745 Å and Zr\(^{4+}\) is 0.86 Å) and charge. Since, both ZP and TP bear a common anion (HPO\(^4-\)), Ti\(^{4+}\) with smaller ionic radii and therefore high charge density, exhibits greater proton conductivity. \( \sigma_{ZTP} \) is higher compared to its single salt counterparts, may be attributed to some structural changes. However, observed conductance depends on concentration of charge carriers, availability of vacant sites, crystal structure, surface morphology, hydrophobicity, presence of interstitial sites, temperature, activation energy etc. Higher conductivity in mixed material zirconium phosphomolybdate (7.49 X 10\(^-5\) S cm\(^{-1} \)) compared to its single salt counterparts [zirconium phosphate (2.63 X 10\(^-6\) S cm\(^{-1} \)) and zirconium molybdate (1.08 X 10\(^-5\) S cm\(^{-1} \))] has also been reported\(^2\).

Arrhenius plots for ZP (Fig. 5a), TP (Fig. 5b) and ZTP (Fig. 5c) shows linearity in temperature range, 363-393 K. \( E_a \) has been found to be 0.92, 2.07 and 0.18 kcal.mol\(^{-1} \) for ZP, TP and ZTP respectively. Lower \( E_a \) values indicate ease of conduction. Such low \( E_a \) values are also observed earlier for particle hydrates\(^9,11\). \( E_a \) values, follow order TP > ZP > ZTP, however, \( \sigma \) values follow the order ZTP > TP > ZP in temperature range 363-393 K. Low \( E_a \) supports high conductance in case of ZTP. Comparing ZP and TP, high \( E_a \) and high \( \sigma \) values are observed for TP. High \( E_a \) and high \( \sigma \) values have also been reported earlier\(^16,20\). \( E_a \) values depend on high density of mobile ions, availability of vacant sites, good connectivity among sites, complexity in structure/steric effect and acidity of metal ion. Stefina et al\(^16\) attributed this behaviour to strong H-bonds resulting in a higher energy requirement for proton jump from one site to another. Depending on predominant factor, \( E_a \) values vary in each case.

Conclusions
ZTP, a TBMA salt, exhibits enhanced proton conductance compared to its single salt counterparts, ZP and TP. However, to obtain better and higher proton conductance, sol gel route for synthesis of ZTP should be modified to get better IEC and hence proton conductance.

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