



Comparative studies on Proton conducting nature of Copper selective tin Zirconium phosphate Cation exchanger with its single Salts counter parts

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Abstract

Tetravalent metal acid salts based cation exchanger; tin zirconium phosphate was synthesized by sol-gel process. The ion exchange capacity, chemical stability, effect of temperature and pH titration studies were carried out to understand the ion exchange capability. The study of effect of temperature on ion exchange capacity of this material indicated the pronounced ion exchange capacity even at elevated temperature. The physico-chemical characterization was studied by elemental analysis, XRD, FTIR and TGA. The thermal analysis depicted the enhanced thermal stability of this material. The X-ray diffraction study showed that the material formed is semicrystalline in nature. The distribution studies of different metal ions on the exchanger were performed in different solvent systems and it was found to be selective for Pb^{II} and Cu^{II} ions. The presence of protons makes the TMA salt, a potential candidate for solid state protonic conduction. In the present endeavour, the proton conduction behaviour of these materials has been studied by measuring specific conductance (S) at different temperatures in the range 30–80°C using Solatron (1255B FRA F11287 Electrochemical Phase) impedance analyzer. The specific conductance values for the single salts counter parts (tin phosphate and zirconium phosphate) have been compared.

Keyword: Tetravalent metal acid, cation exchanger, proton conductivity.

Introduction

Inorganic metal phosphates have interesting properties like protonic and alkali metal conductivity^{1,2}, catalytic³, and ion-exchange^{4,5}. In recent years there are lot of research work, focused at developing new proton conductors and determining their conduction mechanism, which makes its potential use in the field of fuel cell, sensors, water electrolysis units and other electrochemical devices. Fast proton conduction is often observed in inorganic ion exchange materials which contain high valent cations^{1,2}.

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. These types of metal phosphates possess structural hydroxyl protons that are responsible for their ion-exchange behaviour. The number of protons present in the structural hydroxyl groups indicates the potentiality of TMA salts to exhibit as solid state proton conductor. 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 crystallinity⁶. Alberti and coworkers have shown that the protons on the surface conduct a thousand times faster than protons through bulk⁷.

The diffusion and proton transport mechanism in crystalline zirconium phosphate and titanium phosphate has been reported by various workers^{7–16}. An early study on zirconium phosphate with varying crystallinity depicts the importance of degree of crystallinity in the proton conduction^{7,17,18}. Stenina and

coworkers have reported the conduction behaviour of tin phosphate¹⁹. Literature survey reveals that most of the proton transport properties carried out in case of zirconium phosphate and titanium phosphate and not many report in the case of tin phosphate. Mixed materials of class of TMA salts (compounds containing two different cations and given anion or two different anions and a cation) have been widely investigated as ion exchangers and showed enhanced ion exchange properties in comparison to their single salt counterparts.

We therefore considered it worthwhile to study the proton transport properties of mixed material of M(IV) phosphates of the class of TMA salts tin zirconium phosphate, and compare their proton conduction behaviour with its single salts counter parts such as zirconium phosphate and tin phosphate. These materials have been characterized for elemental analysis (ICP-AES), thermal analysis (TGA), 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 30–80°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 on zirconium phosphate (ZrP), tin phosphate (SnP) and tin zirconium phosphate (SnZrP).

Material and Methods

Reagents: Zirconium oxy chloride (Loba Chemie, India), stannic chloride (E.Merck), and sodium dihydrogen phosphate (E.Merck) were used for the synthesis of the exchangers. All other reagents and chemicals used were of analytical grade.

Apparatus and instruments: A glass column was used for column operations. ELICO LI613 pH meter was used for pH measurements. Chemical composition was determined by ICP-AES method using ICP-AE Spectrometer Thermo Electron IRIS Intrepid II. FT-IR Spectrometer model Thermo-Nicolet Avtar 370 for IR studies, X-ray Diffractometer Bruker AXS D8 Advance for X-ray diffraction studies were used. UV Solatron (1255B FRA FI1287 Electrochemical Phase) impedance analyzer was used for conductivity measurements. Perkin Elmer Diamond TG/DTA Analysis System for thermal analysis and an electric shaking machine for shaking were also used.

Synthesis of the exchanger: Zirconium phosphate: Zirconium oxy chloride solution (0.05 M) and sodium dihydrogen phosphate solution (0.05 M) were prepared. Sodium dihydrogen phosphate solution was added to solution of zirconium oxy chloride with constant stirring in different volume ratios so that final volume was 500 mL. The resulting gel was kept for 24 hrs at room temperature maintaining the pH at 1 with 1.0 M NaOH/1.0 M HNO₃. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H⁺ form by treating with 1.0 M HNO₃ for 24 hrs with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60- 100 mesh.

Tin phosphate: Stannic chloride solution (0.05 M) and sodium dihydrogen phosphate solution (0.05 M) were prepared. Sodium dihydrogen phosphate solution was added to stannic chloride solution with constant stirring in different volume ratios so that final volume was 500 mL. The resulting gel was kept for 24 hrs at room temperature maintaining the pH at 1 with 1.0 M NaOH/1.0 M HNO₃. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H⁺ form by treating with 1.0 M HNO₃ for 24 hrs with occasional shaking and intermittent changing of acid. It was then washed with deionized water to remove the excess acid, dried and sieved to obtain particles of 60- 100 mesh.

Tin zirconium phosphate: Zirconium oxy chloride solution (0.05 M), stannic chloride solution (0.05 M) and sodium dihydrogen phosphate solution (0.05 M) were prepared. Sodium dihydrogen phosphate solution was added to mixtures of zirconium oxy chloride solution and stannic chloride solution with constant stirring in different volume ratios so that final volume was 500 mL. The resulting gel was kept for 24 hrs at room temperature maintaining the pH at 1 with 1.0 M NaOH/1.0 M HNO₃. It was then filtered, washed with deionized water and dried. The exchanger was then converted into the H⁺ form by treating with 1.0 M HNO₃ for 24 hrs with occasional shaking and intermittent changing of acid. It was then washed with

deionized water to remove the excess acid, dried and sieved to obtain particles of 60- 100 mesh.

Ion exchange capacity (IEC): The ion exchange capacity of the material was determined by column method. 1.0 g of the exchanger in H⁺ form was taken in a glass column of 1.1 cm diameter. The H⁺ ions were eluted by percolating 100 mL of 1.0 M NaCl solution. The effluent was collected and titrated against standard sodium hydroxide solution. The ion exchange capacity, IEC in meqg⁻¹ was calculated using the formula,

$$IEC = \frac{aV}{w}$$

Where, *a* is the molarity, *v* is the volume of alkali used during titration and, *w* is the weight of the exchanger taken²⁰.

Chemical resistivity: The chemical resistivity of the sample was assessed in mineral acids like HCl, HNO₃ and H₂SO₄, bases like NaOH and KOH and organic solvents like acetic acid, acetone, ethanol and diethyl ether. For this, 0.5 g of the sample was soaked in 50 mL of different solvents, kept for 24 hrs and changes in colour, nature and weight of the sample were noted.

Effect of temperature on IEC: The effect of temperature on ion exchange capacity was studied by heating several 1.0 g samples of the exchanger at different temperatures for 2 hrs in an air oven and Na⁺ ion exchange capacity in meqg⁻¹ was determined by the column method after cooling them to room temperature.

pH titrations: Topp and Pepper method²¹ was used for pH titrations using NaOH/NaCl, KOH/KCl, systems. 0.5 g of exchanger was equilibrated with varying amounts of metal chloride and metal hydroxide solutions. At equilibrium (after equilibration), pH of the solutions was measured and plotted against the milliequivalents of OH⁻ added.

Distribution coefficient (K_d): Distribution studies were carried out for various metal ions in demineralized water by batch process. In this method, 0.1 g of the exchanger (60-100 mesh) was equilibrated with 20 mL of the metal ion solutions for 24 hrs at room temperature. The metal ion concentrations before and after sorption were determined spectrophotometrically/complexometric titration against standard EDTA solution. In the complexometric method, the K_d values were calculated using the formula,

$$K_d = \frac{(I - F)}{F} \times \frac{V}{W}$$

Where, I is the initial volume of EDTA used, F is the final volume of EDTA used, V is the volume of the metal ion solution (mL) and W is the weight of the exchanger²⁰.

Conductivity measurements: The protonic conductivities of the materials were measured using pellets of 13 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 1255B FRA FI1287 Electrochemical Phase impedance analyser over a

frequency range of 5 Hz to 1 MHz at a signal level below 1 V, interfaced to a minicomputer for data collection. The measurements were made in the temperature range 30–80 °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.

Results and Discussion

The exchanger, synthesized ZrP obtained as white solid and SnP and SnZrP obtained as colourless transparent solid. It exhibit good chemical stability in water, acetic acid, 2.0 M NaOH, 2.0 M KOH, 15 M HNO₃, 10 M HCl and 20 M H₂SO₄. Elemental analysis by ICP-AES revealed tin, zirconium, phosphorous ratio of 1: 1: 2.9 for SnZrP and ratio of M:P for SnP and ZrP is 1: 3 and 2:2.9 respectively.

FTIR spectra of SnZrP, SnP and ZrP (figure 1a) showed a broad band in the region ~3444 cm⁻¹ which was assigned to symmetric and asymmetric–OH stretching, while the band at ~1633 cm⁻¹ was attributed to H-O-H bending. A band in the region ~1039 cm⁻¹ was attributed to P=O stretching. A band at ~1384 cm⁻¹ was an evidence for the presence of δ (POH). This indicated the presence of structural hydroxyl protons in SnZrP, which was more evident from the obtained IEC values, whereas in the case of SnP and ZrP there was no prominent peak in that region. Bands at ~615 cm⁻¹ and ~516 cm⁻¹ may be due to the presence of Zr-O and Sn-O bonds.

There was no prominent peak in the x-ray diffractograms of ZrP and SnP which suggested its amorphous nature of the materials whereas some broad peaks were observed in the x-ray diffractogram of SnZrP which suggest its semicrystalline nature of the material (figure 1b).

The thermogram of SnZrP cation exchanger (figure 1c) showed that the weight loss (about 20%) of the ion exchanger up to ~147 °C is due to the removal of free external water molecules²². Further, a gradual loss of mass (about 8%) up to 500 °C may be due to the condensation of hydroxyl groups. Above 500 °C, the gradual loss in weight (about 3%) up to 800 °C was due to the removal of structural water. There was no sudden decrease in the weight loss which indicated that there was no structural change of this material. The percent weight loss with increasing temperature observed by TGA curve for SnZrP was also supported by the thermal stability experiment Figure 1d. The nature of the degradation of SnP and ZrP was similar like SnZrP but the percentage of weight loss was different for three materials. The percentage of weight loss was in the order ZrP > SnP > SnZrP.

Na⁺ ion exchange capacity have been evaluated at room temperature and found to be ZrP, 0.8 meqg⁻¹; SnP, 1.0 meqg⁻¹ and SnZrP, 1.15 meqg⁻¹. It was observed that on heating at different temperatures for 2 hrs, the ion exchange capacity of the dried sample material, SnZrP was not changed as the

temperature increased up to 300°C as shown in figure 1d. Above 300 °C there was slight decrease in ion exchange capacity. However, in respect to ion exchange capacity, this material was found to possess higher thermal stability as the sample maintained 100% of the ion-exchange capacity up to 300 °C. In the case of SnP and ZrP ion exchange capacity decreased in the temperature above 100 °C and the variation of ion exchange capacity of these material with respect to temperature was illustrated in the figure 1d.

All the three materials showed only one inflection point in the pH titration curves which confirm the monofunctional behaviour of the materials (figure 2a, 2b and 2c). pH value of SnZrP, SnP and ZrP when no OH⁻ ions were added to the system is that 3.10, 3.30 and 3.70 which suggest the high acid nature of the materials.

Distribution Studies: In order to explore the potentiality of the newly synthesized cation exchange material in the separation of metal ions, distribution studies for metal ions were performed in different solvent systems table 1. The distribution studies of metal ions showed that the exchanger had very high affinity towards Pb^{II} and Cu^{II} ions in comparison to other metal ions studied. The selectivity was found to be in the order Pb^{II}> Cu^{II}> Zn^{II}> Ca^{II}> Mn^{II}> Mg^{II}> Ni^{II}> Co^{II}> Th^{IV}> Hg^{II}> Bi^{III}. The effect of electrolyte concentrations on distribution coefficients showed that the value decreases with increase in electrolyte concentrations.

Impedance measurements: In complex impedance plots for ZrP, SnP and SnZrP at 303 K, impedance spectra consist of a single depressed semicircle. Sample resistance (R) was measured by extrapolation of high frequency arc crossing to Z axis. Proton conductivity was measured using eq, $\sigma = l/RA$, where σ is conductivity, l is sample thickness and A is electrode area (cm²). Arrhenius plot (log σT vs 1/T) are represented for ZrP, SnP, and SnZrP. Activation energy for each sample was calculated using arrhenius equation [$\sigma = \sigma_0 \exp(-E_a/kT)$] where k is Boltzman constant and T is temperature.

Proton transport includes, transport of proton and any assembly that carries protons. Transport of protons between relatively stationary host anions is termed Grothus or free proton mechanism, which requires close proximity of water molecules, that are firmly held but able to rotate. The low value of E_a depicts that it depends entirely on reorientation step. Transport by other species is called as vehicle mechanism. Here polyatomic ion migrates as entities through bulk materials. Hence E_a is expected to be high. Vehicle mechanism is most frequently observed in aqueous solution and other liquid/melts. Vehicle mechanism is usually restricted to materials with open structures to allow passage of large ions and molecules in solids. The compounds which contain less amount of water would be expected to conduct by vehicle mechanism, in this a nucleophilic group acts as a proton carrier.

Conductivity measured in the range 30–80°C for ZrP, SnP and SnZrP is presented in table 2. As calculated from the electron

impedance spectra, sample ZrP, SnP and SnZrP achieved a proton conductivity of 1.25×10^{-4} , 1.35×10^{-4} and 1.47×10^{-4} S cm^{-1} respectively at 90% relative humidity. Arrhenius plots are presented in figures 3a–c. For all the three materials linearity is observed in the temperature range 30–80°C. From specific conductance for ZrP, SnP, and SnZrP, it is observed that increases with increasing temperature. This fact is also supported by the study of heating effect on IEC, suggesting mechanism of transportation to be grotthus type, where conductivity depends on water ability located on the surface to rotate and participate. Further results are also in agreement with the suggestion that the protons are not able to diffuse along an anhydrous surface, where spacing of –OH groups is too high. Although all the conductivities shown here increase with

increasing temperature, the absolute values of the conductivity clearly vary with each other. The proton migration is dominantly through the Grotthuss mechanism. In this mechanism, the proton transport is mainly caused by the hopping of the protons from one water molecule to another through tunnelling mechanism. To a smaller extent, the proton forms hydrogen bond with the water molecules and exits as H_3O^+ and diffusion of H_3O^+ ions enhances the proton transport. The increase in temperature strongly affects both mechanisms; hopping as well as diffusion becomes faster. The activation energy for the proton migration was calculated and found to be 23 kJmol^{-1} , which is in the range of activation energy for Grotthuss mechanism.

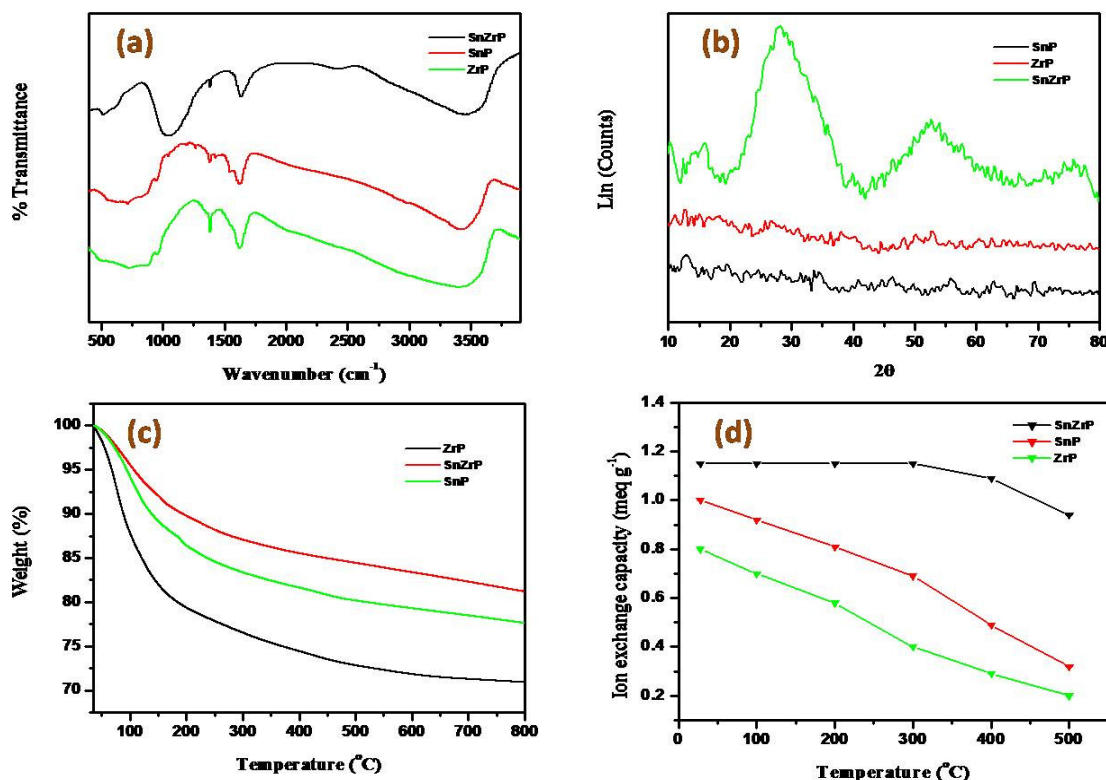


Figure-1

(1a) FTIR spectra of ZrP, SnP and SnZrP, (1b) XRD of ZrP, SnP, and SnZrP, (1c) TGA of ZrP, SnP and SnZrP, and (1d) Effect of temperature on ion exchange capacity of ZrP, SnP, and SnZrP

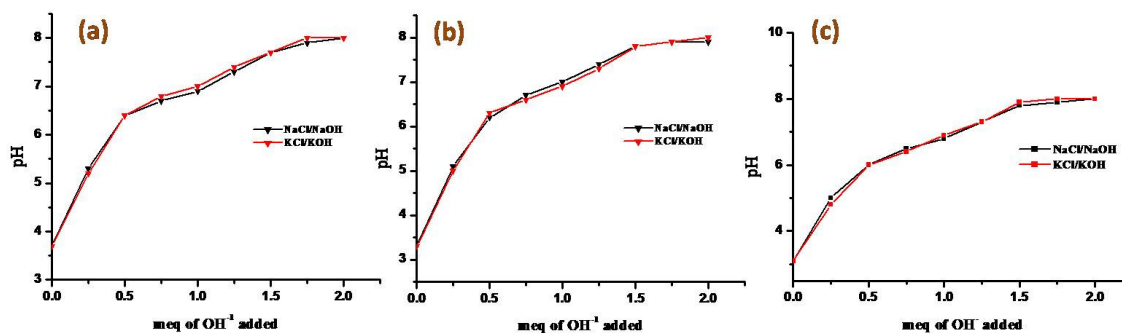


Figure-2

pH titration curve for (a) ZrP, (b) SnP and (c) SnZrP

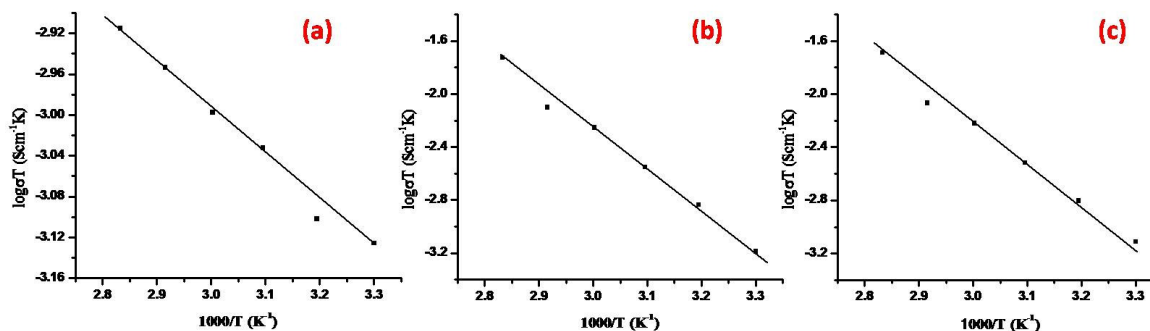


Figure-3
Arrhenius plot for (a) ZrP, (b) SnP and (c) SnZrP in the temperature range of 30-80°C

Table-1
K_d values of various metal ions in different electrolyte

Metal ions	Effect of electrolyte concentration						
	DMW	0.001M HNO ₃	0.01M HNO ₃	0.1M HNO ₃	0.001M NH ₄ NO ₃	0.01M NH ₄ NO ₃	0.1M NH ₄ NO ₃
Pb ^{II}	896.5	665.4	423.9	212.1	720.1	439.2	187.9
Zn ^{II}	213.0	100.0	56.7	4.5	210.0	87.9	23.1
Mn ^{II}	159.4	134.1	98.6	42.1	123.1	67.3	21.2
Ni ^{II}	117.6	100.3	52.1	19.1	99.9	34.0	9.9
Hg ^{II}	60.0	32.0	20.0	8.0	48.0	18.0	2.1
Ca ^{II}	180.1	176.0	98.2	34.6	166.0	67.3	12.0
Co ^{II}	108.7	87.8	42.1	11.1	96.2	45.0	10.0
Cu ^{II}	663.9	611.0	567.0	239.3	659.1	589.1	300.0
Bi ^{III}	45.0	32.0	1.9	NA	30.1	12.0	NA
Mg ^{II}	132.4	129.0	67.3	21.0	130.0	87.2	43.0
Th ^{IV}	72.1	62.0	20.9	4.6	63.0	15.9	NA

NA: No noticeable adsorption

Table-2
Specific conductance of ZrP, SnP and SnZrP at various temperatures

Temperature (K)	Specific Conductivity σ (Scm ⁻¹)		
	ZrP	SnP	SnZrP
303	1.25×10 ⁻⁴	1.35×10 ⁻⁴	1.47×10 ⁻⁴
313	1.35×10 ⁻⁴	1.88×10 ⁻⁴	1.94×10 ⁻⁴
323	1.44×10 ⁻⁴	2.42×10 ⁻⁴	2.49×10 ⁻⁴
333	1.52×10 ⁻⁴	3.15×10 ⁻⁴	3.26×10 ⁻⁴
343	1.54×10 ⁻⁴	3.56×10 ⁻⁴	3.69×10 ⁻⁴
353	1.60×10 ⁻⁴	5.04×10 ⁻⁴	5.24×10 ⁻⁴
Ea/kcalmol ⁻¹	0.24	5.52	5.50

The higher conductivity value of SnZrP compared with SnP and ZrP can correlate with the IEC value of three materials. Higher IEC values indicate more exchangeable protons and hence more available conducting protons. It is agreement with the pH value of the exchangers. Higher value of σ_{SnP} than σ_{ZrP} could be explained due to acidity of cation, which is related to ions size (ionic radii for Sn⁴⁺ is 0.69 Å and Zr⁴⁺ is 0.86 Å) and charge. Since, both ZrP and SnP bear a common anion with smaller ionic radii and therefore high charge density, exhibits greater

proton conductivity. σ_{SnZrP} 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 ($7.49 \times 10^{-5} \text{ Scm}^{-1}$) compared to its single counterparts zirconium phosphate ($2.63 \times 10^{-6} \text{ Scm}^{-1}$) and zirconium molybdate ($1.08 \times 10^{-5} \text{ Scm}^{-1}$) has also been reported²³.

The energy of activation (E_a, kcalmol⁻¹) values observed are 0.24 for ZrP, 5.52 for SnP and 5.50 for SnZrP. Almost similar values of E_a for SnP and SnZrP could be attributed to almost same order of magnitude of conductance in the range 30–80 °C. The activation energy at saturated humidity was less which means the lower energy barrier for the proton conduction. Therefore, both observations indicates that water molecule adsorbed by the mixed material promotes proton conduction to a high degree. This is mainly due to the adsorbed water molecules to form the proton channels in the interlayers of inorganic matrix for the smooth transfer of protons. E_a values follows the order ZrP < SnZrP < SnP however σ values follows the order

ZrP < SnP < SnZrP. It shows that it has no correlation with the order of conductivity of the exchanger presented. The materials SnP, ZrP and SnZrP synthesized in our lab have higher specific conductance compared with other materials discussed in the previous literatures.

Conclusion

Thermally stable semi-crystalline tin zirconium phosphate cation exchanger can be operated at elevated temperature up to 300 °C without any loss in its ion exchange capacity (1.15 meqg⁻¹). It shows selective sorption for Pb^{II} and Cu^{II}. It exhibits enhanced proton conductance (1.47×10⁻⁴ Scm⁻¹) compared to its single salt counter parts, tin phosphate and zirconium phosphate. The material has higher proton conductivity compared to other materials already reported; hence it will be a promising candidate in the field of electrochemical devices.

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