Transport properties in a mixed inorganic ion exchanger—zirconium phosphomolybdate—in comparison to its single salt counterparts

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Abstract. Amorphous inorganic ion exchangers zirconium phosphate, zirconium molybdate and zirconium phosphomolybdate have been prepared and characterized by elemental analysis, TGA, FTIR and surface area measurements. The protonic conductivity in these materials were determined at various temperatures and compared. It was found that the mixed material zirconium phosphomolybdate showed maximum conductivity at all temperatures.

Keywords. Inorganic ion exchangers; protonic conduction; specific conductance.

1. Introduction

In recent years there has been intense research aimed at discovering new proton conductors and the mechanism of conduction in solids. This renewed activity has been driven by the potential use of such compounds in fuel cells, sensors, water electrolysis units and other electrochemical devices.

Inorganic ion exchangers have been extensively studied in the field of separation science and catalysis. But of late attempt has been made to study the transport properties of these materials (Alberti *et al* 1978, 1979). These materials have the property of protonic conduction and the mechanism of diffusion and ionic transport in crystalline α -zirconium phosphate has been studied in detail (Alberti *et al* 1979). They have the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$ where $M = Zr, Ti, Ce$ etc. and $X = P, As, Sb$ etc. The number of water molecules depend upon the method of preparation, drying conditions etc. They have 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 (Clearfield and Berman 1981).

It has been proved that specific conductance of inorganic ion exchangers increase with decreasing crystallinity, which is in agreement with the expectation that the ionic conductance of a solid increases with increase in the number of defects in the crystalline surface (Alberti *et al* 1978). Also it has been found that amorphous materials have more surface area than that of crystalline materials (Clearfield and Berman 1981).

Since until now only single salts, especially α -zirconium phosphate, was studied in detail for the transport properties, it was thought of interest to study the protonic conduction in a mixed material. In the present study, we have prepared and characterized a typical mixed material, amorphous zirconium phosphomolybdate, its transport properties investigated and compared with that of the corresponding amorphous single salts, zirconium phosphate and zirconium molybdate.

2. Experimental

2.1 Preparation of the materials

Zirconium phosphate (ZrP) and zirconium molybdate (ZrMo) were prepared by methods reported earlier (Beena and Chudasama 1995; Shivanekar and Chudasama 1990). Zirconium phosphomolybdate (ZrPMo) was prepared by mixing zirconyl chloride, trisodium orthophosphate and ammonium molybdate in 1:1:1 mole ratio with continuous stirring. The gel thus obtained was kept at room temperature overnight, filtered, washed with conductivity water and dried at 45°C in an oven.

The materials after drying were sized by sieving and converted to the hydrogen form by immersion in 1M HCl, the acid being intermittently replaced, washed till free from the acid and dried again at 45°C and stored at a relative humidity of ~ 80%.

2.2 Elemental analysis

The samples have been analysed for zirconium, molybdenum and phosphorus. Zirconium, molybdenum and phosphorus were determined gravimetrically as zirconium oxide (by cupferron method), molybdenum oxide (by α -benzoin oxime method) and phosphorus as magnesium pyrophosphate respectively.

2.3 Thermal analysis

The thermogravimetric analysis of samples were performed on a Shimadzu DT = 30 thermal analyzer, at a heating rate of 10°C/min.

2.4 FTIR spectra

FTIR spectra of the samples were performed using a KBr-wafer on a Perkin-Elmer FTIR model 1720 $\times$ with Epson Hi 80 Printer/Plotter.

2.5 Surface area measurements

The surface area of the materials were measured by the nitrogen adsorption BET method and recorded on a Carlo-Erba Sorptomatic series – 1800 at – 196°C.

2.6 Determination of ion exchange capacity (i.e.c.)

The i.e.c. of the materials was determined as usual by the column method, 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.

2.7 Conductivity measurements

The electrical conductivity of the solids were measured using pellets of 10 mm diameter and 1.5–2 mm thickness with a relative humidity of ~ 80%. The opposite sides of the

Figure 1. Complex impedance diagram for ZrPMo at 25°C.

pellets were coated with conducting silver paste to ensure good electrical contacts. Impedance measurements were taken by using SOLARTON SI 1260 impedance analyser, over a frequency range of 10 Hz to 32 MHz at a signal level below 1 V, interfaced to a mini computer for data collection. In all cases, since the impedance plots of the materials consist of single depressed semi circle (figure 1), the pellet conductivity was calculated by arc extrapolation to the real axis, taking into account the geometrical sizes of the pellets. The measurements were made in the temperature range of 25–150°C.

3. Results and discussion

All the three materials ZrP, ZrMo, and ZrPMo obtained were white, hard and amorphous in nature. The materials were found to be stable in dilute mineral acids like HCl, H_2SO_4 , HNO_3 and bases like NaOH and KOH up to 4M concentration, and in ethanol, acetic acid and 1M salt solutions.

Chemical analyses indicate the composition of ZrP, ZrMo and ZrPMo to be 1:2, 1:1 and 1:1:1 respectively. Based on these the formula proposed for these compounds are $\text{ZrO}_2 \cdot \text{P}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$, $\text{ZrO}_2 \cdot \text{MoO}_4 \cdot 15\text{H}_2\text{O}$ and $\text{ZrO}_2 \cdot 1/2 \text{P}_2\text{O}_5 \cdot \text{MoO}_4 \cdot 15\text{H}_2\text{O}$ for ZrP, ZrMo and ZrPMo respectively. The number of water molecules were determined from the thermograms of the samples using Alberti's formula (Alberti and Torracca 1968). The Na^+ exchange capacities of ZrP, ZrMo and ZrPMo were found to be 1.01, 1.02 and 1.10 meq/g respectively.

Thermograms of all the materials showed sharp changes within the temperature range of 80–120°C corresponding to the loss of external water molecules after which slow change in weight was observed till 600°C. This may be due to the condensation of structural hydroxyl groups.

FTIR spectra of all the materials showed broad bands in the region $\sim 3400 \text{ cm}^{-1}$. This was attributed to the asymmetric and symmetric hydroxo –OH and aquo –OH stretches. A sharp medium band at $\sim 1620 \text{ cm}^{-1}$ was also observed in all the cases which was attributed to the aquo–(H–O–H) bending. In addition to these bands the FTIR spectrum of ZrMo showed a broad shoulder at 935 cm^{-1} which was attributed to the presence of zirconium oxygen stretching. FTIR spectrum of ZrP showed a sharp medium band at $\sim 970 \text{ cm}^{-1}$ and a broad shoulder at $\sim 1120 \text{ cm}^{-1}$ indicating the

Table 1. Variation of specific conductance (σ) with temperature.

Temp. (°C)	$\sigma(\Omega\text{ cm})^{-1}$		
	ZrP	ZrMo	ZrPMo
25	2.78×10^{-6}	1.12×10^{-5}	1.96×10^{-4}
30	2.63×10^{-6}	1.08×10^{-5}	7.49×10^{-5}
60	7.28×10^{-7}	1.23×10^{-6}	5.87×10^{-5}
90	1.36×10^{-7}	5.20×10^{-7}	1.41×10^{-6}
120	9.27×10^{-8}	3.39×10^{-8}	6.37×10^{-7}
150	3.10×10^{-8}	1.36×10^{-8}	1.77×10^{-7}

presence of asymmetric and symmetric phosphate vibrations. A weak shoulder at 530 cm^{-1} may be attributed to the zirconium–oxygen stretching. The FTIR spectrum of ZrPMo shows two broad shoulders at $\sim 935\text{ cm}^{-1}$ and $\sim 1120\text{ cm}^{-1}$ indicating the presence of zirconium–oxygen stretching and symmetric phosphate vibrations.

Surface area of ZrP, ZrMo and ZrPMo are $48\text{ m}^2/\text{g}$, $25\text{ m}^2/\text{g}$ and $55\text{ m}^2/\text{g}$ respectively.

The presence of protons able to be exchanged and hence able to diffuse through the interspaces, make these materials protonic conductors. It is seen that the value of specific conductivity (σ) of ZrPMo at 25°C is $1.96 \times 10^{-4}\text{ }\Omega^{-1}\text{ cm}^{-1}$ whereas for the corresponding single salts ZrP and ZrMo the value of σ is 2.78×10^{-6} and $1.12 \times 10^{-5}\text{ }\Omega^{-1}\text{ cm}^{-1}$ respectively. For all these materials specific conductivity decreases with increasing temperature (table 1). This is due to the gradual loss of water of hydration as well as the condensation of structural –OH groups. This also suggests the mechanism of transportation as a Grothus type (Clearfield 1988) where the conductivity depends on the ability of water located on the surface to rotate and participate in a Grothus type transport. This also agrees with the suggestion that protons are not able to diffuse along an anhydrous surface where the spacing of the –OH groups is high (Alberti *et al* 1989). Also the fact that the loss of protons resulting from hydroxyl condensation causes a considerable decrease in conductivity indicates that the electrical conduction is protonic also.

The high value of specific conductance in ZrPMo which is of the order of $10^{-4}\text{ }\Omega^{-1}\text{ cm}^{-1}$ is comparable to that of amorphous polymer electrolyte blends prepared by blending poly (propyleneglycol) with poly (ethylene oxide) –NaI electrolyte (Paulmer and Kulkarni 1992). This high value of specific conductance in ZrPMo as compared to the single salts ZrP and ZrMo may be because of its comparatively large surface area. It has been shown earlier in zirconium phosphate that conductivity increases with increase in surface area (Alberti *et al* 1978). The value of σ in ZrPMo is only one order less than that of pellicular zirconium phosphate and colloidal dispersion of α -ZrP ($\sigma \sim 10^{-3}\text{ }\Omega^{-1}\text{ cm}^{-1}$) where the preparation methods are rather difficult (Alberti *et al* 1989). Thus ZrPMo with its easy method of preparation and relatively high value of specific conductance offers as a promising material for solid electrolyte applications.

4. Conclusions

Zirconium phosphomolybdate exhibits better transport properties than the corresponding single salts prepared under the same conditions. The conductivity is essentially

dependent on the surface water of hydration. ZrPMo with its easy method of preparation and comparatively high value of specific conductance is a promising material for solid electrolyte applications.

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