Ion transport in some solid state proton conducting composites studied from volta cell e.m.f. and complex impedance spectroscopy

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Abstract. Proton conducting composites of heteropolyacid hydrates (phosphomolybdic acid $H_3PMo_{12}O_{40}\cdot nH_2O$, PMA; phosphotungstic acid $H_3PW_{12}O_{40}\cdot nH_2O$, PTA) and salt hydrate like $NiCl_2\cdot 6H_2O$ were prepared with insulating Al_2O_3 as dispersoid. The ionic conductivity peaks at two concentrations of Al_2O_3 indicating two percolation thresholds for proton conduction. Two separate experiments were carried out to check the existence of such percolation thresholds viz. the volta battery experiment involving the measurement of e.m.f. of an electrochemical cell with composites of different compositions used as electrolyte and the composition vs conductivity measured by the complex impedance spectroscopy. The presence of two maxima has been attributed to two different percolation thresholds for the two possible mobile protonic species H^+ (H_3O^+) and OH^- arising from the hydrates.

Keywords. Interface; ionic transport; composites.

1. Introduction

Solid state ionic materials are of great interest due to their potential applications in electrochemical devices like batteries, fuel cells, sensors, electrochromic devices etc (Chandra 1981; Laskar and Chandra 1989; Takahashi 1989). Many methods have been adopted to increase the conductivity of crystalline ionic solids. Heterogeneous doping or formation of composites is an effective method to improve the conductivity of ionic materials and conductivity enhancements of ~ 2–4 orders of magnitude have been reported (Liang 1973; Shahi and Wagner 1981; Maier 1987). In general, these are prepared by dispersing different insulating oxides like Al_2O_3, SiO_2, TiO_2, SnO_2, ZrO_2, etc into an ion conducting matrix. A large number of two-phase composite systems with various ion conducting species such as Li^+, Ag^+, Na^+, Cu^+, etc have been investigated (Maier 1995; Agrawal and Gupta 1998). The conductivity–composition isotherm showed a maximum corresponding to some optimum composition (termed as percolation threshold). However, proton conducting composites are not studied much. In the present work, proton conducting composites of acid/salt hydrates with insulating Al_2O_3 as the dispersoid have been prepared and studied. Our motivation of choosing the 'hydrates' as our proton conducting matrix has been the following: Most (Li^+, Ag^+, Na^+ etc) conducting composites used matrices with 'single' cation mobilities but in 'hydrates' there are two likely mobile species (H^+ or

H_3O^+) and OH^-. So, it would be interesting to check whether the composites with single mobile ion matrix and those with two types of mobile species behave differently or not. Further, the protonic species are likely to be more reactive for oxide dispersoids and hence may (or may not) give different interface behaviour.

Two different parameters which depend upon the ionic activity/mobility, characteristic of the solid electrolyte, have been measured: (i) conventional ionic conductivity measurement from impedance spectroscopy, (ii) e.m.f. or volta battery experiment involving galvanic cell anode (chemical potential μ_1) | electrolyte | cathode (chemical potential μ_2) as described below.
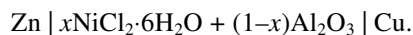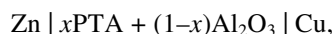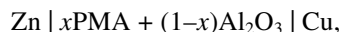
2. Experimental

2.1 *Preparation of composites*

The materials employed PMA, PTA (Alfa, Germany), $NiCl_2\cdot 6H_2O$ (Laboratory Rasayan, India) and Al_2O_3 (Aldrich, USA) were of analytical grade purity. Composites of different stoichiometric ratios of xPMA : $(1-x)$ Al_2O_3, xPTA : $(1-x)Al_2O_3$ and xNiCl$_2\cdot 6H_2O$: $(1-x)Al_2O_3$ (x : $1-x$ is weight ratio) systems were prepared by simple physical grinding method and pellets of 8 mm diameter were made at a pressure of 1 ton/cm^2.
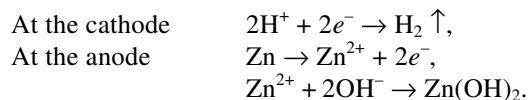
2.2 *Volta battery experiment for different composites*

Volta battery experiment (Tortet *et al* 1996) was carried out on the PMA : Al_2O_3, PTA : Al_2O_3 and $NiCl_2\cdot 6H_2O$:

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Al$_2$O$_3$ systems. A voltaic cell was assembled using Cu and Zn as electrodes. The cell configurations are given by

Zn | xPMA + (1–x)Al$_2$O$_3$ | Cu,

Zn | xPTA + (1–x)Al$_2$O$_3$ | Cu,

Zn | xNiCl$_2$·6H$_2$O + (1–x)Al$_2$O$_3$ | Cu.

The following reactions occur.

At the cathode	$2H^+ + 2e^- \rightarrow H_2 \uparrow$,
At the anode	$Zn \rightarrow Zn^{2+} + 2e^-$,
	$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$.

The generation of e.m.f. implies the motion of ionic species and the magnitude of voltaic e.m.f. obtained for different compositions is a qualitative measure of the relative protonic activity/conductivity. Note that the e.m.f. in such a study has to be measured with very high impedance voltmeter. We used Keithley (2000) multi-meter with an input impedance greater than 10 GΩ.

2.3 *Impedance spectroscopy*

The electrical conductivity of different compositions of the composites was evaluated from the impedance plots taken using Solartron Frequency Response Analyser (model 1250) with an electrochemical interface (1286) in the frequency range 65 Hz–65 kHz.

3. Results and discussion

The variation of voltaic e.m.f. with composition of xPMA + (1–x)Al$_2$O$_3$, xPTA + (1–x)Al$_2$O$_3$ and xNiCl$_2$·6H$_2$O + (1–x)Al$_2$O$_3$ are shown in figure 1. In the case of
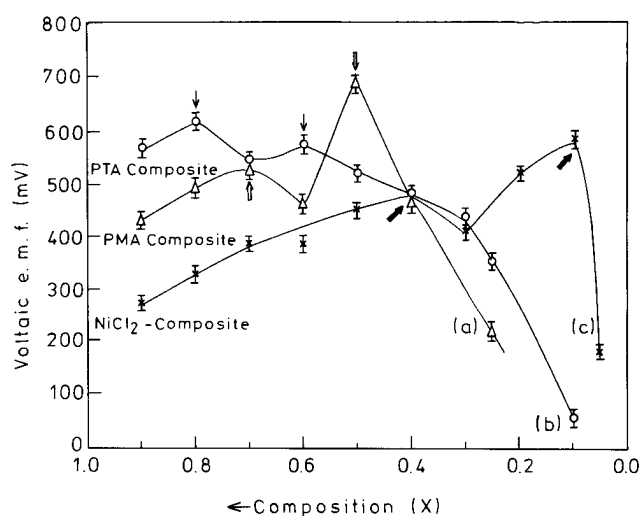
xPMA + (1–x)Al$_2$O$_3$, with the addition of Al$_2$O$_3$, the voltaic e.m.f. attains first maximum at $x = 0.7$. With further addition of Al$_2$O$_3$, the e.m.f. decreases. An interesting feature is an increase in e.m.f. with further increase of alumina content and a second maximum occurs at $x = 0.5$. The e.m.f. then drops due to the blocking effect of Al$_2$O$_3$. Similarly, in xPTA + (1–x)Al$_2$O$_3$, the e.m.f. attains first maximum at $x = 0.8$ followed by a second maximum at $x = 0.6$. In the case of xNiCl$_2$·6H$_2$O + (1–x)Al$_2$O$_3$, the e.m.f. vs composition exhibits two maxima at $x = 0.4$ and 0.1.

To check the authenticity and reliability of the results obtained from the volta battery experiment, we adopted two cross check routes as given below:

(I) We have chosen a well established composite system in which the ion conducting matrix consists of 'single' mobile species and the conductivity–composition isotherm has been earlier found to show only 'one' maximum by other workers. The system so chosen is AgI : αAl$_2$O$_3$ which is reported by Shahi and Wagner (1981) to show only one broad maximum in the conductivity–composition isotherm as shown in figure 2. We applied volta battery experiment to confirm the above conclusion using the electrochemical cell with the configuration Ag | AgI : αAl$_2$O$_3$ | C + I$_2$. The variation of the measured e.m.f. along with σ (reported by Shahi and Wagner 1981) as a function of composition are shown in figure 2. Both are surprisingly similar (i.e. occurrence of one broad maximum at 30 wt% of Al$_2$O$_3$). This gives credence to the volta battery experiment described above.

(II) We carried out the complex impedance spectroscopic studies of the proton conducting composites PMA : Al$_2$O$_3$, PTA : Al$_2$O$_3$ and NiCl$_2$·6H$_2$O : Al$_2$O$_3$ for

Figure 1. Variation of voltaic e.m.f. with composition of (a) xPMA : (1–x)Al$_2$O$_3$, (b) xPTA : (1–x)Al$_2$O$_3$ and (c) xNiCl$_2$·6H$_2$O : (1–x)Al$_2$O$_3$ composite systems.

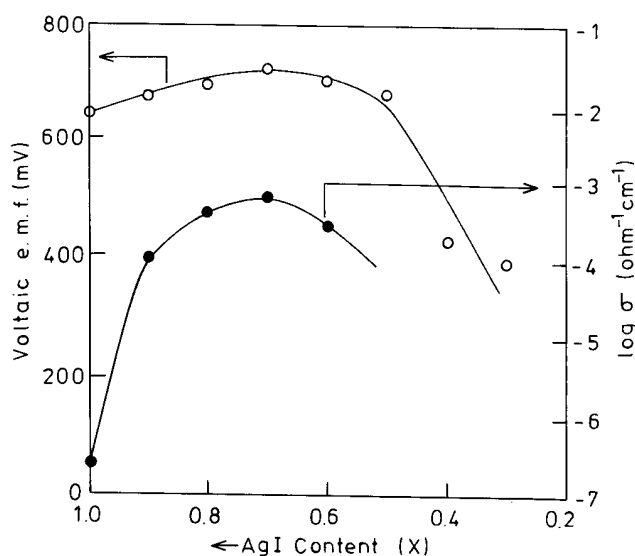**Figure 2.** Variation of voltaic e.m.f. with composition (O) of xAgI : (1–x)Al$_2$O$_3$ along with composition dependence of conductivity (●) (reported by Shahi and Wagner 1981).

which we had seen the occurrence of two maxima in the volta e.m.f. measurement. The electrical conductivity of different compositions of the composites was evaluated from the impedance plots. Typical impedance plots for a few composites for the case of PMA : Al_2O_3 are shown in figure 3. Qualitatively similar curves were obtained for all other composites also. The intercept of the high frequency arc on the Z'-axis gives the value of the bulk resistance, R_b, from which the bulk conductivity can be calculated knowing the dimensions of the sample. The variation of bulk electrical conductivity with composition of xPMA + $(1-x)Al_2O_3$, xPTA + $(1-x)Al_2O_3$ and xNiCl$_2$·6H$_2$O + $(1-x)Al_2O_3$ are shown in figure 4 (curves a–c, respectively). In the case of xPMA + $(1-x)Al_2O_3$ system, the conductivity attains first maximum at $x = 0.7$. With further increase of Al_2O_3 content, σ decreases. But, it has been found that the conductivity again starts increasing with further addition of alumina and a second maximum occurs at $x = 0.5$. Then, the conductivity drops. Similarly, in xPTA + $(1-x)Al_2O_3$, the conductivity–composition isotherm exhibits two maxima at $x = 0.8$ and 0.6. In xNiCl$_2$·6H$_2$O + $(1-x)Al_2O_3$, the first maximum in conductivity has been observed at $x = 0.4$ followed by a second maximum at $x = 0.1$. The conductivity–composition isotherm also indicates the presence of two maxima in

these composites confirming the volta battery studies described earlier in this paper.

Thus, the above two checks authenticate the existence of two maxima in the conductivity–composition isotherm. To find an explanation, we scanned the literature data and could find some systems like PEO–LiClO$_4$–αAl$_2$O$_3$ (Wieczorek *et al* 1996), PEO–LiClO$_4$–AlCl$_3$ (Wieczorek *et al* 1996), PEO–NaClO$_4$–SnO$_2$ (Thakur *et al* 1998), PEO–NaI–Na$_2$SiO$_3$ (Thakur *et al* 1999), PEO–NaI–SnO$_2$ (Hashmi *et al* 2000), RbNO$_3$–Al$_2$O$_3$ (Zhu and Mellander 1995) etc on which experimental data (actual data points) do show the probable existence of two peaks. However, it has been found that either due emphasis was not given or hypothetical explanations were offered by authors like two peaks are due to two mobile species Rb$^+$ and interfacial proton (H$^+$) conduction in RbNO$_3$: Al$_2$O$_3$ system (Zhu and Mellander 1995) or it may be due to various acid-base reactions occurring at the interface (Wieczorek *et al* 1996).

From our above systematic and motivated studies, it appears that the existence of two percolation thresholds in a few composites needs careful consideration. We consider the following tentative models to find a qualitative explanation for the occurrence of two maxima in the e.m.f. and σ vs composition studies:
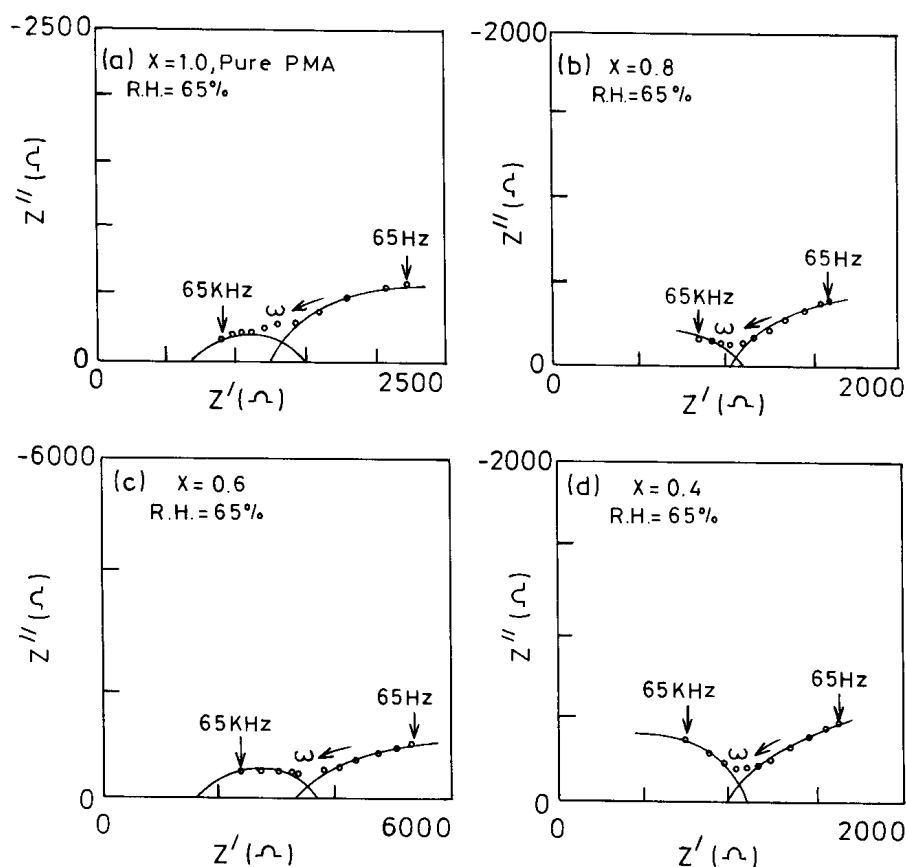

Figure 3. Typical room temperature complex impedance plots for a few compositions of xPMA + $(1-x)$ Al$_2$O$_3$ composite system.
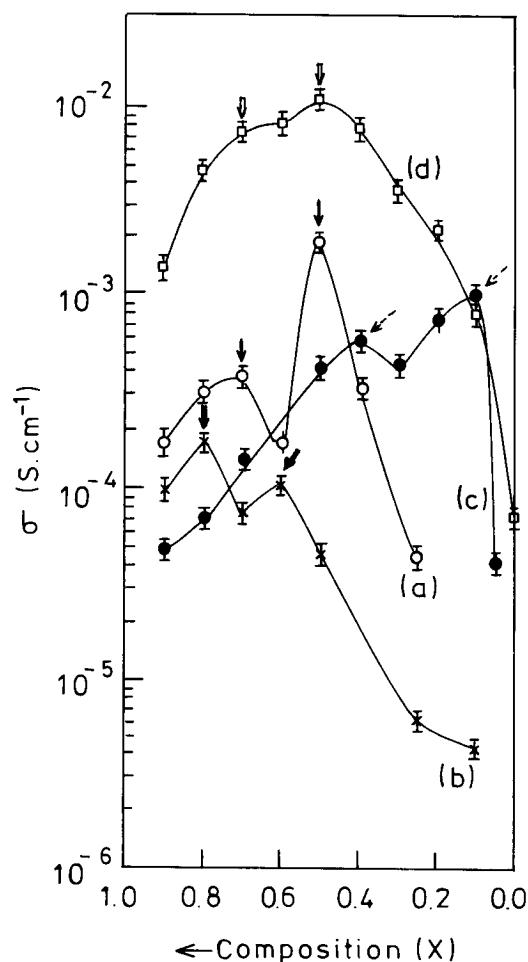
Figure 4. Composition dependence of room temperature bulk conductivity of (a) xPMA : $(1-x)$Al$_2$O$_3$, (b) xPTA : $(1-x)$Al$_2$O$_3$, (c) xNiCl$_2$·6H$_2$O : $(1-x)$Al$_2$O$_3$ and (d) xPTA : $(1-x)$Al$_2$(SO$_4$)$_3$· 16H$_2$O composite systems.

(I) The ion conducting matrix possibly consists of two types of mobile species (H$^+$/H$_3$O$^+$ and OH$^-$) and the two types of species follow different thresholds and the resultant of the two gives rise to two maxima. The presence of both cations and anions (H$^+$/H$_3$O$^+$ or OH$^-$) as mobile species has been demonstrated from the coulometric studies for many proton conducting hydrates (Chandra *et al* 1986, 1989; Hashmi *et al* 1992). The mobility and interface percolation thresholds for the two mobile species may be different. This is schematically shown in figure 5. The net σ vs composition will obviously be the sum of the two percolation thresholds giving two maxima (Lakshmi and Chandra 2001) as observed by us in this paper.

(II) Alternatively, a new high conducting interface is getting formed at the PMA or PTA or NiCl$_2$: Al$_2$O$_3$ interface. Thus, two interface situations arise : PMA or PTA or NiCl$_2$: Al$_2$O$_3$ interface (type I) and new interface compound : Al$_2$O$_3$ interface (type II) giving rise to two maxima.
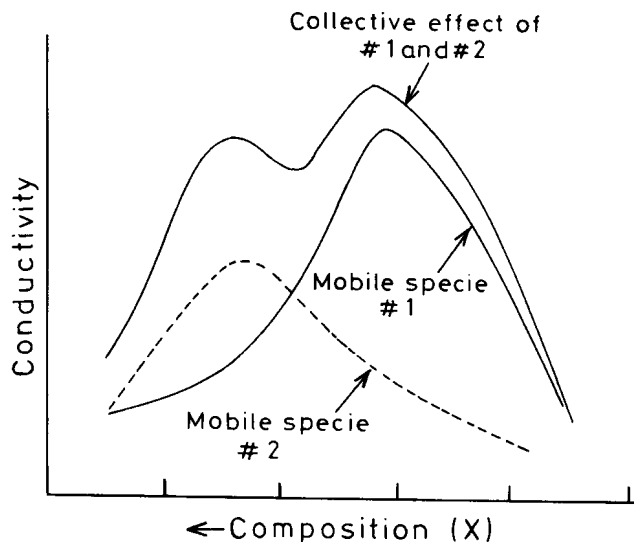

Figure 5. Schematic representation of modelled different percolation thresholds for two different mobile species, the collective effect of which may result in the σ vs composition plots.

Our present data cannot unequivocally establish either of the above models since two types of mobile species are possible and also a new interface compound has been detected (though a very small amount) from XRD and DTA/TGA studies (Lakshmi and Chandra 2001). However, we have also studied a proton conducting composite PTA : Al$_2$(SO$_4$)$_3$·16H$_2$O in which another proton conducting hydrate {Al$_2$(SO$_4$)$_3$·16H$_2$O} has been used as the dispersoid in which 'no evidence' for the formation of any new interface compound has been observed (Lakshmi and Chandra 2002) and yet the conductivity vs composition plot (figure 4, curve d) of xPTA + $(1-x)$Al$_2$(SO$_4$)$_3$· 16H$_2$O shows two maxima.

4. Conclusions

The protonic conductivity of PMA or PTA or NiCl$_2$· 6H$_2$O in the solid state is shown to increase on forming their composites with Al$_2$O$_3$. Two conductivity dependent measurements viz. volta battery and direct impedance spectroscopy, have been carried out and the σ vs composition plots show two maxima in variance with the existing literature data giving one maximum only. This has been assigned to the existence of two types of mobile ionic species (H$^+$/H$_3$O$^+$, OH$^-$) leading to two different percolation thresholds for conductivity enhancement.

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