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Evidence of failure of hopping model of ionic conductivity in phosphomolybdic acid studied by a.c. conductivity measurements

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The a.c. conductivity measurement has been used to probe into the possible conduction mechanisms (Vehicle or Hopping) in proton conducting acid hydrate Phosphomolybdic acid $H_3PO_4{\cdot}12MoO_3{\cdot}nH_2O$. The magnitude of hopping rate and its temperature dependence evaluated from a.c. conductivity data does not favour the hopping mechanism of conduction. The value of activation energy ($Ea \sim 0.76$ eV) supports the vehicle mechanism of ion transport. © *1999 Kluwer Academic Publishers*

1. Introduction

Solid state proton (H^+) conductors [1] belong to the general class of ionic solids (termed as fast ion conductors or solid electrolytes) which have high ionic conductivity. These materials have recently become important due to their application in H_2/O_2 fuel cells, batteries, gas sensors, etc. Salt/acid hydrates are included in one of the important groups of effective proton conductors studied for room temperature applications [2]. In these materials, the possible proton transport mechanism could be hopping (Grotthus) or vehicle. The hopping model for ion transport is quite successful for Ag^+, Cu^+, Li^+ etc. conductors, but for solid-state H^+ conductors it is still uncertain [3]. To determine the possible transport mechanism in ion/proton conductors it requires a combination of many experimental tools. The determination of carrier concentration and the hopping rate can be easily made possible by a.c. conductivity measurement. The advantage of this method [4] is it avoids the necessity of non-blocking electrodes that are required in the d.c. technique and to separate the grain boundary and the bulk phenomena in the polycrystalline materials. The study of a.c. conductivity measurement with dielectric response is one of the methods to gain insight into the hopping mechanism of the ionic conductors [5, 6].

In this paper we report the measurement of a.c. conductivity with frequency of a proton-conducting hydrate, the heteropolyacid hydrate phosphomolybdic acid ($H_3PO_4{\cdot}12MoO_3{\cdot}nH_2O$, abbreviated as PMA) and attempt to explain the proton transport in terms of the hopping transport and vehicle mechanisms.

2. Theory and methodology

The a.c. conductivity $\sigma(\omega)$ of hopping ion conductors is given by [7]

$$\sigma(\omega) = \sigma(0) + A\omega^n \tag{1}$$

where ω is the angular frequency, $\sigma(0)$ corresponds to the frequency independent plateau in $\sigma(\omega)$ which is called the d.c. conductivity of the material and A is a frequency-dependent parameter. This frequency-independent conductivity (d.c. conductivity) must be obtained at high frequency, where the electrode and the grain boundary effects are negligible in polycrystalline samples. Almond *et al.* [6] suggested a simple relationship between $\sigma(0)$ and the a.c. coefficient A for estimating the ion hopping rates from the a.c. conductivity measurements by assuming that these were related to the same basic dielectric response in the a.c. field. The dielectric constant χ' and the dielectric loss χ'' can be determined from the value of the measured capacitance and conductance at different frequencies (ω) as given under

$$\chi'(\omega) = C/C_0 \tag{2}$$

$$\chi''(\omega) = \sigma(\omega)/\varepsilon_0(\omega) \tag{3}$$

where C_0 is the geometrical capacitance of the sample electrode assembly without the sample. The values of dielectric constant have been found to be large for superionic materials because of their high conductivity [5].

In hopping ion conductors the dielectric loss χ'' is given by [8]

$$\chi''(\omega) = (\omega/\omega_p)^{n_1-1} + (\omega/\omega_p)^{n_2-1} \tag{4}$$

where ω_p is a characteristic frequency (which is a measure of hopping rate) and n_1 and n_2 are the slopes of log σ vs. log ω curve (Fig. lb) in the low and high frequency dispersion region. In special case, when $n_1 = 0$ (i.e. no low frequency dispersion) and $n_2 = n$ (Fig. 1a)

$$\sigma(\omega) = K\omega_p + K(\omega_p)^{1-n}\omega^n \tag{5}$$

where K is a constant of proportionality and ω_p is the hopping (frequency) rate. The hopping rate may be obtained by the Equation 5

$$\begin{aligned}\sigma(\omega) &= K\omega_p\big[1 + (\omega/\omega_p)^n\big] \\ &= \sigma(0)\big[1 + (\omega/\omega_p)^n\big].\end{aligned} \tag{6}$$

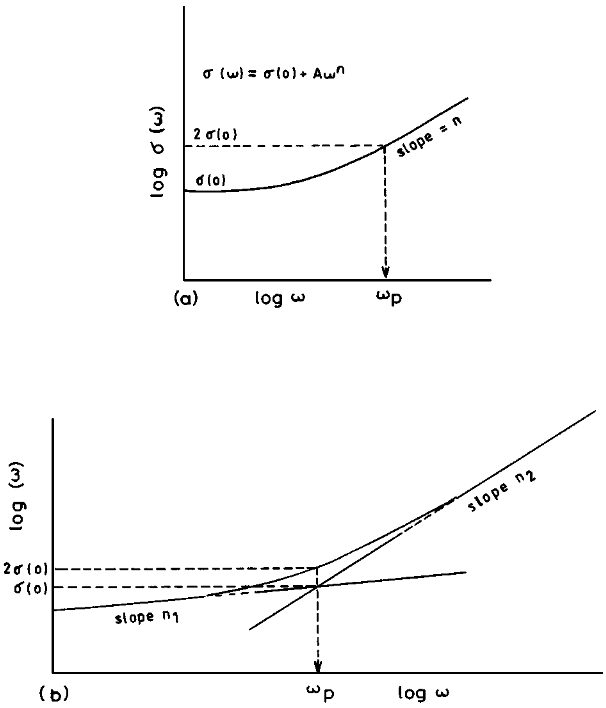

Figure 1 (a) Characteristic of a.c. conductivity of materials for which $n_1 = 0$ no low frequency dispersion. (b) Characteristic of a.c. conductivity of materials for which the two slopes n_1 and n_2 (low and high frequency dispersion) are present.

This expression helps in estimating the hopping rate. It is obvious from Equation 6 that at $\omega_p = \omega$

$$\sigma(\omega) = 2\sigma(0)$$

If we know $\sigma(0)$, we can locate $2\sigma(0)$ and the frequency corresponding to $2\sigma(0)$ shall give ω_p. Two situations arise, as has been discussed earlier: (i) $\log \sigma(\omega)$ vs. $\log \omega$ plot with one slope as in Fig. 1(a) or (ii) plot with two slopes as in Fig. 1(b). For the Fig. 1(a) case, conductivity values extrapolated to low frequencies give $\sigma(0)$. Then obtaining $2\sigma(0)$ and ω_p is a straightforward evaluation from Fig. 1(a). For a two slope (n_1 and n_2) system, the intersection of straight lines defining slopes n_1 and n_2 gives $\sigma(0)$, $2\sigma(0)$ and ω_p as is shown in Fig. 1(b).

3. Experimental

The material employed phosphomolybdic acid ($H_3PO_4 \cdot 12MoO_3 \cdot nH_2O$, Alfa, Germany) was of analytical grade purity. For the electrical conductivity measurements, pellets were prepared at a pressure of 1.0×10^3 Kg cm^{-2}. The diameter of the pellet was 0.8 cm. Graphite paste (Eltech Corp., India) was used for the electrodes. The a.c. conductivity was measured

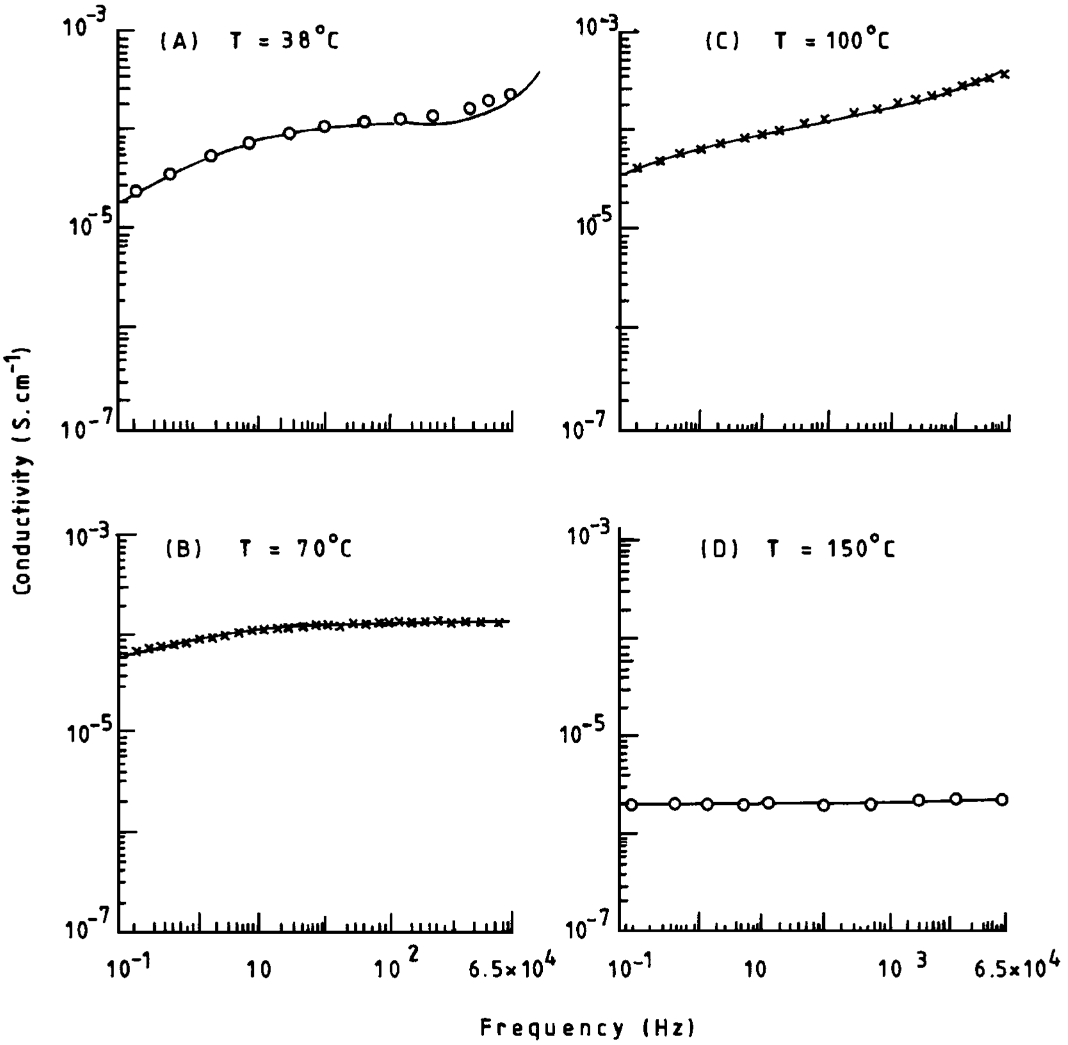

Figure 2 Variation of a.c. conductivity with frequency at (a) $T = 38\,^\circ$C, (b) $T = 70\,^\circ$C, (c) $T = 100\,^\circ$C and (d) $T = 150\,^\circ$C.

using a Solartron FRA, 1250 with an ECI 1286 coupled to an HP computer in the frequency range 0.1 Hz to 65 KHz. The measurements were carried out at different temperatures.

4. Results and discussion

The values of a.c. conductivity of $H_3PO_4{\cdot}12MoO_3{\cdot}nH_2O$ as a function of frequency at different temperatures is shown in Fig. 2 (a slow heating rate ~2 °C/min. was maintained). The presence of two slopes indicates low as well as high frequency dispersion. It is obvious from Fig. 2 that the two slopes can be seen in the data obtained below 100 °C, but they are not so evident in the data at 150 °C, possibly because of dehydration of $H_3PO_4{\cdot}12MoO_3{\cdot}nH_2O$ above ~104 °C [9]. As was explained earlier, we have calculated $\sigma(0)$ and ω_p from the result of Fig. 2. They are plotted in Fig. 3 and the calculated values of dielectric constant and dielectric loss with frequency are shown in Fig. 4.

The d.c. conductivity $\sigma(0)$ initially increases with the temperature attains a maximum at ~80 °C and then starts decreasing (Fig. 3). In the temperature range (14 – 85 °C) this shows a "Arrhenius type thermally activated process" with the activation energy $Ea = 0.76$ eV. The d.c. conductivity $\sigma(0)$ is controlled by hopping rate as well as the number of charge carriers ($\sigma = n \cdot q \cdot \mu$ where mobility μ depends upon the hopping rate). As has been explained, at $T < 70$ °C as $\sigma(0)$ increases the value of ω_p also increases, but at higher temperatures $\sigma(0)$ decreases while ω_p continues to increase (at a faster rate). The decrease in $\sigma(0)$ is ascribed to the loss of water in PMA, which was the source of the H^+ charge carriers. The loss of water molecules decreases the number of charge carriers and hence a decrease in conductivity results. The loss of water would also lead to many vacant sites which may make the hopping rate high, as is observed in Fig. 3. However, the more disturbing fact is the magnitude of the hopping rate. The value of ω_p changes from ~10^2 to $10^5 s^{-1}$. These values of ω_p are low. Such low values of ion motion are indicative of translation motion rather than real hopping. This suggests that hopping is not the mechanism responsible for proton transport in PMA. The more likely mechanism can be inferred as a vehicle mechanism. The possible vehicles are H_3O^+ and OH^- in PMA [10]. There are many studies which show that H_3O^+ moves with activation energy $Ea = 0.8$ eV [11]. The activation energy evaluated from our data of log σ vs. $1/T$ (in the temperature range less than <100 °C i.e. before dehydration) is Ea = 0.76 eV.

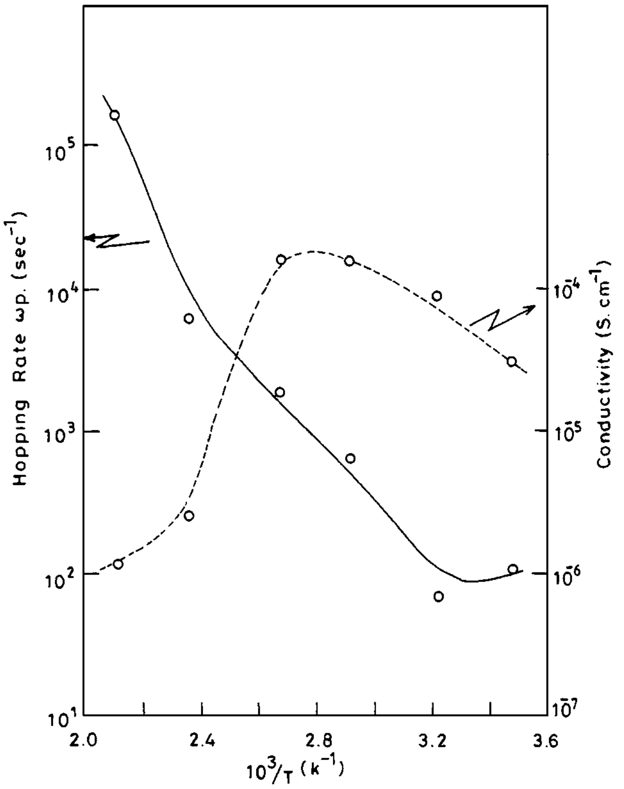

Figure 3 Variation of d.c. conductivity $\sigma(0)$ and hopping rate (ω_p) with the temperature.

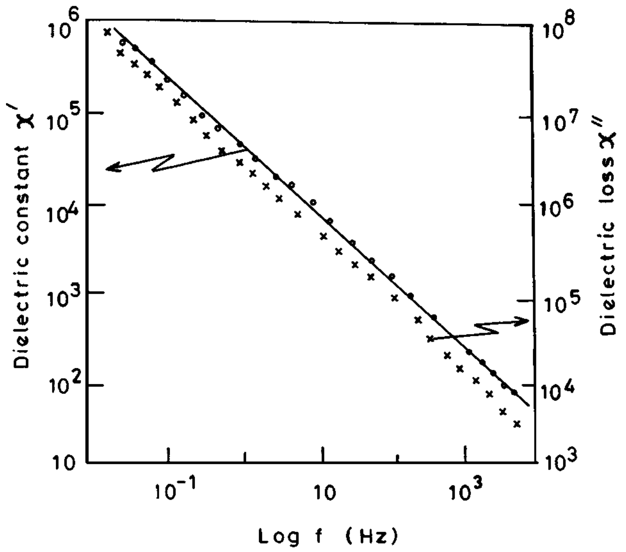

Figure 4 Variation of dielectric constant $\chi'(\omega)$ and dielectric loss $\chi''(\omega)$ with the temperature.

5. Conclusion

Assuming a hopping conduction mechanism, the hopping rate calculated from a.c. conductivity data is unrealistic for PMA. Therefore, a vehicle transport mechanism is more likely.

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