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Experimental studies on the ionic (protonic) transport in ammonium para-tungstate pentahydrate

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Abstract. Proton transport in ammonium para-tungstate pentahydrate $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}\cdot 5\text{H}_2\text{O}$ ($\text{APT}\cdot 5\text{H}_2\text{O}$) has been established using coulometry, transient ionic current, IR and electrical conductivity measurements along with the TGA/DTA results of Kiss and co-workers. The mobile ions are NH_4^+ , H^+ and O^{2-} . The ions (H^+ and O^{2-}) are the products of electrolysis of the inter-layer water. The temperature dependence of the electrical conductivity has been correlated with the accompanying dehydration and de-ammoniation reaction of $\text{APT}\cdot 5\text{H}_2\text{O}$.

1. Introduction

Proton-conducting solid electrolytes have recently attracted attention because of their potential use as solid electrolytes in fuel cells, batteries, hydrogen sensors, electrochromic displays or capacitors (Jensen 1985, Chandra *et al* 1986, Jensen and Kleitz 1981, Goodenough *et al* 1982, 1985, Iwahara 1988, Chandra 1989). Many of these applications need proton conductors with good mechanical properties, and chemical and thermal stability in the temperature range 100–300 °C. Only a few good proton conductors have been investigated that even marginally satisfy the above conditions. The best room temperature proton conductors are some hydrates, e.g. $\text{H}_2\text{UO}_2\text{PO}_4\cdot 4\text{H}_2\text{O}$ and $\text{H}_2\text{UO}_2\text{AsO}_4\cdot 4\text{H}_2\text{O}$ (Howe and Shilton 1979), $\text{H}_3\text{PMO}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 29\text{H}_2\text{O}$ (Nakamura *et al* 1979). These are thermally unstable materials above 70 °C due to dehydration. Some sintered oxides (e.g. SrCeO_3 -based sinters doped with Mg, Yb, Y or Sc) have also been reported which exhibit good protonic conduction at high temperature (about 1000 °C) in hydrogen and/or humid atmosphere (Iwahara 1988). A literature scan shows that many solid hydrates show good proton conduction. The present paper describes details of our investigations carried out on Ammonium para-tungstate pentahydrate ($\text{APT}\cdot 5\text{H}_2\text{O}$) for which a preliminary report was made by us (Tolpadi *et al* 1986).

Ammonium para-tungstate (APT) is an industrially important material since it acts as the starting material for manufacturing tungsten filament for incandescent light sources. A number of physical and chemical studies have already been made, such as thermo-condensation, thermal decomposition, IR and x-rays, phase diagram studies etc (Kiss 1973, Kiss and Chadik-Major 1973, Kiss *et al* 1972, 1978, 1982, Bartha *et al* 1979). The crystal structure of $\text{APT}\cdot 5\text{H}_2\text{O}$ has been obtained by D'Amour and Allmann (1972) by x-ray diffraction method. It has a monoclinic structure, crystallising in the space

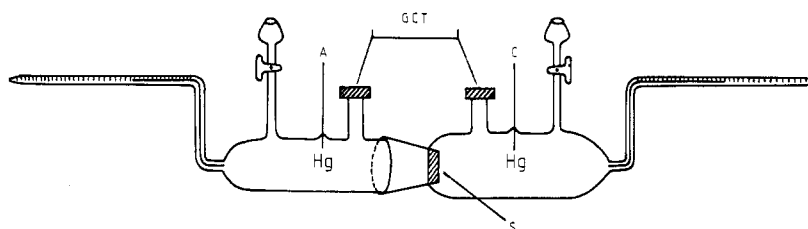


Figure 1. DC electrolysis cell or coulometer: A, anode; C, cathode; GCT, gas chromatographic tube with rubber stopper; s, sample.

group $P2_1/n$ $a = 15.08 \text{ \AA}$, $c = 11.00 \text{ \AA}$, $\beta = 109.40$, $z = 2$. The NH_4^+ ions and H_2O molecules surround the complex anion $(\text{H}_2\text{W}_{12}\text{O}_{42})^{10-}$ in the overall $\text{APT} \cdot 5\text{H}_2\text{O}$ structure. The NH_4^+ ions occupy the sites at the surface of the anion, subjected to strong libration. A small chain of $\text{H}_2\text{O}-\text{H}_2\text{O}$ linkage is also present within the structure with a bond length of 2.83 \AA .

In the present paper, we have explored the possibility of proton conduction in $\text{APT} \cdot 5\text{H}_2\text{O}$. A wide variety of techniques such as coulometry, transient ionic current, IR and electrical conductivity measurement, have been used to establish the proton transport mechanism. In our earlier preliminary paper (Tolpadi *et al* 1986), we were not able to explain properly the σ against $1/T$ behaviour and also we took only H^+ and O^{2-} to be moving under the DC field. The gas chromatographic and chemical analysis results reported in the present paper show the movement of NH_4^+ ions as well as H^+ and O^{2-} . A correlation between our σ against $1/T$ with the TGA/DTA studies of Kiss *et al* has been made. Transient ionic current studies are also reported for determining the ion mobilities.

2. Experimental procedure

2.1. Transference number and mobility measurements

The ionic transference number was measured by using two methods: (i) Wagner's polarisation method; and (ii) a direct electrolysis method. In the polarisation method, the current passing through the pellet of the sample (pressed at 6000 lbs cm^{-2}) was monitored as a function of time under a constant voltage (6 V). Vacuum-evaporated thick silver coatings were used as blocking electrodes. Care was taken to check the leakage of any gas collected at or near the electrodes. The ionic transference number t_{ion} was calculated by using the formula

$$t_{\text{ion}} = (i_T - i_e)/i_T \quad (1)$$

where i_T is the total initial current and i_e is the residual electronic current after the sample has been fully polarised. The polarisation method fails to indicate which cation or anion is responsible for the ion transport. The electrolysis method or coulometry is a more direct way of measuring the transference number. In the present investigation, we suspected that both cationic H^+ (and/or NH_4^+) and anionic O^{2-} species were being transported as electrolysis products. Hence, we used a modified double-arm coulometer shown, as in figure 1, specially fitted with rubber stoppers from which the gases could be taken out for gas chromatography, with the help of syringe. The volumes of the gases evolved at both the cathode and anode ends could be measured by monitoring the

movement of mercury columns. A pellet of the sample was mounted using Araldite on the cone face separating the cathode and anode ends. Electrical contacts at two faces of the pellet were made with platinum wire electrodes dipped in mercury. The electrolysis was carried out at a constant current. The hydrogen, collected at the cathode, was tested with the help of the Tracer Instruments model 540 gas chromatograph.

The transient ionic current (TIC) measurement technique was used to detect the number of types of mobile ionic species and to evaluate their mobility. In this method, the sample is first polarised and then the transient ionic current is monitored as a function of time, after reversing the polarity of the polarising field. Details of the experimental technique have been reported elsewhere (Chandra *et al* 1988). The $APT \cdot 5H_2O$ sample was GR grade supplied by BDH, England. The transference number and mobility measurements were carried out at room temperature (about 300 K).

2.2. IR measurement

The IR spectra of the original sample and the electrolysed samples scraped from the cathode and anode surfaces were recorded. The electrolysed samples were obtained after the coulometric experiment. The spectra were recorded in KBr pellets (pressed at $20\,000\text{ lbs cm}^{-2}$). For the purposes of comparison equal amounts of sample (original powder, scraped from the surface near the cathode/anode) were used in the KBr pellets for the three cases. A Perkin-Elmer 783 IR spectrophotometer was used to record the spectra.

2.3. Electrical conductivity measurements

The electrical conductivity measurements were carried out on the polycrystalline pellets (1 mm thick and 1 cm diameter) pressed at $10\,000\text{ lbs cm}^{-2}$. The measurements were carried out in the temperature range 258–473 K with the cell geometry $Ag/APT \cdot 5H_2O/Ag$ in a static air atmosphere (relative humidity about 60%)[†]. The DC conductivity was evaluated from the complex-admittance ($B-G$) plots. The values of susceptance (B) and conductance (G) at different frequencies were measured using a Hewlett-Packard 4274A LCR meter. The sample temperature was measured and controlled with the help of Century Instruments model 806 temperature indicator and controller. Colloidal silver paint (Electrodag 915, Acheson Colloidal Co.) was used for the electrodes.

3. Results and discussion

3.1. Transference number and mobility

In the Wagner's polarisation method, the transference number t_{ion} was calculated from figure 2 and (1) and the value of t_{ion} was found to be about 0.99. This tells us that the transport is mainly ionic. However, it fails to tell which cation and/or anion is responsible for the ion transport. To determine this the coulometric investigation was carried out. The following results were obtained.

(i) On passing a constant current ($108\ \mu A$) through the sample placed in the coulometer, gases evolved both at the cathode and the anode sides. The volumes of the gases evolved at the cathode and the anode are shown in figure 3.

[†] The conductivity of $APT \cdot 5H_2O$ is strongly humidity dependent. The details on the humidity dependence of conductivity will be reported elsewhere. (7th International Conference on Solid State Ionics, Hakone, Japan, November 1989.)

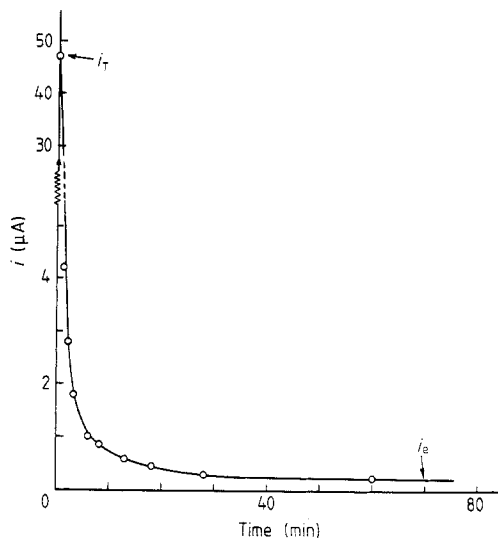


Figure 2. Variation of current as a function of time.

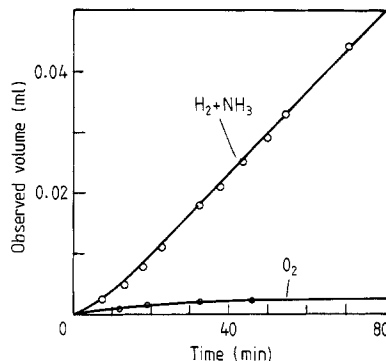


Figure 3. The volume of gases evolved for a constant current ($108 \mu\text{A}$) as a function of time.

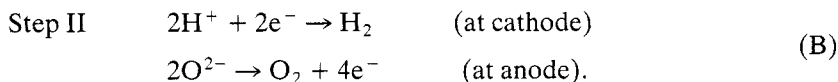
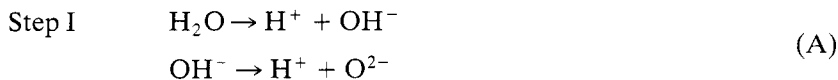
(ii) The sample surfaces got somewhat modified on both sides after electrolysis. The surface on the anode side gets blackened within a few minutes. On the cathode side, the surface acquires a *very feeble* greyish colour if kept in contact with the mercury electrode for a very long time. The anode-side darkening is primarily due to HgO formation (see later in this section) while the charge-transfer surface reaction responsible for the cathode surface change could not be assessed because it was very feeble.

(iii) The gases collected at the cathode were subjected to gas chromatography. The amount of hydrogen in the gas was about 70%. For the other 30%, some other gases were expected to be evolved.

(iv) The cathode-side gas was also tested chemically and the presence of ammonia was confirmed, along with H_2 . It is reasonable to assume that the remaining 30% of the gas at cathode is ammonia, although no quantitative estimation was carried out.

(v) Gases collected at the anode side are assumed to be mainly O_2 , though no direct test could be made because of non-availability of equipment.

The evolution of gases both at the cathode and anode sides suggests the possible electrolysis of water of crystallisation in $\text{APT} \cdot 5\text{H}_2\text{O}$. H_2 and O_2 gases evolve as electrolysis products at the cathode and anode respectively. The blackening at both sides of the sample after electrolysis suggests an electrode–electrolyte charge transfer reaction at both ends. In $\text{APT} \cdot 5\text{H}_2\text{O}$, there are four interlayer water molecules, whereas one molecule is coordinated. These four interlayer water molecules may get electrolysed on the application of DC electric field and the following reactions take place at the electrodes:



From figure 3 it is observed that the volume of the gas evolved at the cathode is more

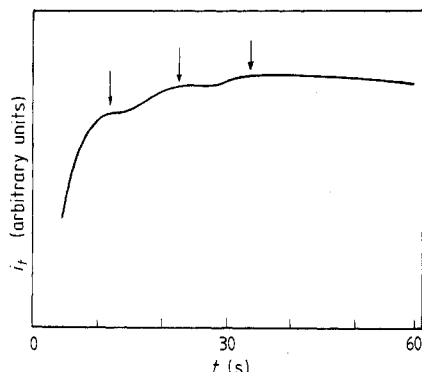
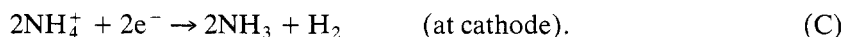


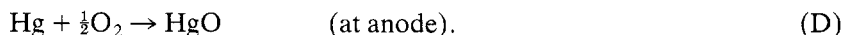
Figure 4. Plot of transient ionic current (i_t) against time (t).

than twice the anode gas whereas, according to the well known laws of electrolysis of water, the volume of hydrogen must be double that of oxygen. This suggests that some other gases are also evolving at the cathode, in addition to H_2 . From the chemical test of the gas evolved at the cathode, ammonia was detected as described earlier. Thus, it is concluded that, on application of a DC electric field, both hydrogen and ammonia gases evolve at the cathode and oxygen gas is liberated at the anode. Ammonia is liberated at the cathode following the reaction:



Therefore, the evolution of H_2 and NH_3 gases at the cathode and O_2 at the anode suggest that H^+ , NH_4^+ and O^{2-} are the mobile ions produced by the application of the DC electric field.

From the gas chromatographic study, 70% hydrogen was observed on the cathode side. The rest is ammonia, as confirmed by a chemical test. The NH_4^+ ion transference number $t_{NH_4^+}$ has been calculated directly and is found to be about 0.13. The total amount of hydrogen gas comprises the hydrogen evolved due to the H^+ ion movement (the electrolysis product of H_2O) (reaction B) and the H_2 liberated from the NH_4^+ ions (reaction C). The H^+ ion transference number was calculated after eliminating the hydrogen gas contribution from NH_4^+ ions and is found to be $t_{H^+} \approx 0.46$. The O^{2-} transference number was calculated directly from the anode-side gas and is found to be $t_{O^{2-}} \approx 0.14$. Using Wagner's polarisation technique, the total ionic transference number is observed to be $t_{ion} \approx 0.99$. Therefore, the O^{2-} transference number must be $t_{O^{2-}} = t_{ion} - t_+(t_{NH_4^+} + t_{H^+}) = 0.40$, which is expected to be nearly equal to t_{H^+} (about 0.46) due to the electrolysis of H_2O . The large discrepancy between the directly observed value of $t_{O^{2-}}$ and the calculated value given above can be explained on the basis of the following observation. At the anode side, a strong blackening of the surface in contact with mercury has been observed. This is attributed to the formation of HgO film (confirmed by IR data—§ 3.2) as a result of the reaction



This would mean that a part of O_2 reacting at the anode is lost in the above reaction and the volume of the gas evolved is less than the volume of the actual O^{2-} transported through the sample. This would lead to an underestimation of $t_{O^{2-}}$ by the coulometric method. The weak blackening at the cathode end is due to the formation of a possibly lesser amount of the charge transfer product, which is difficult to identify.

Several mobile ionic species in $APT \cdot 5H_2O$ have also been confirmed by transient ionic current measurement. Three peaks observed in the transient ionic current i_t against time t plot (figure 4), are indicative of three types of mobile ionic species, that is, NH_4^+ ,

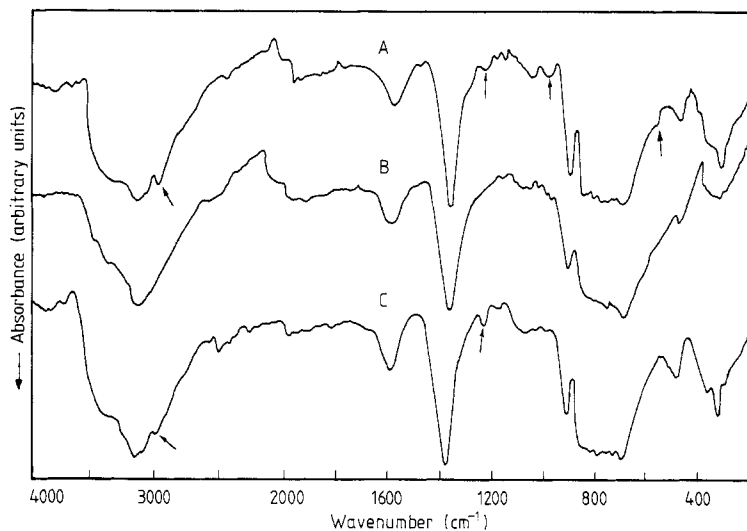


Figure 5. IR absorption spectra of original sample B, along with electrolysed materials near C, cathode, and A, anode.

H^+ and O^{2-} . The mobility values calculated for the three mobile ions corresponding to the three peaks are:

$$\mu_1 = 2.27 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$

$$\mu_2 = 1.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$

$$\mu_3 = 9.1 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}.$$

On the basis of the relative ionic size, the steric consideration suggests that a large mobility is likely for smaller ions. With this assumption, we expect $\mu_{\text{H}^+} > \mu_{\text{NH}_4^+} > \mu_{\text{O}^{2-}}$ as the ionic radii of H^+ , NH_4^+ and O^{2-} are 0.5 Å, 1.42 Å and 1.76 Å, respectively. Therefore, the μ_1 , μ_2 and μ_3 values respectively refer to the values of mobilities of H^+ , NH_4^+ and O^{2-} . This identification is tentative. No measurement of mobility is available in the literature and so direct comparison is not possible. Nonetheless, the value of $\mu_{\text{H}^+} \approx 2.27 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is comparable to μ_{H^+} (about $1.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) estimated for ammonium dihydrogen phosphate (ADP), which is a simple system (Chandra and Hashmi 1989).

3.2. IR spectral study

From the coulometric investigation, we concluded that some H^+ , NH_4^+ and O^{2-} are transported out of the sample on the application of the DC electric field. The change in the electrolysed sample on the application of the DC electric field has been identified by comparing the IR spectra of the original and electrolysed samples. The IR spectra of the samples scraped from the pellet near the cathode and anode ends after electrolysis, along with that for the original sample, are shown in figure 5. The following changes in the spectra are observed.

(i) Two new peaks at 1240 cm^{-1} and 3000 cm^{-1} appear in the electrolysed sample, which are assigned to NH_3 bending (NH_4^+ ion in the lattice partially give NH_3 bonding after H^+ is discharged) and N–H stretching of NH_3 , respectively. It is well known that

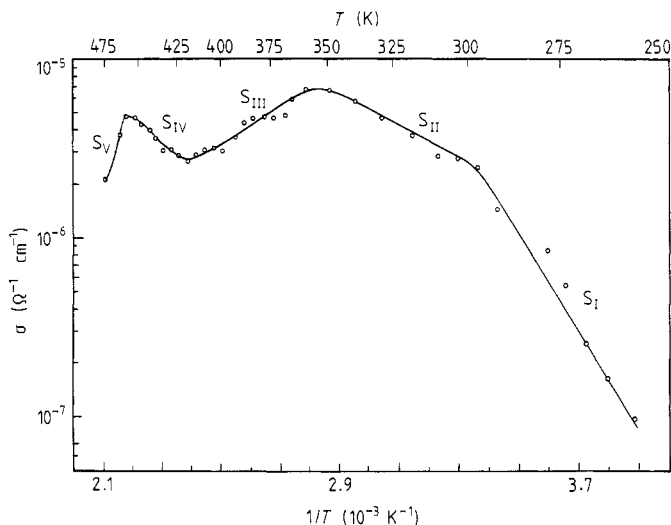


Figure 6. The DC bulk conductivity as a function of temperature: $E_a = 0.64 \text{ eV}$.

when the symmetry of a molecule or ion is reduced, some degenerate modes of vibration become non-degenerate and the number of peaks in the vibrational spectra increases. The same situation occurs in the case of $\text{APT}\cdot 5\text{H}_2\text{O}$. The number of peaks in the stretching and bending regions of N–H vibration is found to be increased after electrolyzing the sample. The NH_4^+ ions have T_{dh} symmetry that is more than the C_{3v} symmetry of the NH_3 molecules. The appearance of one extra peak in the bending region of NH_3 at 1240 cm^{-1} and one in the stretching region at 3000 cm^{-1} indicates the presence of NH_3 molecules (along with NH_4^+ ions) in the electrolysed sample. The presence of NH_3 in the sample after charge transport had taken place, and also its presence in the gases evolved at the cathode, have to be simultaneously reconciled. The latter confirms that one of the mobile species is NH_4^+ ions, which give NH_3 and H_2 as a result of electrode reaction (C) given earlier. Possibly only a part of this NH_3 is being released, while some is diffusing back into the system.

(ii) One new peak at 1000 cm^{-1} and another weak peak at 575 cm^{-1} are found in the sample taken from the anode side. These are attributed to the electrode reaction product HgO , formed due to the reaction of discharging O^{2-} with the mercury of the coulometer.

(iii) Some changes are also observed at about 2500 cm^{-1} that we could not identify.

(iv) In the range $200\text{--}600 \text{ cm}^{-1}$ there are also changes. For example, on the anode side a peak appears at 575 cm^{-1} , which is due to HgO as explained earlier. The broad peak at around 300 cm^{-1} splits into three relatively sharp peaks that we could not identify.

3.3. Electrical conductivity

The temperature dependence of DC conductivity (evaluated from the experimental B–G plots) is shown in figure 6. These measurements have been taken up to a temperature of only 474 K, because fast dissociation of the compound starts after this temperature caused by the simultaneous evolution of ammonia and water vapours as suggested in TGA and DTA results of Kiss *et al* (1972).

The conductivity variation with temperature (figure 6) shows a complex behaviour. The temperature range of interest has been divided into different regions (S_I , S_{II} , S_{III} ,

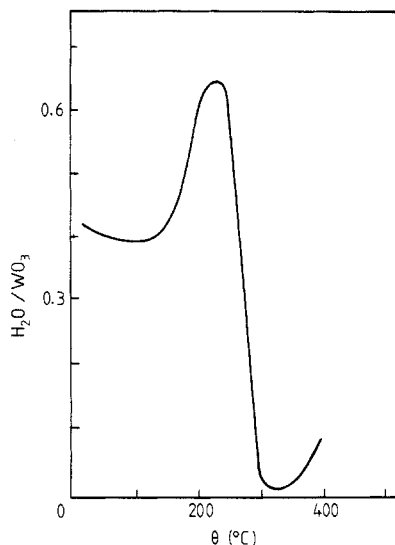


Figure 7. Rehydration capacity of the intermediate phases of $\text{APT} \cdot 5\text{H}_2\text{O}$ (after Kiss *et al* 1978).

S_{IV} and S_{V}) on the basis of different steps of variations in conductivity. In the S_{I} -region (figure 6) the conductivity increases sharply up to 293 K. It may be explained in terms of Arrhenius-type thermally activated process. The activation energy for this region is calculated to be 0.64 eV. In the S_{II} -region, the increase in conductivity becomes slower and starts decreasing after 353 K in the S_{III} -region and shows a minima at 418 K. These variations can be correlated with the decomposition/dehydration reaction given by Kiss *et al* (1972) by simultaneous TGA and IR studies. According to these studies, various intermediate compounds of $\text{APT} \cdot 5\text{H}_2\text{O}$ exist in different temperature ranges. A partial dehydration occurs in the temperature range 293–403 K. The S_{II} -region may be assigned to the pre-transition state, in which slight dehydration starts, following which a decrease in conductivity occurs in the S_{III} -region owing to faster dehydration.

In the S_{IV} -region, the conductivity starts increasing again after 418 K. In the TG studies (Kiss *et al* 1972, 1978), it was discussed that the onset of the release of dry ammonia due to the thermal decomposition of $(\text{NH}_4)_2\text{O}$ unit into NH_3 leaves behind H_2O molecules in the lattice, and the sample becomes relatively rehydrated. A rehydration curve is shown in figure 7 (Kiss *et al* 1978). The enhancement of the conductivity in the S_{IV} -region is explained in terms of this rehydration. A rapid decrease in conductivity in the S_{V} -region after 450 K is due to the evolution of the rehydrating water along with NH_3 .

Thus, it can be summarized that the S_{I} -region is characteristic of the material $\text{APT} \cdot 5\text{H}_2\text{O}$, while the other regions (S_{II} , S_{III} , S_{IV} and S_{V}) are due to the variable composition phases following the reaction of dehydration and de-ammoniation.

4. Conclusion

Combining all the electrical, thermal and spectroscopic studies of $\text{APT} \cdot 5\text{H}_2\text{O}$, described above, the following tentative conclusions are drawn regarding the ion transport. Three types of ionic carriers are present as evidenced by TIC experiment. Protons for transport are provided by the electrolysis of inter-layer water of crystallisation (which also provides O^{2-} ions for motion). In $\text{APT} \cdot 5\text{H}_2\text{O}$, four water molecules are inter-layered, whereas

one is coordinated. The coordinated water molecules, which are strongly bonded making the $(H_2W_{12}O_{42})^{10-}$ complex anion, are not likely to contribute to the conduction. Inter-layer water molecules are likely to contribute to the ion transport. Short-range chains of inter-layered H_2O-H_2O linkage (bond length 2.83 Å) occur, through which the translation motion of H^+ ion is possible.

Another ionic species contributing to the ion transport is NH_4^+ . The evolution of ammonia during electrolysis at the cathode end suggests the movement of NH_4^+ ions following the 'vehicle mechanism', i.e. NH_4^+ ions move as such in the bulk. The NH_4^+ ions, occupying the sites at the surface of the complex anion $(H_2W_{12}O_{42})^{10-}$, are subjected to strong librational motion (Evans and Prince 1983), and can easily be dissociated under the influence of a DC electric field.

Acknowledgments

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