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Proton Transport Studies in Dehydrated Salts: $AlNH_4(SO_4)_2$ and $FeSO_4$

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Dehydrated aluminium ammonium sulphate and ferrous sulphate have shown good protonic behaviour (H^+ ion movement) after the insertion of external hydrogen in the intermediate temperature range (200–400°C) as studied by polarization experiment, IR spectroscopy, electrochemical e.m.f. measurement and electrical conductivity measurement in air and hydrogen ambient.

Key Words: Dehydrated salt, Electrical conductivity, Electrochemical e.m.f., Proton conduction.

INTRODUCTION

The high temperature proton conductors are of special interest in the solid state ionic materials[1, 2] due to their potential applications in electrochemical devices, like fuel cells, gas sensors and steam electrolyzers. Most of the good proton conductors are hydrates or hydrogen bonded materials[3–6] which are unstable at high temperatures. For the fuel cell application generally 200°C or more is the preferable temperature due to good thermodynamic efficiency[7]. Many sintered oxides like $SrCeO_3$, $BaCeO_3$, $SrZrO_3$ doped with Y_2O_3, Yb_2O_3 etc. which are *p*-type semiconductors, show proton transport at high temperatures (600–1000°C) in H_2/humid ambient [8–10]. A series of materials based on $KTaO_3$ doped with Ni, Fe, Cu or Li_5AlO_5[11–13] show protonic behaviour at intermediate temperature ranges (200–500°C). In the present paper, we communicate that the dehydrated aluminium ammonium sulphate [$AlNH_4(SO_4)_2$] and ferrous sulphate ($FeSO_4$) can sustain proton conduction in the temperature range (200–400°C). The thermal and transport behaviour of aluminium ammonium sulphate and ferrous sulphate[14] at low temperature have already been studied. On the basis of the following studies we demonstrate that these dehydrated materials are proton conductors at intermediate temperature range: (i) ion/proton behaviour in hydrogen ambient, (ii) increase in conductivity in H_2 atmosphere, (iii) electrochemical EMF study of concentration cell P_{H_2O}-I (air)/dehydrated solid electrolyte/P_{H_2O}-II (air) and hydrogen-oxygen cell P_{H_2}/dehydrated solid electrolyte/P_{O_2} (air), (iv) IR spectral studies looking for the presence of —OH bonds in H_2 ambient.

EXPERIMENTAL

The starting materials aluminium ammonium sulphate and ferrous sulphate [$AlNH_4(SO_4)_2 \cdot 12H_2O$ and $FeSO_4 \cdot 7H_2O$ (Glaxo, India)] were of the analytical grade of purity. The dehydration temperatures of these salts were obtained by DTA/TGA studies[14–17]. For the dehydrated powder the polycrystalline hydrated salts were kept in an oven [$AlNH_4(SO)_2 \cdot 2H_2O$ at 240°C and $FeSO_4 \cdot 7H_2O$ at 300°C] for 24 h. The dehydrated salts were cooled in a desiccator to room temperature. Pellets were prepared by Beckmann's evacuable die to avoid the possible rehydration.

To determine the nature of mobile species (*i.e.*, transference number measurement) Wagner's polarisation method[18] was used. In this method, a thick silver coating was used as a blocking electrode and platinum paste as the second electrode. The complete polarization cell assembly[5] was placed in a temperature controlled furnace. To polarize the sample, a small d.c. potential is applied across the sample. The current is monitored as a function of time till the current saturates. The current decreases with time due to the formation of a polarization cloud at the blocking electrode which prevents further flow of the ionic species. In the current *vs.* time plot, the initial total current (i_T) is the sum of the current contributed by both ionic as well as electronic species. The final residual current (i_e) is due to electronic conduction only. Therefore the ionic transference number (t_{ion}) is given by

$$t_{ion} = 1 - \frac{\sigma_e}{\sigma_T}$$

$$= 1 - \frac{i_e}{i_T}$$

where σ_e and σ_T are the electronic and total conductivity respectively. However, the above method cannot identify exactly whether the conductivity of the material is due to electrons (σ_e) or holes (σ_h). The theory of non-ionic contribution in predominantly ionic conductors was proposed by Wagner and Wagner[18] and was later used by Ilschner[19]. In the cell design, they used one blocking electrode and another non-blocking electrode. The mobile ionic charge carriers move under the applied potential (of polarity) and get dissolved in the non-blocking electrode. As the supply of the species cannot be maintained by the other side electrode (*i.e.*, blocking electrode) the current will decrease with time. The final residual current will only be due to the non-ionic charge carrier. The final residual current at every voltage is monitored as a function of the applied voltage. According to Wagner and Wagner[18] this current may be expressed as:

$$i_{e,h} = i_e + i_h \tag{1}$$

$$I_{e,h} = \frac{RTA}{LF}\left[\sigma_e\left\{1 - \exp\frac{-VF}{RT}\right\} + \sigma_h\left\{\exp\frac{VF}{RT} - 1\right\}\right] \tag{2}$$

where R is the gas constant, F is the Faraday's constant and T is the absolute temperature. A and L are area and thickness of the pellet respectively, V is the applied voltage, $I_{e,h}$ is the total non-ionic current (due to electron + hole), i_e and

i_h are the currents due to electrons and holes respectively. The variation of residual non-ionic current (*i.e.*, after full polarization has been achieved) is a function of applied potential. There are the following different cases summarized below:

(i) If $\sigma_e \gg \sigma_h$, then

$$I_{e,h} = I_e = \frac{RTA}{LF}\left[\sigma_e\left\{1 - \exp\frac{-VF}{RT}\right\}\right] \qquad (3)$$

For large value of V, the current saturates to the following value:

$$I_e = \frac{RTA}{LF}[\sigma_e] \qquad (4)$$

(ii) If $\sigma_e \ll \sigma_h$, then

$$I_{e,h} = I_h = \frac{RTA}{LF}\left[\sigma_h\left\{\exp\frac{VF}{RT} - 1\right\}\right]$$

$$\approx \frac{RTA}{LF}\left[\sigma_h\left\{\exp\frac{VF}{RT}\right\}\right] \qquad (5)$$

That is, the current varies exponentially with V. When extrapolated to V = 0 this gives the value of I_h for(V = 0.

$$I_h \approx \frac{RTA}{LF}[\sigma_h] \qquad (6)$$

In the present investigation, the sample is polarized at some fixed voltage and the residual current was measured by the sensitive Keithley Source Measure Unit Model 236 (sensitivity –0.1/A) as the current was generally less than 10^{-8} A. The above residual current measurement was repeated for different voltages so that the nature of V *vs.* I behaviour could be ascertained. Subsequently, the values of σ_e and σ_h could be calculated from the 1-V characteristics using the above equations.

For exploratory studies on proton conductors, the electrochemical e.m.f. measurement across the concentration cell is a good method, particularly at higher temperature, where many methods fail. For this we used a concentration cell with the following configuration:

$P_{H_2}(p')$	■	Proton conductor	■	$P_{H_2}(p'')$

The potential difference developed across it is given by Nernst's equation[20]

$$E = t\frac{RT}{2F}\ln\left[\frac{p'}{p''}\right]$$

where t is the transference number p′ and p″ are the partial pressures of gases. By this method, several workers have demonstrated the presence of protonic conduction[8, 21, 22].

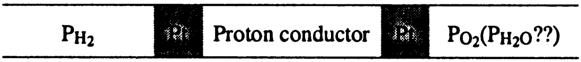
Suppose the concentration cell is obtained by a combination of dry /wet air as

$P_{H_2O}(I)P_{O_2}(I)$	■	Proton conductor	■	$P_{H_2O}(II)P_{O_2}(II)$

The e.m.f. of the cell is given by

$$E = \frac{RT}{2F} \ln \left[\frac{p_{H_2O}(I)}{p_{H_2O}(II)}\right]\left[\frac{p_{O_2}(II)}{p_{O_2}(I)}\right]^{1/2} \tag{8}$$

Now, let us take another type of concentration cell which uses H_2 and O_2 in the two compartments.

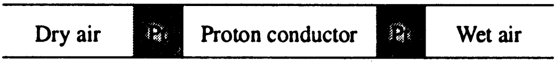


In this cell, the proton has a tendency to migrate across the proton conductor towards the oxygen electrode where it is discharged to form water vapour. Therefore, the e.m.f is given by

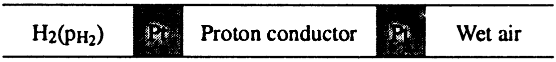
$$E = E^0 - \frac{RT}{2F} \ln \left[\frac{p_{H_2O}(I)}{p_{H_2} p_{O_2}^{1/2}}\right] \tag{9}$$

where, $P_{H_2}$and P_{O_2} are the partial pressures of the hydrogen and oxygen respectively. In this method, it is important to avoid the leakage between the anode and the cathode compartments. Two types of concentration cells were used for the present study

Cell 1



Cell 2



For assembling cell (i), gas outlet 2 was closed and gas inlet 2 was connected to a bottle containing P_2O_5, so that the air dries up before entering the cell. Gas inlet 1 and gas outlet 1 were connected by a rubber tubing to a water bottle for providing wet air. For assembling cell (ii), gas inlet 1 was connected to a hydrogen cylinder and the gas was allowed to bubble out through outlet 1. Further, gas inlet 2 was left open to ambient air.

The bulk electrical conductivity measurement was carried our by complex impedance/admittance plot method with the help of computer controlled "Schlumberger Solartron 1250 frequency response analyser" coupled with the 1286 electrochemical interface. The electrical conductivity of dehydrated salts was measured with the help of a spring loaded sample holder placed in a closed chamber. All the measurements were taken in three different ambients (air, vacuum and hydrogen) with varying temperature. The frequency range of measurement was 1 Hz to 65 kHz.

The infrared spectra was recorded by Perkin-Elemer IR spectrophotometer (model 883). The spectra were recorded on a thin transparent pellet of dehydrated salt dispersed in KBr in the ratio of 1 : 100. A temperature controlled sample holder/cryostat suitable for the temperature range 150–600 K was used for temperature dependent studies.

RESULTS AND DISCUSSION

Nature of Charge Carriers in Dehydrated Salts

Transference number measurements in air and hydrogen ambient: The transference numbers of $AlNH_4(SO_4)_2$ and $FeSO_4$ were evaluated at T = 250°C in air and hydrogen ambient by Wagner's polarization method. The current *vs.* time plot for dehydrated aluminium ammonium sulphate and ferrous sulphate are shown in Fig. 1. The ionic transference number (t_{ion}) has been evaluated by

$$t_{ion} = \left(\frac{i_T - i_{e,h}}{i_T}\right) \qquad (10)$$

where i_T is the initial total current and $i_{e,h}$ is the final current after almost complete polarization. Calculated values of t_{ion} in air and hydrogen ambient are listed in Table-1. Following interesting inference can be drawn from these results:

Both dehydrated salts are essentially non-ionic in air. However, in the presence of hydrogen, they show the ionic behaviour as is clear from Fig. 1 with respective t_{ion} values shown in Table-1. This gives the "first indication" that the dehydrated salts can possibly sustain protonic conduction at elevated temperatures in H_2 atmosphere.

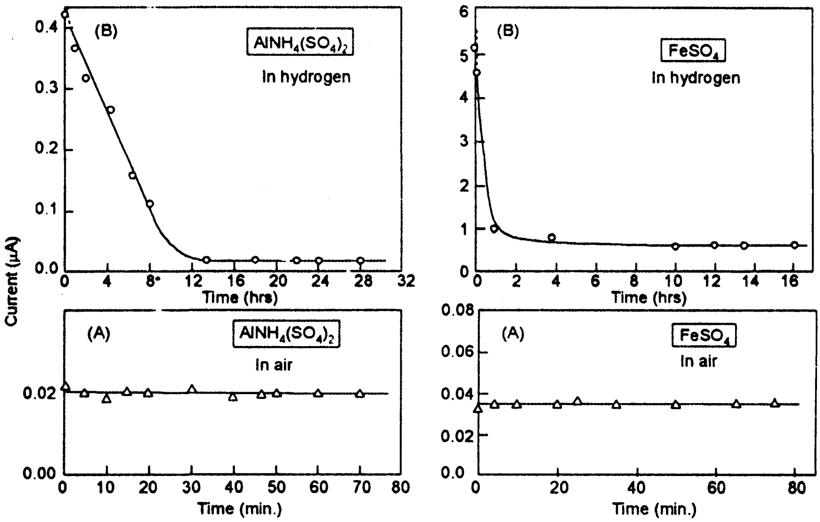


Fig. 1. Variation of polarization current with time for $AlNH_4(SO_4)_2$ and $FeSO_4$ at 250°C

TABLE-1
VALUE OF TRANSFERENCE NUMBER (t_{ion}) IN AI RAND HYDROGEN AMBIENT

S.No.	Dehydrated salts	$(t_{ion})_{Air}$	$(t_{ion})_{Hydrogen}$
1.	$AlNH_4(SO_4)_2$	≈ 0	≈ 0.952
2.	$FeSO_4$	≈ 0	≈ 0.910

Non-ionic part of conductivity in air ambient by I-V measurements: The above polarization experiments have shown that the dehydrated salts behave principally as non-ionic conductors in air. This non-ionic conduction may be due to holes and/or electrons.

For the determination of the relative contributions of the electron and hole conduction, we used Wagner's method. The sample was placed between ion blocking and a reversible electrode. A typical cell configuration is

(–) M | | MX | | Inert electrode (+)

where MX is the solid electrolyte in which the electron/hole conductivity is desired to be measured. A d.c. voltage (less than the dissociation voltage of the material) is applied and the "residual final current" due to the electrons and holes is measured for different voltages V. With the increasing potential V the electronic part of the current tends to assume a saturation value (RTA/LF) σ_e while on the other hand the contribution of hole increases exponentially. The conductivities due to electrons and holes are given by

$$\sigma_e = \frac{LF}{RTA} i_e \tag{11}$$

$$\sigma_h = \frac{LF}{RTA} i_h \tag{12}$$

where i_e is the measured saturation plateau current and i_h is the value of current obtained by extrapolating in I *vs.* V plot to V = 0 . The I-V measurements were carrried out only at one representative temperature of 250°C .

In the present study, the pellets of dehydrated aluminium ammonium sulphate and ferrous sulphate with platinum paste electrodes were held in a spring-loaded flat plate cell assembly. The I-V characteristics of these salts (after allowing sufficient time for polarization, if any) are given in Fig. 2. In the I-V characteristic for the dehydrated aluminium ammonium sulphate, there is a small plateau region (typical of i_e) as well as exponentially increasing current (giving the value of i_h when extrapolated to V = 0). Therefore we can conclude that the conduction is partially through electrons and partially through holes. The values of σ_e and σ_h evaluated by using equations (11) and (12) are

$$\sigma_e = 1.3 \times 10^{-8}\ \mathrm{s\ cm^{-1}}$$

$$\sigma_h = 0.3 \times 10^{-8}\ \mathrm{s\ cm^{-1}}$$

The electrical conductivity σ as measured by impedance spectroscopy is 1.6×10^{-8} s cm^{-1} which agrees with the present evaluated value of ($\sigma_e + \sigma_h$).

The dehydrated ferrous sulphate I-V characteristic does not show i_e or σ_e related plateau and the current increases exponentially at high applied voltages, which is typical of hole conduction. The σ_h so evaluated is about 54×10^{-7}s cm^{-1} which is in reasonable agreement with that measured with impedance spectroscopy (approximately 6×10^{-7} s cm^{-1}).

Determination of ionic (or protonic) conduction in hydrogen ambient by electrochemical EMF measurement

A concentration cell of the following configuration, using the specimen as electrolyte diaphragm is assembled:

Gas I (pI)	Pt	Proton conductor	Pt	Gas II (pI)

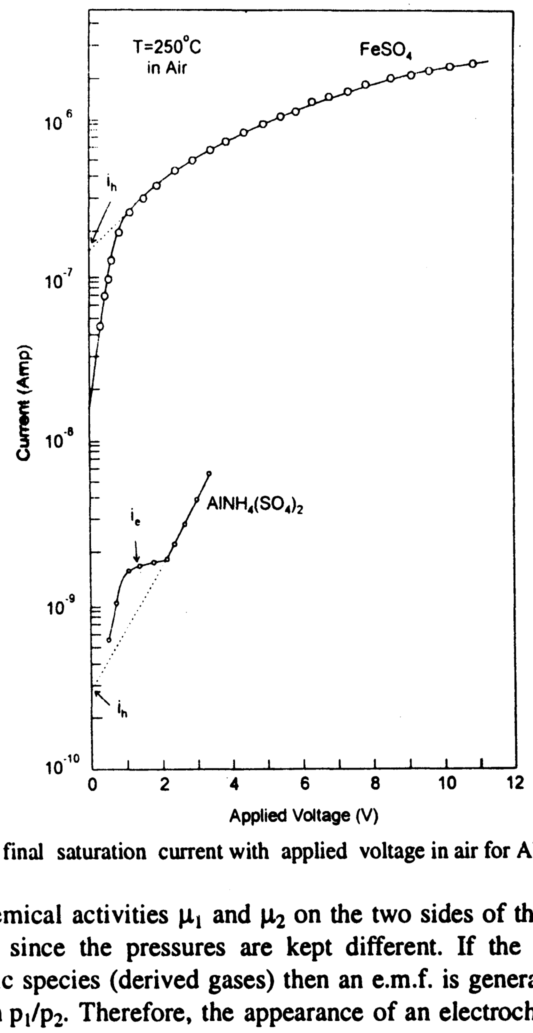


Fig. 2. Variation of final saturation current with applied voltage in air for $AlNH_4(SO_4)_2$ and $FeSO_4$

The electrochemical activities μ_1 and μ_2 on the two sides of the electrolytes will be different since the pressures are kept different. If the electrolyte is permeable to ionic species (derived gases) then an e.m.f. is generated, which is proportional to $\ln p_1/p_2$. Therefore, the appearance of an electrochemical e.m.f. in a concentration cell is an indication of possible mobilities of gaseous ionic species in the electrolyte.

In the present study, we suspect protonic conduction; the protonic species (H^+, O^-) can be derived from H_2 or H_2O. Hence the following cell geometries were assembled:

(i) Cell I: Wet air, Pt | Dehydrated salt | Pt, dry air.
(ii) Cell II: H_2, Pt | Dehydrated salt | Pt, air.
(iii) Cell III: Dry air, Pt | Dehydrated salt | Pt, dry air.

The first two cells are asymmetric with different activity of the protonic species on the two electrode sides while (iii) is symmetric. The cell (iii) was purposefully assembled to check that the electrochemical e.m.f. developed in cell (i) or (ii) is genuinely due to the presence of higher activity of protonic species on one side. The cell (iii) gives nearly zero voltage as expected since the electrochemical activity on the two sides is the same. However, cell (i) and cell (ii) gave genuine electrochemical e.m.f. typical of a concentration cell. The electrochemical e.m.f.s generated for cell (i) and cell (ii) using the dehydrated salts as an electrolyte are given in Table-2.

TABLE-2
ELECTROCHEMICAL e.m.f. OF THE DEHYDRATED SALTS AT 200° AND 250°C

S. No.	Materials	Cell type			
		Wet air | | Dry air		Air (p_{low}) | | Hydrogen	
		200°C	250°C	200°C	250°C
1.	$AlNH_4(SO_4)_2$	1.2 mV	13.7 mV	51.5 mV	32.0 mV
2.	$FeSO_4$	11.4 mV	34.0 mV	260.0 mV	188.0 mV

In both dehydrated salts [$AlNH_4(SO_4)_2$ and $FeSO_4$], almost similar results are obtained. The generation of electrochemical e.m.f. is briefly described below:

The e.m.f. is generated in the dehydrated salts due to the following reactions:

(a) Cell I: wet air, Pt | dehydrated salt | Pt, dry air

On wet air side electrode the electrode reaction is:

$$H_2O \rightarrow 2H^+ + \tfrac{1}{2} O_2 + 2e^-$$

while on the dry air side electrode, the electrode reaction is:

$$2H^+ + \tfrac{1}{2} O_2 + 2e^- \rightarrow H_2O$$

The humidity level on the wet air side of the cell was created by connecting the compartment with a tube whose other end was dipped in a water vessel kept far away from the furnace. The dry air used was essentially ambient air with R.H. 40% corresponding to P_{H_2O} *ca.* 3 torr at room temperature. The actual value of P_{H_2O} either on the wet air side or dry air side could not be measured at the elevated temperature of 250°C where the measure ments on dehydrated salts were being performed.

The e.m.f. of the above concentration cell in which the partial pressure of H_2O is different $p_{H_2O}(I) > p_{H_2O}(II)$ in the different electrode compartments separated by the proton conductor diaphragm can be expressed as[8]

$$E = \frac{RT}{2F} \ln \left[\frac{p_{H_2O}(I)}{p_{H_2O}(II)} \right]$$

where F is Faraday's constant and R is the gas constant. As predicted by the above equation, the e.m.f. generated is higher at higher T (Table-2) but actual calculations could not be done due to lack of knowledge of $p_{H_2O}(I)$ and $p_{H_2O}(II)$ at the elevated temperatures.

(b) For cell II: H_2 (P *ca.* 1 atm) Pt | dehydrated salt | Pt air (p *ca.* 0.1 atm)

On the H_2 side electrode the reaction is

$$H_2 \rightarrow 2H^+ + 2e^-$$

The H^+ migrate through the electrolyte and the reaction on air (or oxygen) side electrode is

$$2H^+ + \tfrac{1}{2} O_2 + 2e^- \rightarrow H_2O$$

The generated electrochemical e.m.f. (E) will be governed by the equation (9). This equation predicts that the e.m.f. would be lower for higher temperatures and has also been observed by us. Again we could not calculate the actual e.m.f. due to the lack of the measured value of P_{H_2O} of the reaction product. However, it may be noted that an agreement between $(EMF)_{cal}$ and $(EMF)_{exp}$ is not generally expected due to the uncertainty in the estimation of P_{H_2O}, an insufficient knowledge of electrode activity/interface condition and because the continuously varying partial pressure of the product H_2O vapour with time disturbs the pressure condition. Nonetheless, the approximate agreement along with the trends of experimental/theoretical temperature dependence of e.m.f. gives credence to our interpretation based on the basis of protonic conductivity.

Infrared spectral studies

The results obtained by the IR spectral studies of $AlNH_4(SO_4)_2$ and $FeSO_4$ are indicative of the fact that these dehydrated salts can sustain proton (H^+ or OH^-) mobility in hydrogen ambient at elevated temperatures 200–250°C. Therefore, it is expected that the hydrogen diffusion coefficient would be high at these temperatures. The diffusing hydrogen may form —OH bonds with the sulphate oxygen and/or also alter other bondings. This means that the IR spectra of the dehydrated salts heated in hydrogen ambient would show significant changes while such changes are not expected when heated in dry air/vacuum. Therefore the *in-situ* IR-spectral studies have been carried our at 250°C under

—dehydrated salts kept in vacuum at 250°C, and

—dehydrated salts kept in hydrogen at 250°C for sufficiently long time

so that the equilibration is fully attained. (The time for $AlNH_4(SO_4)_2$ is 1 h and for $FeSO_4$ is 24 h, which is guided by the time dependence study of conductivity discussed in a later section).

The IR spectra of the dehydrated salts taken with the sample kept in vacuum and hydrogen atmosphere at 250°C are shown in Fig. 3.

Both spectra are qualitatively similar for all cases. We have to take a closer look in the —OH bond region since our aim is to identify the possible formation

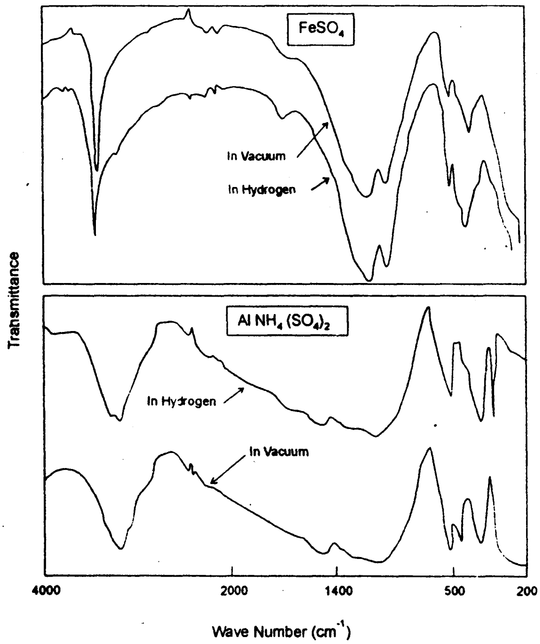


Fig. 3. IR spectra of $AlNH_4(SO_4)_2$ and $FeSO_4$ at 250°C

of new —OH bands due to the diffusing hydrogen. The region of strong —OH peak in the IR spectra is 3600–3000 cm^{-1}.[22] So we present an enlarged view of this region in the IR spectrum for the salts in Fig. 4.

Ideally, in the fully dehydrated salt —OH peak in the *ca.* 3200 cm^{-1} region is not expected. However, we do see a residual —OH absorption peak even in the dehydrated sample placed in vacuum. This may be due to the ineffective N_2 purging in our instrument (and/or some residual —OH bands in KBr or the sample). The important information of our present interest is to study the change (if any)[23] in the —OH peak when the IR spectrum is recorded in hydrogen ambient. A comparison of the area under —OH peak with the sample in vacuum and sample after having been placed in hydrogen ambient (as shown in Fig. 4 for $AlNH_4(SO_4)_2$ and $FeSO_4$ respectively) shows that an enhancement (*ca.* 1.5 times) in the area under —OH peak has occurred possibly due to the formation of new —OH bonds by the hydrogen diffusing in the lattice.

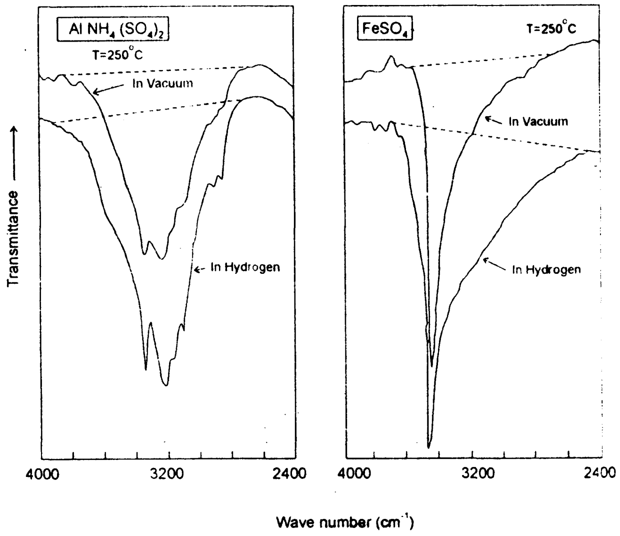


Fig. 4. IR spectra (region 4000–2400 cm^{-1}) of $AlNH_4(SO_4)_2$ and $FeSO_4$

Temperature Dependence of Conductivity

The bulk electrical conductivity of the dehydrated salts was evaluated from the complex impedance plots in the temperature range (200–400°C) for the samples placed in three different atmospheres (air, vacuum and hydrogen). All the measurements were done on dehydrated pellets with porous platinum electrodes. The electrical conductivities of dehydrated salts were evaluated from complex-impedance plots as a function of time and temperature in three different atmospheres as given in Figs. 5 and 6.

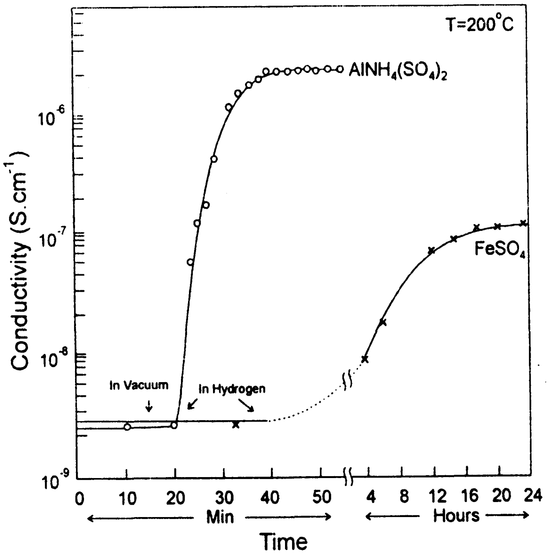


Fig. 5. Variation of electrical conductivity of $AlNH_4(SO_4)_2$ and $FeSO_4$ with time after the insertion of hydrogen (the conductivity of t = 0 min is σ_{vacuum})

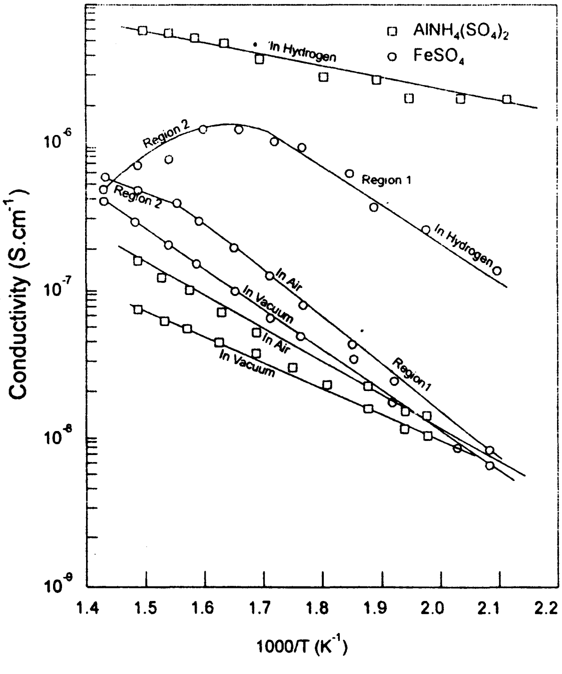


Fig. 6. Variation of electrical conductivity of $AlNH_4(SO_4)_2$ and $FeSO_4$ with temperature in three ambients (*i.e.*, air, vacuum and hydrogen)

Enhancement of conductivity in H_2 ambient: In the dehydrated salts the conductivity increases after inserting hydrogen into the chamber. Earlier it is discussed that the material changes its conductivity behaviour from non-ionic to ionic when placed in H_2 ambient. However, it has been found that the uptake of hydrogen in the dehydrated salts is slow and it takes some time for the conductivity value ($\sigma_{hydrogen}$) to equilibrate.

The variation of conductivity with time after the insertion of hydrogen in the conductivity cell chamber is shown in Fig. 5. It is clear that the equilibration is faster (30–40 min) for $AlNH_4(SO_4)_2$ while it takes a very long time (> 24 h) in the case of $FeSO_4$ to equilibrate. It is interesting to note that the number of water molecules removed during dehydration for the $AlNH_4(SO_4)_2$ is large (*i.e.*, 12) while for $FeSO_4$ it is small (*i.e.*, 7). The variation of equilibration time (for σ- values) as a function of the number of molecules of water of crystallization removed on dehydration (or what was present in the original salt) more voids are created in those lattices from which more water molecules have been removed and hence they follow faster reaction kinetics to equilibrate in hydrogen ambient. However, this is only an empirical observation.

σ vs 1/T measurement: The log σ *vs.* 1/T plots are shown in Fig. 6 for samples placed in vacuum, air and hydrogen. Sufficient time was always allowed for equilibration whenever ambient was changed. The log σ *vs.* 1/T plots are linear in the region 1 (referred to in the figure) and it can be represented by the Arrhenius type expression:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{14}$$

where σ_0 is the pre-exponential factor and E_a is the activation energy. The values of σ_0 and E_a are given in Table-3.

TABLE-3

VALUES OF σ_0 AND E_a OF DEHYDRATED SALTS

Dehydrated Salts	Ambients	σ_0 (s cm^{-1})	E_a (eV)
1. $AlNH_4(SO_4)_2$	Air	3.8×10^{-4}	0.45
	Vacuum	3.1×10^{-5}	0.34
	Hydrogen	5.8×10^{-6}	0.04
2. $FeSO_4$	Air	3.5×10^{-2}	0.64
	Vacuum	2.2×10^{-1}	0.66
	Hydrogen	2.7×10^{-3}	0.40

In $AlNH_4(SO_4)_2$ there is only a linear region in the entire temperature range studied by us but in $FeSO_4$ the deviation from linear behaviour starts at *ca.* 340°C in air and hydrogen. This effect is more prominent in the case of hydrogen ambient. It is reported in literature[25] that $FeSO_4$ has a dissociation temperature of *ca.* 480°C. The present trend is possibly a reflection of a pre-dissociation effect. The dissociation seems to be assisted by hydrogen ambient.

Conclusion

From transference number, electrochemical e.m.f. measurement and σ *vs.* 1/T studies, it is shown that the dehydrated aluminium ammonium sulphate and ferrous sulphate are primarily non-ionic in air in the temperature range 200–400°C and become ionic (protonic) in hydrogen ambient. The non-ionic part of the conductivity in air is due to holes in $FeSO_4$ while it is *ca.* 20% due to holes and *ca.* 80% due to electron in $AlNH_4(SO_4)_2$. This study proposes an alternative set of materials (*i.e.*, dehydrated salts) as possible proton conductors for intermediate temperature range.

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