

Thermal and Ion Transport Studies in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

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The proton transport in ferrous sulphate has been established using different techniques like thin layer chromatography, differential thermal analysis/thermal gravimetric analysis, polarization, coulometry and electrical conductivity measurements. The possible charge carriers in hydrogen bonded or hydrate materials are protons (*i.e.*, H^+ or OH^-) which are generated on the electrolysis of the water of crystallization and provide the protonic conductions.

Key Words: Salt hydrates, Rehydration, Ionic/protonic conductivity, Mobility, TIC.

INTRODUCTION

Recently, there has been a strong demand of solid proton conductors to build "All Solid State Electrochemical Devices"^{1–4}. It is well-known that hydrated solid state polycrystalline materials conduct the protons more or less in their crystal structure. Some hydrated crystalline compound based on metal oxide cluster or polyoxometallate anion such as $\text{PMo}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ shows a very high ionic conductivity, as high as $10^{-1} \text{ S} \cdot \text{cm}^{-1}$ at room temperature⁵. Mostly the proton conductors are hydrates/hydrogen bonded materials^{6–8} (*e.g.*, $\text{MoO}_2 \cdot 2\text{H}_2\text{O}$, $\text{APT} \cdot 5\text{H}_2\text{O}$, HUP, PTA, etc.), some polymers ($\text{PEO-NH}_4\text{ClO}_4$, $\text{PEO-NH}_4\text{I}$), some ferroelectric materials (ADP, KDP), some glasses, geis and some dispersed phase composite materials (like Al_2O_3 dispersed in PMA, PTA)^{9–12} also. In hydrated salts, the high content of water (which facilitates the high protonic conductivity) gives the advantage on the other groups of materials in device application¹³. Some wet-coated thin film is also reported for high protonic conductivity¹⁴. In this paper, we deal with the detailed thermal and rehydration studies and protonic conduction in a hydrated salt, Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) at temperature (RT–120°C). The proton conducting behaviour has been established with different experimental techniques like DTA and TGA, IR, TIC and electrical conductivity measurements.

EXPERIMENTAL

The salt hydrate ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Glaxo, India) was of the analytical grade of purity. All the pellets were prepared on a pressure of 7.5 kg cm^{-2} for the experimental characterizations.

Thermal analysis was carried out by Linseis (2045) DTA/TGA/DTG instrument on a constant heating rate of 5°C/min in the temperature range of 27°C–350°C. Alumina powder was used as a reference material. To study the rehydration of the dehydrated salt¹⁵: (i) FeSO₄·7H₂O was heated in an oven at 325°C for 24 h [it is expected that if this dehydrated salt is exposed in the ambient (R.H. *ca.* 60%), it regains its water of crystallization from the atmosphere]. (ii) The dehydrated salt pellet/powder was kept in an electronic balance (sensitivity *ca.* ± 0.0001 g) and the change in mass with time was recorded.

Infrared spectroscopy is an important tool for studying vibrations of different groups/fingerprints present in the compound. Therefore, structural changes introduced on thermal dehydration or by any other cause would be reflected in the IR spectra of the salt. To record the IR spectra the salt was dispersed in KBr powder in the ratio 1 : 100. Thin pellets were made and their IR spectra were recorded by Perkin-Elmer infrared spectrophotometer 778 model.

The total ionic transport number was measured by Wagner's method of polarization¹⁶. In this method, the sample pellet is sandwiched between a blocking and a non-blocking electrode. For the mobile protonic species (due to their gaseous nature), no ideal blocking electrodes are available. As a compromise, we use the thick silver coating as a blocking electrode. To polarize the sample a constant d.c. potential was applied across the cell such that the mobile ionic species moves toward the blocking electrodes. The experimental arrangement is shown in Fig. 1. The current passing through the sample was monitored as a function of time for a sufficiently long time to allow the sample get fully polarized. In the current vs. time plot, the initial total current (*i*_T) is the sum of the current contributed by both the ionic as well as the electronic species. The final *i*_e, the residual current is due to electronic conduction only. The total ionic transference number (*t*_{ion}) is given as

$$\begin{aligned} t_{\text{ion}} &= 1 - \frac{\sigma_e}{\sigma_T} \\ &= 1 - \frac{i_e}{i_T} \end{aligned} \quad (1)$$

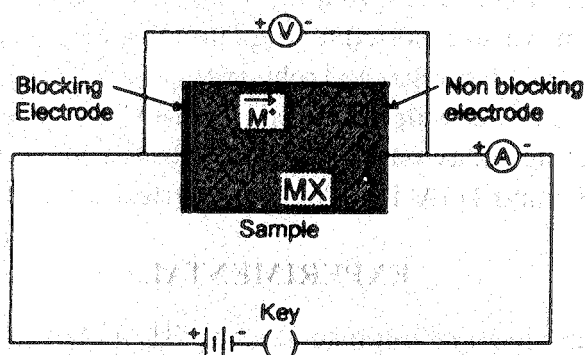


Fig. 1. Experimental arrangement for measuring transference number by Wagner's method of polarization

To check the nature of the mobile species in FeSO₄·7H₂O, coulometry technique¹⁷ (double arm coulometer)¹⁸ was applied. The pellet was mounted by

epoxy in the coulometer and a very small current was applied. Now, we measured the volume of the gas evolved on both sides (cathodes and anodes) of the coulometer as a function of time. The electrolysis was carried out by passing a small current (i) through the sample for a fixed time (t). The total charge (Q) passed through the sample is ($i \times t$). The charge equivalent (Q') corresponding to each mobile species can be calculated by Avogadro's law and the volume of the gas evolved on the electrodes. The observed volume (V_2) of the gas evolved at anode or the cathode side at RT (T_2) is first converted to the corresponding volume at NTP (P_1, T_1) by the equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (2)$$

where P_2 is the corrected pressure. The transference number t_i of the different gaseous species is evaluated by the formula

$$t_i = \frac{Q'}{Q} \quad (3)$$

where Q' is the charge equivalent to the volume of the gases evolved.

To confirm the number of mobile species we used the transient ionic current (TIC) method¹⁹. In this method, a sample pellet was placed in between two blocking electrodes and polarised by the application of small dc potential. The mobile ionic species accumulate at their respective electrodes resulting in polarization. On reversing the polarity of the applied field, these ionic species start to move in the reverse direction. Since different ions have different mobilities, they reach their counter electrodes at different times giving peaks in the current vs. time plot. By measuring the time (τ) taken for each peak, the mobility μ of the mobile ionic species can be calculated as

$$\begin{aligned} \mu &= \frac{\text{Velocity}}{\text{Electrical field}} = \frac{l/\tau}{V/l} \\ &= \frac{l^2}{V\tau} \end{aligned} \quad (4)$$

where l is the thickness of the sample, τ is the time of flight and V is the applied potential.

The electrical conductivity measurement was carried out by complex impedance/admittance plot with the help of computer controlled "Schulmberger Solartron 1250 frequency response analyzer coupled with 1286 electrochemical interface". The electrical conductivity was measured with varying temperature and humidity. The frequency range of measurement was 1 Hz to 65 kHz.

RESULTS AND DISCUSSION

(a) Structural and Thermal Properties

Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is green in colour and occurs in nature in crystalline form as an oxidation product of iron containing sulphide called melanterite. It belongs to a series of compound ($\text{M}^{2+}\text{SO}_4 \cdot n\text{H}_2\text{O}$), where M^{2+} is

Fe^{2+} cation with an appropriate ionic radius 0.7 Å. Many hydrates with $n = 1, 4, 5, 6$ and 7 are known.

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is monoclinic and crystalline in a space group $\text{C}_{2h}^5\text{P}_{21/c}$ with

Fe(1) :	(2a)	0	0	0 : 0	1/2	1/2
Fe(2) :	(2d)	1/2	1/2	0 : 12	0	1.2

and all other atoms in the general position

$$(4e) + (xyz, 1/2 - y, z + 1/2)$$

with the lattice parameters

$$a = 14.072 \text{ \AA}$$

$$b = 6.503 \text{ \AA}$$

$$c = 11.041 \text{ \AA} \text{ and } \beta = 105^\circ 36' 1''$$

There are four formula units per unit cell. The iron ions occupy a special position such that each iron ion is surrounded octahedrally by six water oxygens. The mean bond length $\text{Fe}-\text{O}(\text{w})$ is 2.12 Å and $\text{O}\cdots\text{H}-\text{H}$ is 2.82 Å. The bond length of Fe^{2+} to non-coordinated water is 2.19 Å.

To study the thermal behaviour, we recorded (shown in Fig. 2) the DTA/TGA curve of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the temperature range 27–350°C. In TGA, there are distinctly three steps 28–90°C, 90–135°C, 135–300°C in which the weight loss occurs. In the temperature range 28–90°C the weight loss is *ca.* 17% which means the loss of three water molecules from the lattice. In the second step (temperature range 90–135°C) the weight loss obtained is again *ca.* 17% meaning a loss of

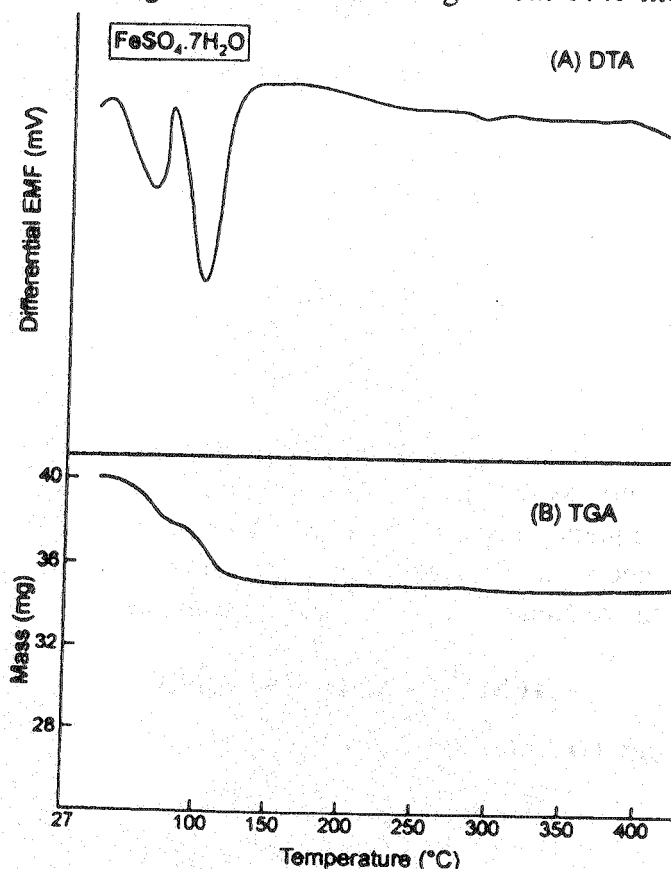
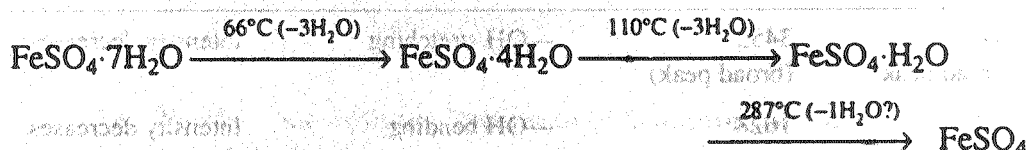


Fig. 2. DTA and TGA curve of ferrous sulphate

further three water molecules. In the temperature range $135\text{--}300^\circ\text{C}$ the loss in weight is 2% which is slightly less than one molecule of water left in the lattice. In the formula $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ the total water content is 40% but the loss of water due to dehydration is only 36%. These results agree with Duval (1963)²¹, who has also shown that ferrous sulphate really does not carry 7 water molecules and the actual water of crystallization is between 6 and 7. In the DTA traces, there are three endothermic peaks at 66° , 110° and 287°C . The peak at 66°C is due to the loss of three water molecules from the lattice. The peak at 110°C is related with fast or violent removal of further three water molecules. This process is called as boiling of ferrous sulphate²². There is a very small peak at 287°C which may be due to the loss of the last removable water of crystallization.

The phase transition behaviour of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ can be summarized as:



The changes appearing after dehydration are also confirmed by infrared spectroscopy. We recorded the IR spectra of hydrated and dehydrated salts. These salts were dispersed in KBr in the ratio (1 : 100) and IR spectra were recorded as shown in Fig. 3 after preparing the pellets of the powder. The assignments of various groups recorded (before and after heating) are given in Table-1. In the hydrated salt, there is a strong and very broad band obtained in the region $2800\text{--}3400\text{ cm}^{-1}$ related with the —OH stretching mode and other —OH related band, namely, —OH bending *ca.* 1650 cm^{-1} . On dehydration, the intensity of the peak decreases considerably/disappears. The reduction in the peak intensity supports the conclusion regarding the dehydration by DTA/TGA studies. The ν_3 , ν_1 and ν_4 modes of SO_4^{2-} respectively appear at *ca.* 1100 cm^{-1} , *ca.* 950 cm^{-1} and 650 cm^{-1} within $\pm 40\text{ cm}^{-1}$.

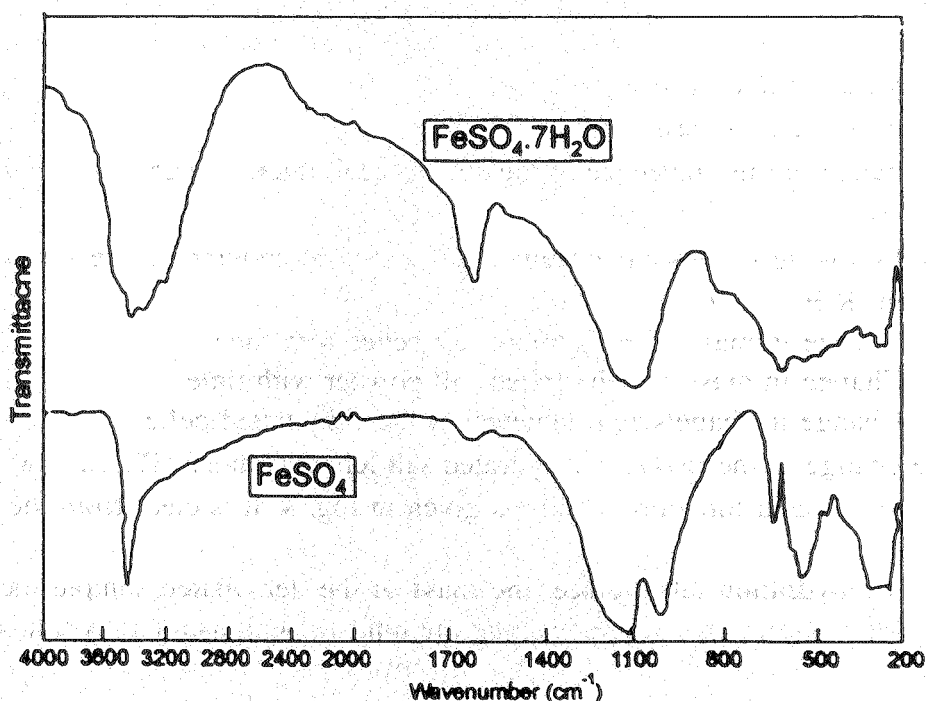


Fig. 3. Infrared spectra of hydrated and dehydrated ferrous sulphate

Evidence of ν_2 mode at 470 cm^{-1} is also present but is not very clear due to its low intensity and the presence of many likely liberation modes. The SO_4 group is surrounded by the water of crystallization molecules and hence their removal on dehydration changes the symmetry. In the present case ν_3 , ν_1 and ν_4 peaks after dehydration respectively are 1098 – 1125 , 990 – 1018 and 616 – 642 cm^{-1} . These peaks in the dehydrated samples are more sharper and well defined.

TABLE-I
THE ASSIGNMENT OF VARIOUS GROUPS OF VIBRATIONS IN $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Band position in hydrated salts (cm^{-1})	Band position in dehydrated salts (cm^{-1})	Assignments ²⁷	Remarks (Effects after dehydration)
3461 (broad peak)	3455 (broad peak)	—OH stretching	Intensity decreases
1624	1628	—OH bending	Intensity decreases
1098	1125	ν_3 mode of sulphate group	Sharp and well defined peak
990	1018	ν_1 mode of sulphate group	Sharp and well defined peak
616	642	ν_4 mode of sulphate group	Sharp and well defined peak

(b) Rehydration of Dehydrated Salts

The dehydrated salt hydrates are expected to take up water molecules from the ambient (rehydration) since the original salt prefers to have water of crystallization for attaining the stable structure. Therefore, it would be interesting and useful to know the rehydration behaviour of the sample left under RT ambient. The rehydration may lead to

- an increase in mass, and
- change in the shape/size of the pellet due to interlayer absorption of water molecules.

The following studies have been carried out in room temperature atmospheric condition (R.H. ca. 60%).

- Change in mass of dehydrated salt pellet with time.
- Change in mass of dehydrated salt powder with time.
- Change in shape/size (diameter) of the dehydrated pellet.

The change in the mass of dehydrated salt left in ambient (RT ca. 300 K and RH ca. 60%) as a function of time is given in Fig. 4. It is clear from the figure that:

- as rehydration takes place, the mass of the dehydrated sample increases and saturates to a value defining the limit of permissible rehydration;
- the increase in mass in FeSO_4 is astonishingly low and indicates as if it is not taking back all its lost seven water molecules.

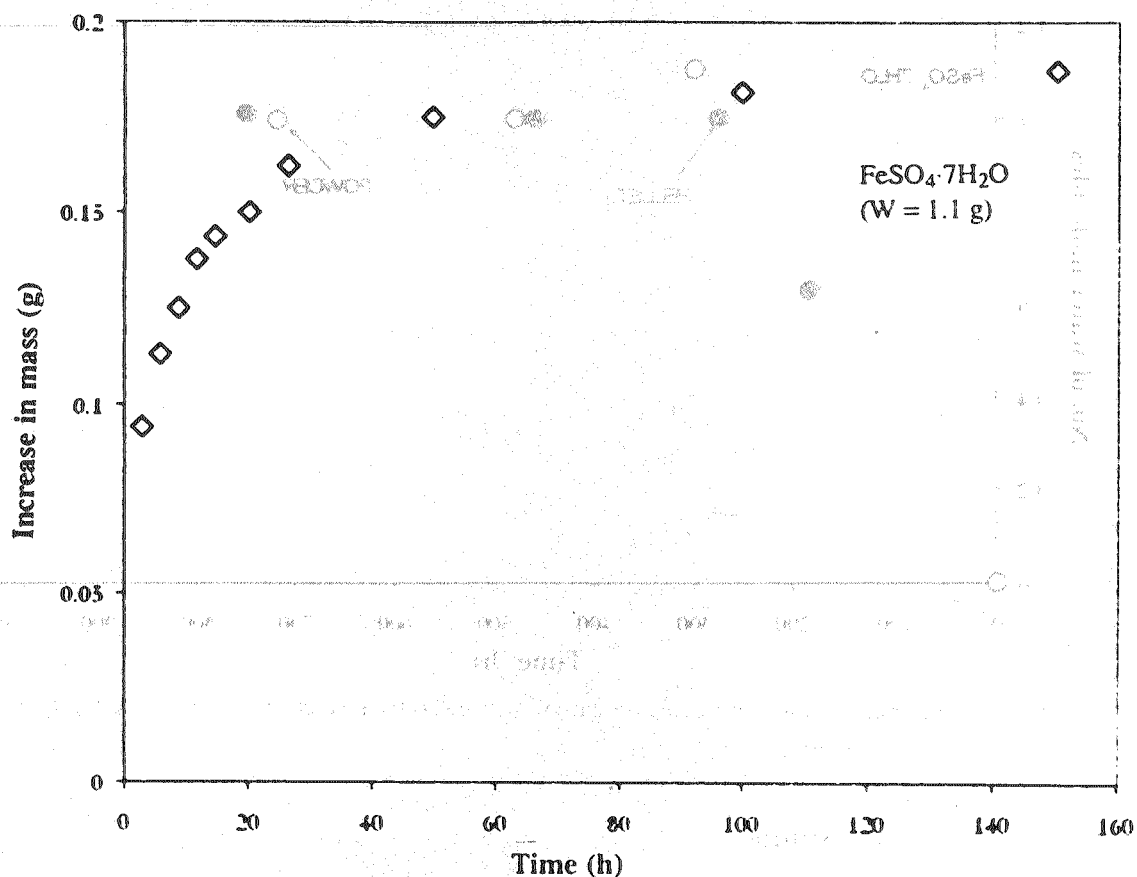


Fig. 4. Change in mass of dehydrated ferrous sulphate as a function of time

We have reconverted the data of change in mass as a function of time into the data of regained water molecules as follows. Let m_0 be the mass of dehydrated salt which becomes m_1 after a particular time t . Therefore, the number of water molecules (x) regained in time t is given by

$$x = \left(\frac{M_s}{M_w} \right) \left\{ \frac{m_1 - m_0}{m_0} \right\} \quad (5)$$

where M_s and M_w are respectively the molecular weights of the dehydrated salts and one water molecule.

The number of water molecules regained by the dehydrated salt after different intervals of the time is shown in Fig. 5. In the present case, the regaining of water molecule is extremely slow. In fact after *ca.* 600 h the number of water molecules regained is only one while the water of crystallization lost during dehydration was 7. So, rehydration of FeSO_4 is not a favoured process.

Visually it was observed that the shape and size of the pellets of dehydrated salts change on rehydration. In FeSO_4 , the pellet retained its shape reasonably up to *ca.* 600 h, because the regaining of their lost water molecule in this case is extremely slow and only a part (one of seven) of the lost water molecule is regained.

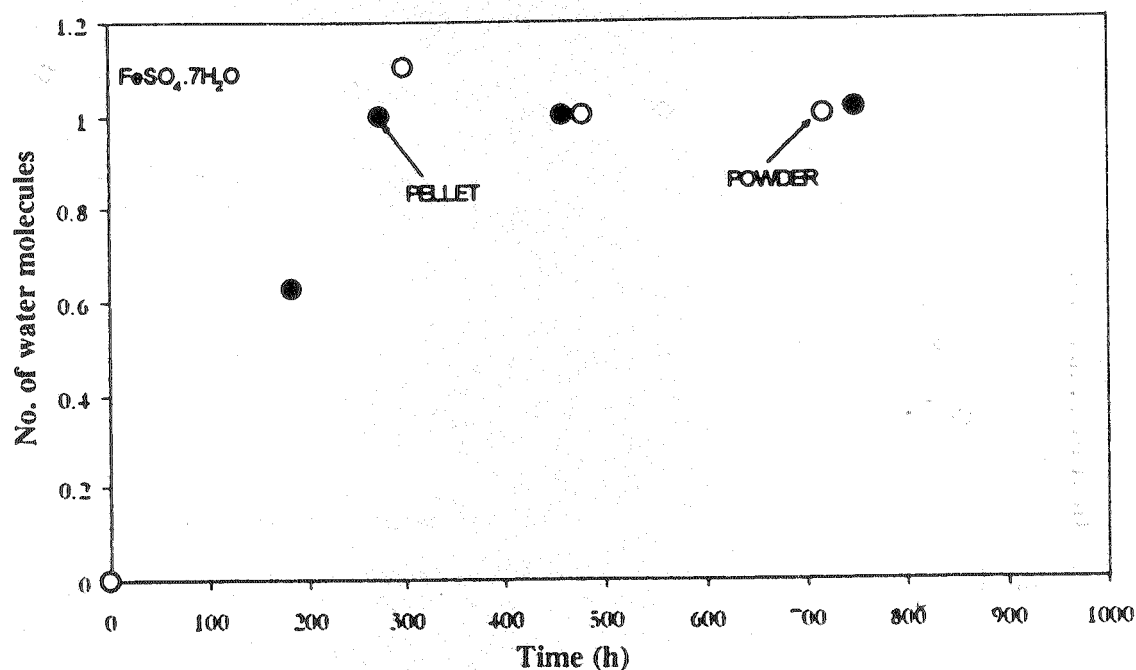


Fig. 5. The number of water molecules regained by FeSO_4 as a function of time (filled dot for powder and open dot for pellet)

(c) Ion Transport Studies

The following studies are reported in order to gain some insight into the mechanism of charge transport in them:

- (i) Transference number:
 - (a) Total ionic transport number by Wagner's polarisation method.
 - (b) Cationic and anionic transference number by coulometry.
- (ii) Mobility by transient ionic current (TIC) technique.
- (iii) IR spectroscopy on sample before and after the ionic transport has occurred to get clues about possible transport mechanism.
- (iv) Electrical conductivity (by impedance spectroscopy) as a function of temperature and humidity.

(i) Transference Number Measurement

(a) **Total ionic transport number by Wagner's polarisation method:** To evaluate the value of t_{ion} , Wagner's polarization method has been applied. In this, we monitor the current with time, the initial current i_{initial} and final current after polarization i_{final} are evaluated by the I vs. t curve. The ionic transference number was calculated using the equation

$$t_{\text{ion}} = \frac{t_{\text{initial}} - t_{\text{final}}}{t_{\text{initial}}} \quad (6)$$

The current vs. time plot for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is shown in Fig. 6. The calculated value of ionic transference number is 0.91. This value is, at best, qualitative because of the:

- (1) Non-availability of ideal blocking electrodes, and
- (2) Uncertainty in measurement of true i_{initial} .

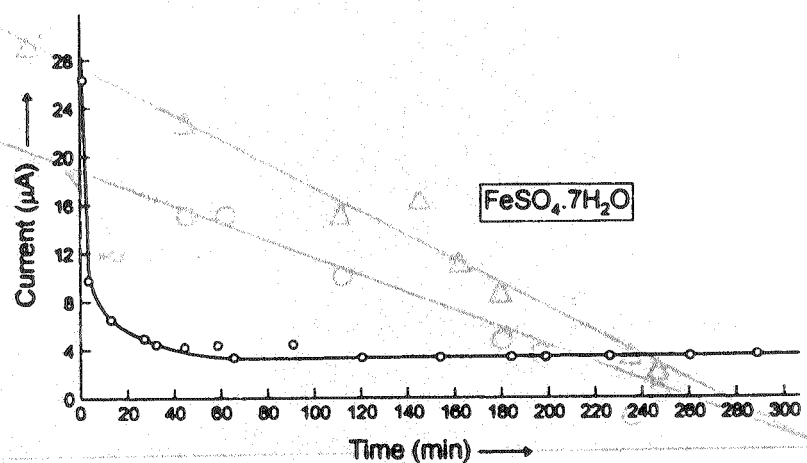


Fig. 6. Current vs. time plot in a typical Wagner's polarisation plot on $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ pellet

To study the cationic and anionic contribution in protonic conductors (where the discharging species at electrodes are gas) a double arm coulometer (Fig. 7) was used. In this technique, a constant d.c. current is passed through the sample pellet mounted in the coulometer. The volume of the gas evolved on the anode and cathode side are measured and analyzed. In $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ pellet, after passing a d.c. current gases evolved both at the anode and cathode sides (Fig. 8) indicating the mobility of both cationic (possibly H^+) as well as anionic species (possibly OH^-). The cathode side gas has been tested using gas chromatography and found to be hydrogen. The likely mechanism of the evolution of H_2 at cathode and O_2 at the anode is discussed elsewhere²³. The calculated cationic and anionic contributions are 68% (t_{H^+}) and 22% (t_{OH^-}). This value is similar to the value obtained by total ionic transference number (91%).

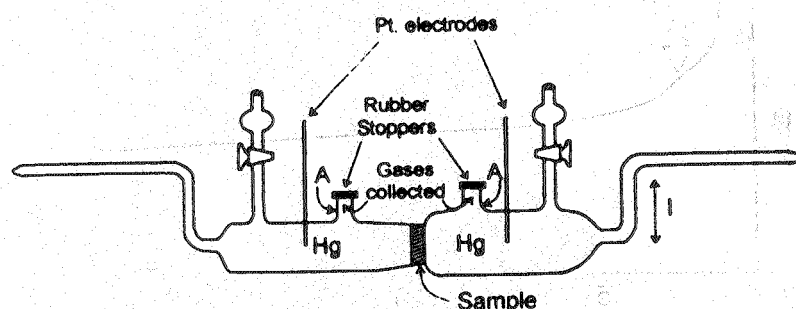


Fig. 7. Double arm electrolysis cell (coulometer) for proton conductor

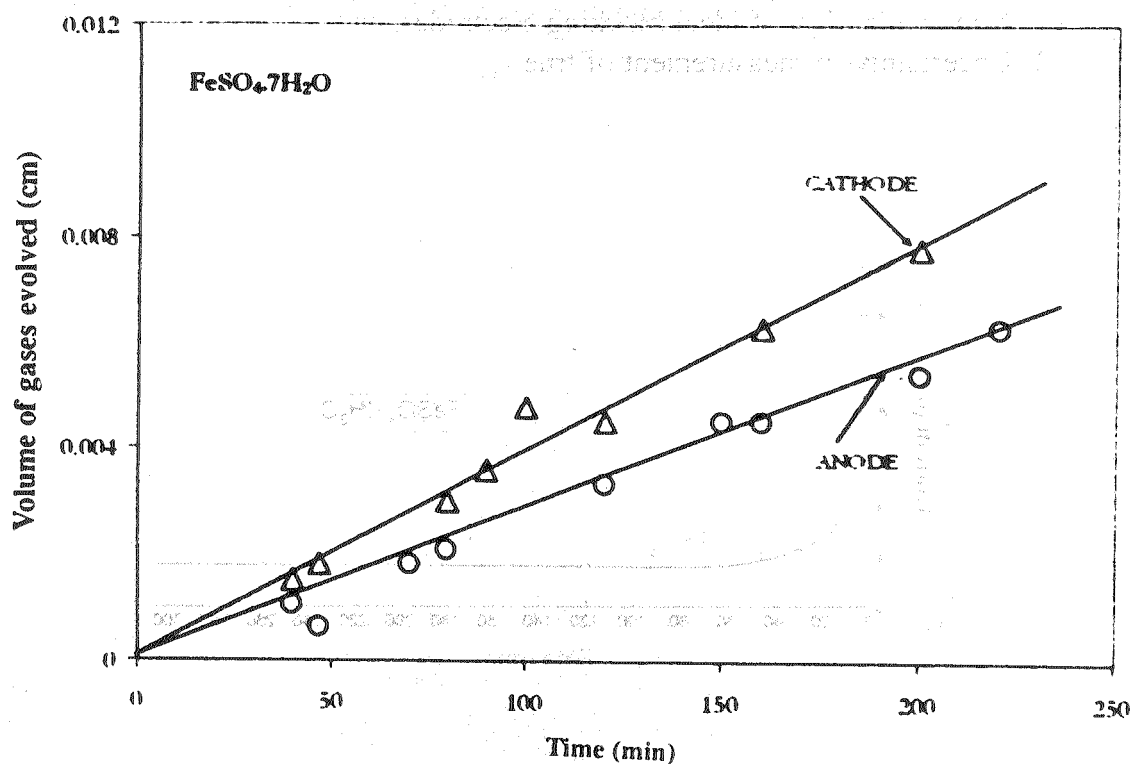


Fig. 8. The volume of the gas evolved in FeSO₄·7H₂O on the cathode side (hollow dot) and anode side of the coulometer as a function of time (applied current *ca.* 15 μ A).

(ii) Ionic Mobility Measurement and IR Spectral Study

Transient ionic current (TIC) measurement method has been widely used to find the number of "type of mobile ionic species" as well as their respective mobilities²⁴. The current vs. time plot for FeSO₄·7H₂O is shown in Fig. 9. Here

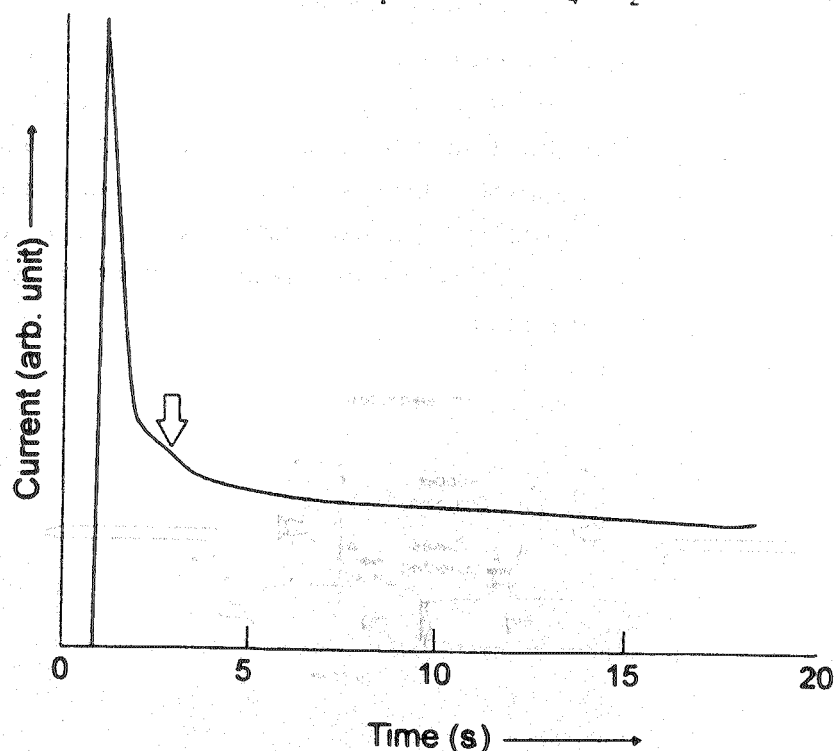


Fig. 9. Current vs. time plot of transient ionic current measurement on FeSO₄·7H₂O

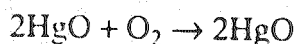
a single broad peak can be observed. This could be due to the fact that either there is only one type of mobile species or there are still two types of mobile species with nearly same mobilities which could not be resolved in TIC experiment. The latter look more reasonable since the likely species in this system may also be arising from the equation



The calculated value of mobility $\mu_1 = \mu_2 = \mu = 2.5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

From coulometry and TIC measurements, it is clear that H^+ and OH^- are the two possible ionic species. These discharge themselves as gaseous products (H_2 or O_2) at the electrodes on the application of dc electric field. Thus the electrolysed sample is expected to have different stoichiometric composition than the original sample.

The IR spectra (essentially a fingerprint of various groups present in the material) of the original and electrolyzed samples were recorded and it is expected that both should be different. To check this, nearly equal amounts of original and scraped samples from the cathode and anode sides of the electrolyzed pellet were dispersed in KBr in the ratio 1 : 100, thin pellet prepared and IR spectrum recorded. Fig. 10 shows the IR spectra of (a) unelectrolyzed original sample, (b) electrolyzed sample scraped from the cathode and (c) electrolyzed sample scraped from near the anode. The assignments of the peak of original and electrolyzed samples are given in Table-2. The appearance of new HgO peak in IR spectrum of the scraped sample of anode side is due to the surface reaction between discharging O_2 and the mercury electrode in contact



or

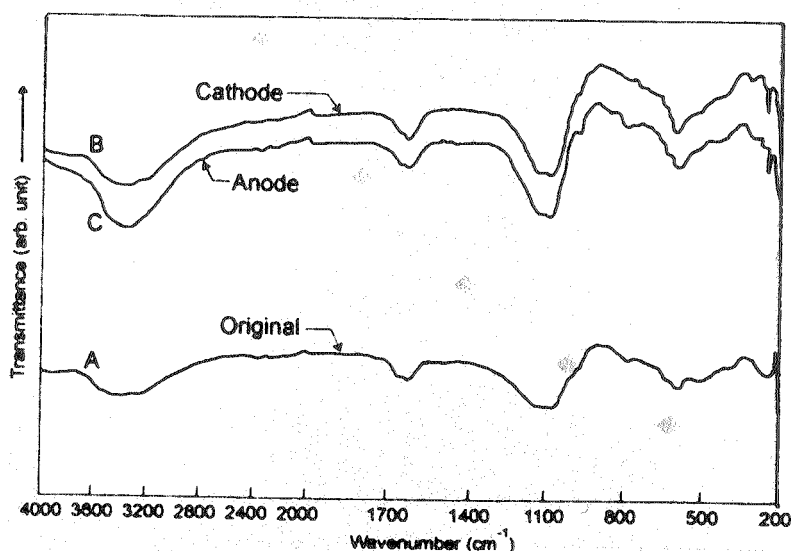


Fig. 10. IR spectra of original and electrolyzed (from cathode and anode side) samples

TABLE-2
THE IR BAND POSITIONS AND THEIR ASSIGNMENT OF THE ORIGINAL AND ELECTROLYZED $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Original sample	Electrolyzed sample		Assignments	Remarks
	Cathode side	Anode side		
3441	3375	3393	—OH stretching	
1625	1624	1623	—OH bending	
1097	1093	1140	ν_3 mode of sulphate group	
—	—	860	HgO peak	New peak
—	—	805	HgO peak	New peak
620	625	615	ν_4 of sulphate group	

(iii) Electrical Conductivity Measurements

The electrical conductivity was evaluated using complex impedance/admittance plots. Measurements were done in the frequency range 1 Hz–65 kHz. These measurements were done on the polycrystalline pellet using silver paste on both faces as an electrode. For polycrystalline sample, the control of pelletizing pressure is an important parameter because it changes the packing (and hence the grain boundary effects). Further this is more important for material with water of crystallization (or hydrates) since by using too high pressure it may result in partial dehydration. The electrical conductivity at room temperature as a function of pelletizing pressure is shown in Fig. 11. This indicates that the conductivity of the

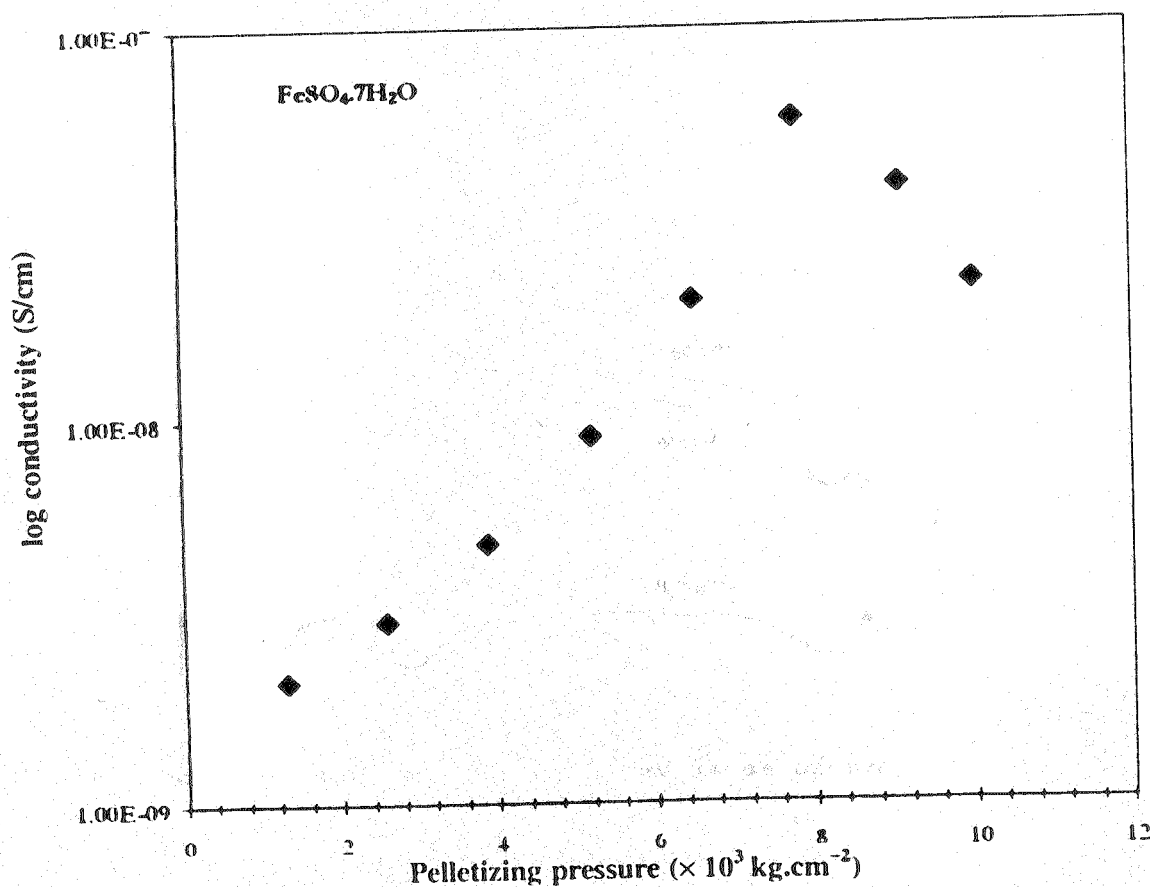


Fig. 11. Pressure dependence of electrical conductivity of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ pellet

pellet for low pelletizing pressure is lower because of poor packing. Again, at high pressure, the conductivity values show a decreasing trend. This is probably due to the removal of some of the water of crystallization by the high pressure applied for pelletizing. At high pressure the pellet becomes sticky and wet in the pelletizing die. For further conductivity measurement the best pressure is 7.5 kg/cm^2 .

Some typical impedance/admittance plots for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are shown in Fig. 12. The bulk electrical conductivity of the hydrated salts as a function of temperature is shown in Fig. 13. This figure shows that with increasing temperature the conductivity initially increases, attains a maxima and then decreases. The $\log \sigma$ vs. $1/T$ plots in the temperature range $25\text{--}45^\circ\text{C}$ are somewhat linear which suggests a "thermally activated Arrhenius type"²⁵ conductivity

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{KT}\right) \quad (10)$$

in the limited temperature range of measurement. In this expression σ_0 is the pre-exponential factor and E_a is the activation energy. The calculated values of σ_0 and E_a are $6.0 \times 10^{-2} \text{ S-cm}^{-1}$ and 0.31 eV respectively. The Arrhenius type linearity is only in a very short span of temperature; therefore, these values (σ_0 and E_a) are best tentative. At higher temperature (more than 150°C), the measurements are not possible because the leaving water molecules which are pending during dehydration lead to self-dissolution²⁶ to the salt and the pellet becomes sticky/wet.

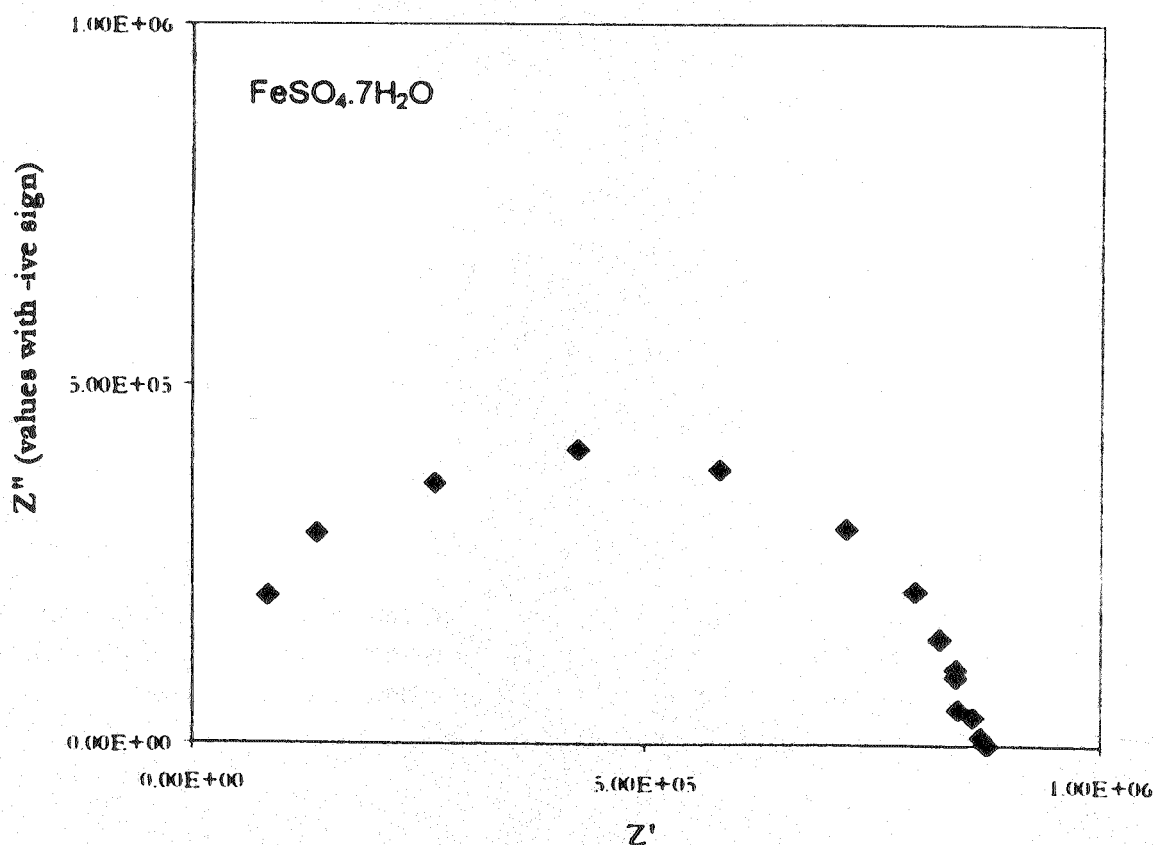


Fig. 12. A typical complex impedance plot for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ pellet at $T = 303 \text{ K}$

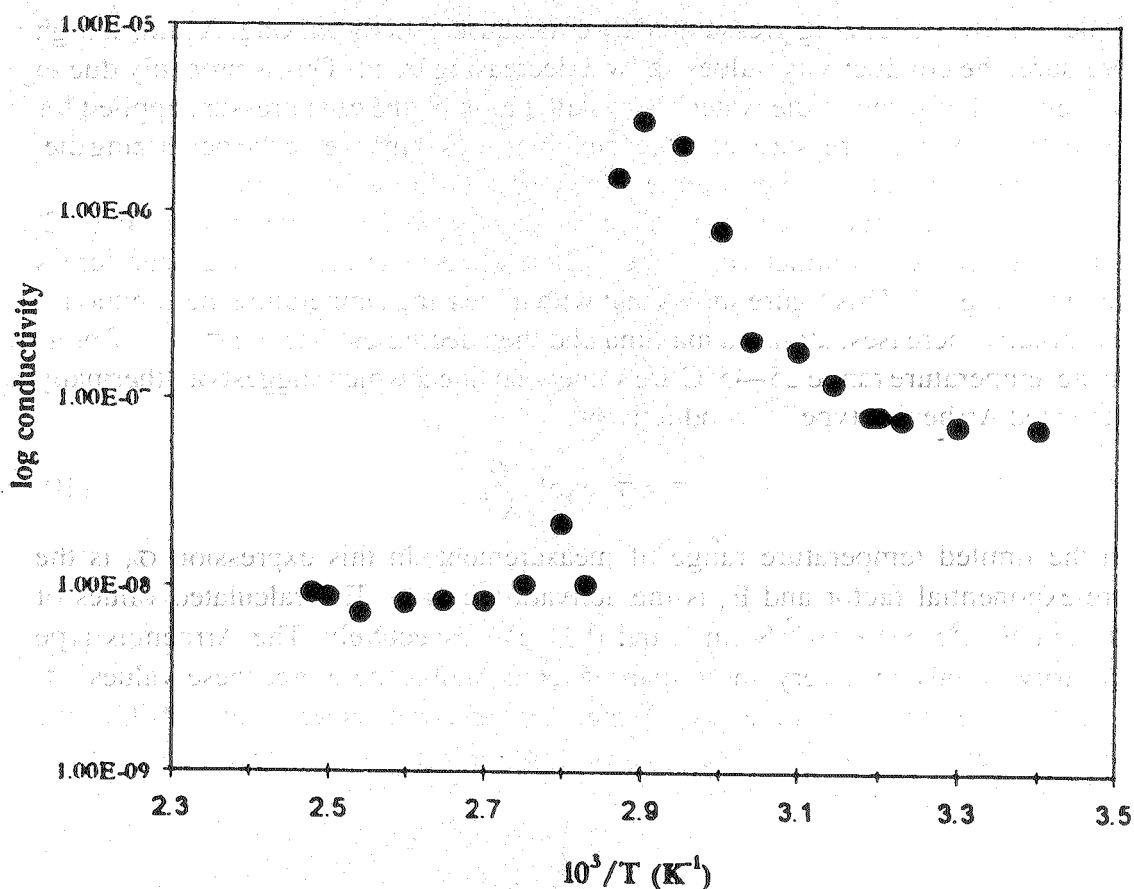


Fig. 13. Temperature dependence of bulk electrical conductivity of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ pellet

In general the ionic conductivity is expressed as

$$\sigma = \sum_i n_i q_i \mu_i \quad (11)$$

Here n_i is the number of charge carriers, q_i is the charge and μ_i is the ionic mobility. In $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, there are two types of charge carriers, viz., cations (H^+) and anions (OH^-). So the equation (11) can be written as

$$\sigma = \sigma_{\text{cation}} + \sigma_{\text{anion}}$$

where

$$\sigma_{\text{cation}} = n^+ \mu^+ q$$

$$\sigma_{\text{anion}} = n^- \mu^- q$$

where n^+ , n^- and μ^+ , μ^- are the respective numbers and mobilities of cation and anion. The values of σ_{cation} and σ_{anion} can also be written in terms of transference numbers. We can calculate the number of cations and anions as follows:

$$n_{\text{cation}} = \left(\frac{t_{\text{cation}} \cdot \sigma}{\mu^+} \right) q \quad (12)$$

$$n_{\text{anion}} = \left(\frac{t_{\text{anion}} \cdot \sigma}{\mu^-} \right) q \quad (13)$$

The values of μ^+ and μ^- are calculated by TIC experiment and t_{cation} and t_{anion} by coulometry. The calculated values are

$$\begin{aligned}\sigma_{\text{measured at RT}} &= 2.7 \times 10^{-7} \text{ S cm}^{-1} \\ \sigma_{\text{cation calculated}} &= 1.85 \times 10^{-7} \text{ S cm}^{-1} \\ \sigma_{\text{anion calculated}} &= 6.9 \times 10^{-8} \text{ S cm}^{-1}\end{aligned}$$

Calculated values of

$$\begin{aligned}n_{\text{cation}} &= 4.4 \times 10^{14} \text{ cm}^{-3} \\ n_{\text{anion}} &= 1.5 \times 10^{14} \text{ cm}^{-3}\end{aligned}$$

The variation of conductivity as a function of relative humidity is shown in Fig. 14. In the figure the conductivity initially increases at a faster rate up to R.H. *ca.* 50%, then slows down and finally after R.H. *ca.* 85% it increases rapidly again. This increase may be an artifact because of surface dissolution of the salt due to high humidity content in the ambient.

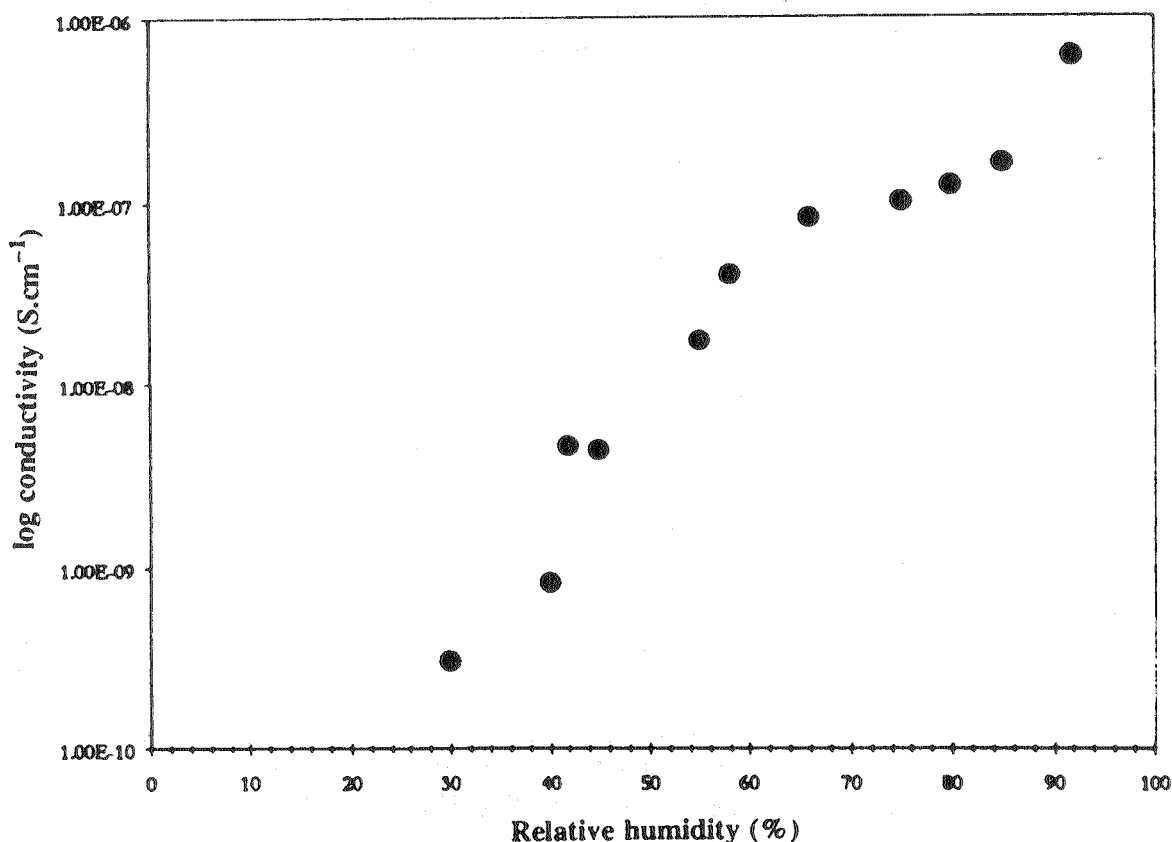


Fig. 14. Humidity dependence of electrical conductivity of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ pellet

Conclusions

On the basis of above observations it is clear that hydrated ferrous sulphate has a good protonic behaviour in the temperature range RT–100°C. The thermal studies are indicative of removal of water of crystallization in three different steps. In rehydration, only last stepped removed water has regained. In $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, rehydration is not a favourable process. Coulometry suggests two types of mobile species H^+ and OH^- with nearly same mobility ($\mu = 2.5 \times 10^{-3} \text{ cm}^2/\text{V sec}$).

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REFERENCES

1. S. Chandra, *Superionic Solids: Principles and Applications*, North Holland, Amsterdam (1981).
2. J. Jensen and M. Kleitz, *Solid State Protonic Conductors-I*, Odense University Press, Denmark (1981).
3. S. Chandra, in: A.L. Lasker and S. Chandra, (Eds.), *Superionic Solids and Solid Electrolytes: Recent Trends*, Academic Press, New York, p. 185 (1989).
4. M. Hibino, T. Kusakabe and T. Kudo, in: B.V.R. Chowdari, H.L. Yoo, G.M. Choi and J.H. Lee (Eds.), *Solid State Ionics: Science and Technology*, World Scientific Pub. Co., p. 275 (1998).
5. O. Nakamura, T. Kodama, I. Ogino and Y. Miyake, *Chem. Lett.*, **1**, 17 (1979).
6. S. Chandra, *Material Science Forum-I*, 153 (1984).
7. J. Livage, *Solid State Ionics*, **50**, 307 (1992).
8. M. Nogami, K. Miyamura and Y. Abe, *J. Electrochem. Soc.*, **144**, 121 (1997).
9. C.C. Liang, *J. Electrochem. Soc.*, **120**, 1289 (1973).
10. K. Shahi and J.B. Wagner, *J. Phys. Chem. Solids*, **43**, 713 (1982).
11. J. Maier, *J. Phys. Chem. Solids*, **46**, 309 (1985).
12. N. Lakshmi, K. Pandey, P.K. Singh and S. Chandra, in: B.V.R. Chowdari, H.L. Yoo, G.M. Choi and J.H. Lee (Eds.), *Solid State Ionic: Science and Technology*, World Scientific Pub. Co., p. 65 (1998).
13. S.A. Hashmi, D.K. Rai and S. Chandra, *J. Mat. Sci.*, **27**, 175 (1992).
14. H. Okamoto, K. Yamnaka and T. Kudo, *Mat. Res. Bull.*, **21**, 551 (1986).
15. K. Pandey, S.A. Hashmi and S. Chandra, in: B.V.R. Chowdari, H.L. Yoo, G.M. Choi and J.H. Lee (Eds.), *Solid State Ionics: Material and Applications*, World Scientific Pub. Co., p. 689 (1992).
16. J.B. Wagner and C. Wagner, *J. Chem. Phys.*, **26**, 1597 (1957).
17. C. Tubandt, *Z. Anorg. Allgen. Chem.*, **110**, 234 (1920a).
18. S. Chandra, N. Singh and B. Singh, *Solid State Communi.*, **57**, 519 (1986b).
19. S. Chandra, S.K. Tolpadi and S.A. Hashmi, *Solid State Ionics*, **28-30**, 651 (1988).
20. R.W.G. Wyckoff, *Crystal Structure*, Vol. 3, Interscience Publishers, Inc., New York (1960).
21. C. Duval, *Inorganic Thermogravimetric Analysis*, Elsevier Publ. Comp., Amsterdam, London-New York (1963).
22. L.G. Berg, and A.V. Nikolaev, *IZV Akad. Nauk SSSR*, 865 (1940).
23. K. Pandey and M.M. Dwivedi, *Science Lett.*, **25**, 99 (2002).
24. K. Pandey, Ph.D. Thesis, B.H.U., Varanasi (1995).
25. Ph. Colombon, *Proton Conductors: Solid, Membrane and Gels: Materials and Devices*, Cambridge University Press (1992).
26. A.B. Gancy, J.M. Rao and W.M. Wanner, *J. Am. Ceram. Soc.*, **64**, 119 (1981).
27. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York (1986).