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Study of Dehydrated Salts: Electrolyte for Intermediate Temperature Fuel Cell

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Abstract

Fuel cells are receiving growing interest in recent years since they represent one of the most promising energy source to reduce pollutant emission. We propose some new dehydrated salts as an electrolyte in the intermediate temperature fuel cell. The proton conduction in the dehydrated salts was established by the study of DTA/TGA, infrared spectroscopic study, transference number, bulk electrical conductivity measurement and emf study. The electrical conductivity of the dehydrated salts becomes ionic and increases 100-1000 times in the hydrogen ambient with respect to vacuum.

Keywords: hydrogen-oxygen, fuel cell, proton conductor, dehydrated salt, electrochemical emf.

Introduction

In the present scenario, because of the increasing energy demand and the growing concern about the limited fossil fuel, the scientific community has focused its attention towards the development of alternating power generation technologies with the potential for low pollution. Usually the solar cells and the fuel cells are the main sources of the non conventional energy. These non conventional energy sources are advantageous because they are clean and economical. Recently, the proton conducting materials (as an electrolyte) have become the hot contenders for the electrochemical device applications like batteries, fuel cell and sensors [1-4]. Most of the good proton conductors are hydrates or hydrogen bonded materials which are unstable at high temperatures. For the fuel cell applications, generally 200 °C or more is the preferable

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temperature due to good thermodynamic efficiency. Many sintered oxides like SrCeO₃, BaCeO₃, SrZrO₃ doped with Y₂O₃, Yb₂O₃, etc., which are p-type semiconductors, show proton conducting behavior at high temperature in H₂/humid ambient [5-7]. A series of materials KTaO₃ doped with Ni, Fe or Li₅AlO₅ show protonic behavior at intermediate temperature range (200-500 °C) [8-12]. In the present communication, we report the proton conducting behavior of some specific salt hydrates (i.e. Al₂(SO₄)₃.16H₂O, AlNH₄(SO₄)₂.12H₂O and FeSO₄.7H₂O), which show a good conduction in the hydrated state as well as after the dehydration in the intermediate temperature range (200-400 °C). This unusual behavior of the dehydrated salts makes it a best candidate for electrochemical application. The proton conduction in the dehydrated salts was established by the study of DTA/TGA, transference number, bulk electrical conductivity measurement and emf study.

Experimental techniques

Dehydration of salt hydrates and ion transport study

Salt hydrates (namely aluminum sulphate, aluminum ammonium sulphate and ferrous sulphate) are of analytical grade. These salts are dehydrated by heating the samples at 300 °C, 220 °C and 300 °C, respectively, in an oven. The dehydration of the salts is confirmed by the TGA record as shown in Fig. 1.



Figure 1. TGA spectra of three salts: $Al_2(SO_4)_3.16H_2O$, $AlNH_4(SO_4)_2.12H_2O$ and $FeSO_4.7H_2O$.

From the TGA, it is clear that all three salt hydrates are not completely dehydrated in a single step. For example, in the first step, aluminum sulphate losses two water molecules of crystallization up to 120 °C; in the second step (up to 145 °C) next eight water molecules and finally the last six water molecules were removed from the lattice up to 300 °C [13]. Dehydration of $Al_2(SO_4)_3.16H_2O$ is given as

$$Al_{2}(SO_{4})_{3}.16H_{2}O \xrightarrow{120^{\circ}C} Al_{2}(SO_{4})_{3}.14H_{2}O \xrightarrow{145^{\circ}C} \xrightarrow{-8H_{2}O} \xrightarrow{-8H_{2}O} Al_{2}(SO_{4})_{3}.6H_{2}O \xrightarrow{300^{\circ}C} Al_{2}(SO_{4})_{3}$$
(1)

For aluminum ammonium sulphate, Duval (1959) [14], proposed a mechanism for weight loss by assigning $AlNH_4(SO_4)_2.12H_2O$ the chemical formula NH_4 $[Al(H_2O)_2(SO_6H_4)_2]6H_2O$. On heating there is a loss of 6 molecules of water of crystallization up to 120 °C, then a subsequent loss of 4 water molecules at ~140 °C comes from group (SO₆H₄)₂, leaving behind the SO₄⁻⁻ group. Finally, the last two molecules of water attached to Al ion are removed at 220 °C. Phase transition behaviour can be summarized as

$$\operatorname{AlNH}_{4}(\operatorname{SO}_{4})_{2}.12\operatorname{H}_{2}\operatorname{O} \xrightarrow{110^{\circ}C} -6H_{2O} \rightarrow \operatorname{AlNH}_{4}(\operatorname{SO}_{4})_{2}.6\operatorname{H}_{2}\operatorname{O} \xrightarrow{140^{\circ}C} -4H_{2O} \rightarrow \operatorname{AlNH}_{4}(\operatorname{SO}_{4})_{2}.2\operatorname{H}_{2}\operatorname{O} \xrightarrow{220^{\circ}C} -2H_{2O} \rightarrow \operatorname{AlNH}_{4}(\operatorname{SO}_{4})_{2} \qquad (2)$$

In ferrous sulphate, there is the loss of first three water molecules up to 66 °C, next three are removed from the lattice up to 110 °C, and final removable water of crystallization gets off at 287 °C [15]. In ferrous sulphate, this can be summarized as

$$\operatorname{FeSO}_{4}.7\operatorname{H}_{2}\operatorname{O} \xrightarrow{66^{\circ}C}{-3H_{2}O} \operatorname{FeSO}_{4}.4\operatorname{H}_{2}\operatorname{O} \xrightarrow{110^{\circ}C}{-3H_{2}O} \rightarrow \xrightarrow{110^{\circ}C} \operatorname{FeSO}_{4}.\operatorname{H}_{2}\operatorname{O} \xrightarrow{287^{\circ}C}{-H_{2}O} \operatorname{FeSO}_{4}$$
(3)

If this powder is again kept in humid ambient, these water molecules may be reabsorbed. The dehydrated samples were ground and palletized in a evaccuable die (to avoid the rehydration problem) in the form of a pellet (d = 6 mm and thickness 2 mm).

To determine the nature of mobile species (i.e. transference number measurement), Wagner's method of polarization [16] has been used. In this, we record the current as a function of time on application of a small dc potential on the sample. The initial current ($i_{initial}$) and the final current after the complete polarization (i_{final}) were evaluated by the current - time plot. The ionic transference number (t_{ion}) is given by

$$t_{ion} = \frac{i_{initial} - i_{final}}{i_{initial}}$$

In the case of dehydrated salt, Wagner's method is unable to exactly predict whether the conductivity is due to electrons (σ_e) or holes (σ_h). The theory of nonionic contribution in the predominantly ionic conductor was proposed by Wagner and later used by Ilschner [17]. According to this theory, the current may be expressed as

$$\mathbf{I}_{e,h} = \mathbf{I}_e + \mathbf{I}_h$$

$$I_{e,h} = \frac{RTA}{LF} \left[\sigma_e \left\{ 1 - e^{\frac{-VF}{RT}} \right\} + \sigma_h \left\{ e^{\frac{VF}{RT}} - 1 \right\} \right]$$
(4)

where R is the gas constant, T is the absolute temperature, F is Faraday's constant, 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 electrons and holes), i_e and i_h are the current due to the electrons and the holes, respectively. The variation of residual non ionic current (i.e. after full polarization) has been achieved as a function of applied potential. There are the following possibilities:

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

$$I_{e,h} = I_e = \frac{RTA}{LF} \left[\sigma_e \left\{ 1 - e^{\frac{-VF}{RT}} \right\} \right]$$

For large value of V, the current saturates to

$$I_e = \frac{RTA}{LF}[\sigma_e] \tag{5}$$

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

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

i.e., the current varies exponentially with V. When extrapolated to V = 0, this gives the value of I_h as

$$I_h = \frac{RTA}{LF} \left[\sigma_h \right] \tag{6}$$

The sample is polarized at some fixed voltage and the residual current was measured by Keithley SMU-236. The value of σ_e and σ_h could be calculated from the I-V characteristics using the above equations.

The infrared spectra of dehydrated salts were recorded by Perkin-Elmer IR spectrophotometer. For the high temperature measurement, a temperature controlled evacuable cryostat with KBr window, suitable for the temperature range 150-600 K (Specac, model 5757) was used. A sample (with KBr) pallet was mounted inside the cell. This cell also has gas flow attachment. During the experiment, hydrogen is flowing continuously in the cell. After the time of equilibration, the spectrum was recorded.

The bulk electrical conductivity measurement was carried out by complex impedance/admittance plot method with the help of a "Solartron 1250 FRA" coupled with the 1286 ECI. The high temperature electrical conductivity of dehydrated salts was measured with the help of spring loaded sample holder placed in a closed furnace.

Cell geometry used

To establish a protonic behavior at high temperature, the electrochemical emf measurement across the concentration cell is the best technique. Some important concentration cell geometries are

(i) Cell-IA

	P _{H2(p')}	Pt-electrode*	Dehydrated salt	Pt-electrode*	P _{H2(p'')}
*To construct the porous Pt-electrode, it is necessary to fire the Pt-paste at 250 °C.					at 250 °C.

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

$$E = t \frac{RT}{2F} \ln \left[\frac{p'}{p''} \right]$$
⁽⁷⁾

where t is the transference number, and p' and p" are the partial pressures of gases.

(ii) Cell-IB

P_{H2O(I)}P_{O2(I)}Pt-electrode Dehydrated salt Pt-electrode P_{H2O(II)}P_{O2(II)}

In the concentration cell having dry/ wet air combination, the emf of the cell is given by

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

(iii) Cell-II

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

In this cell, the proton has tendency to migrate across the proton conductor towards the oxygen where it is discharged to form water vapor. Therefore, the emf is given by

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

(9)

where P_{H2} and P_{O2} 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	Dry air // Dehydrated salt pellet // Wet ai
Call 2	II // Debudneted celt mellet // ain

Cell-2 $H_{2 (pH2)}$ // Dehydrated salt pellet // air

For the dry air we connect the assembly to P_2O_5 (with R.H.< 25%) and for wet air it is connected to water bottle. Porous platinum paste was used as electrode on the both faces of the pellet.

Results and discussion

Transference number (t_{ion}) of dehydrated salts (i.e., $Al_2(SO_4)_3$, $AlNH_4(SO_4)_2$ and FeSO₄) was measured by Wagner's method of polarization at 250 °C in vacuum and hydrogen ambient. In vacuum/low pressure air t_{ion} of the dehydrated salts were found to be ~ zero. This is an indication of non ionic (or electronic) nature of mobile species in vacuum. But in the hydrogen ambient, the nature of dehydrated salts was completely changed and showed ionic behavior. The change

of non ionic to ionic nature in hydrogen ambient give the preliminary indication that dehydrated salts can sustain the protonic conduction at elevated temperatures. The change in nature of dehydrated salts is explained as follows: in the presence of hydrogen, it (protons) is considered to be localized between the nearest neighboring oxide ions, forming a hydrogen bond with oxide in the lattice, producing hydroxide groups and electrons as follows

$$\frac{1}{2}H_{2(g)} + O_o^x = OH_o^* + e^{\prime} \tag{10}$$

One could believe that proton could migrate by hopping from the OH_o^* site to oxide ion site at a normal lattice site nearly causing the protonic conductivity [18-21]. Calculated values of transference number in both atmospheres are given in Table 1.

S.No.	Materials	t _{ion} (in air)	t _{ion} (in hydrogen)
1.	$Al_2(SO_4)_3$	≈ 0.0	≈ 0.80
2.	$AINH_2(SO_4)_2$	≈0.0	≈ 0.95
3.	FeSO ₄	≈0.0	≈ 0.90

Table 1. Values of t_{ion} in air and hydrogen for the dehydrated salts at T=250 °C.

To determine the relative contribution of electrons and holes conduction separately, we use Ilschner's method. In this technique, the dehydrated salt pellet was sandwiched between ion blocking and a reversible electrode. A small dc voltage (always smaller than the dissociation potential of the material) was applied and the final "residual current" was measured. In I-V plot, the electronic part of the current tends to reach 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

$$\sigma_{\rm e} = (\rm LF/RTA) \, i_{\rm e} \tag{11}$$

and

$$\sigma_{\rm h} = (\rm LF/RTA) \, i_{\rm h} \tag{12}$$

where i_e is the measured saturation plateau current and i_h is the value of current obtained by extrapolating the exponentially increasing part at V = 0 (in I-V plot). The pellets of dehydrated salts with platinum electrodes were held in a spring loaded flat plate cell assembly. The I-V characteristics of these salts (after allowing the sufficient time for polarization, if any) are given in Fig. 2. The variation of current with voltage in Al₂(SO₄)₃ and FeSO₄ shows only an exponential increase (giving the value of i_h when extrapolated to V = 0), but in AlNH₄(SO₄)₂, a small plateau region (typical of i_e) as well as an exponential increase of current, were observed. This infers that Al₂(SO₄)₃ and FeSO₄ both dehydrated salts are basically hole conductor in air/ vacuum (since the necessary plateau of i_e is absent). The calculated values of σ_e and σ_h along with σ_{meas} by complex impedance method are listed in Table 2.



Figure 2. Variation of final saturation current with applied voltage in air for $Al_2(SO_4)_3$, $AlNH_4(SO_4)_2$ and $FeSO_4$.

Table 2. Calculated values of electronic and hole conductivities in dehydrated salt electrolyte in air ambient at T=250 °C.

S.No.	Electrolyte	$\sigma_{electronic}$	σ_{hole}	Calculated	Experimental
		(S/cm)	(S/cm)	$\sigma_{total}(S/cm)$	$\sigma_{total}(S/cm)$
1.	$Al_2(SO_4)_3$		$\sim 9.0 \mathrm{x} 10^{-9}$	9.0x10 ⁻⁹	7.0×10^{-9}
2.	$AlNH_4(SO_4)_2$	1.3×10^{-8}	0.3×10^{-8}	1.6×10^{-8}	1.6×10^{-8}
3.	FeSO ₄		5.4×10^{-7}	5.4×10^{-7}	5.4×10^{-7}

The results obtained by transference number measurement for dehydrated salts are indicative of the fact that they can sustain proton (H^+ or OH⁻) mobility in hydrogen ambient at elevated temperature ~ 200-250 °C. Therefore, it is also expected that the hydrogen diffusion coefficient would be high at these temperatures. To confirm the facts in-situ IR spectral studies have been carried out 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. The IR spectra of dehydrated salts in vacuum and hydrogen atmosphere at 250 °C are shown in Fig. 3.



Figure 3. Infrared spectra of $Al_2(SO_4)_3$, $AlNH_4(SO_4)_2$ and $FeSO_4$.

The spectra in vacuum and hydrogen are qualitatively similar in all respect. The closer look of –OH bond region shows a possible formation of new –OH bonding due to the diffusion of external hydrogen in lattice. The region of strong-OH peak in the spectra is 3600-3000 cm⁻¹. Ideally, in the fully dehydrated salt –OH peak at ~ 3200 cm⁻¹ region is not expected. However, we do see a residual –OH absorption peak even in the hydrated sample placed in vacuum. This may be possible due to the ineffective N₂ purging of the instrument (and/or some residual –OH bands in KBr or the sample). The important point of our present interest is to study the change (if any) in –OH peak when the IR spectrum is recorded in hydrogen ambient. A comparison of the area under –OH peak in vacuum, and in hydrogen ambient shows an enhancement (~1.5 times). It is possibly due to the formation of new –OH bonds by the hydrogen diffusing in the salt lattice.

The electrical conductivity of dehydrated salts at temperature range 200-400 °C in various environments was measured by complex impedance plot.

Enhancement of conductivity in H_2 ambient

In dehydrated salts the conductivity increases after inserting hydrogen into the chamber. The material changes their conductivity from non-ionic to ionic when placed in the H₂ ambient. However, the uptake of hydrogen in dehydrated salts is slow. It takes some time (few minutes to hour) to reach the steady state of conductivity value ($\sigma_{hvdrogen}$). The variation of conductivity with time after the

insertion of hydrogen is shown in Fig. 4. It is clear that the equilibration is faster (30-40 min) for Al₂(SO₄)₃ and AlNH₄(SO₄)₂, while it takes a very long time (>24 h) in the case of FeSO₄. It is interesting to note that there is a correlation between the number of water molecules removed during dehydration and the equilibration time (σ value). The equilibration time of σ in hydrogen ambient for five dehydrated salts [i.e., CaSO₄, FeSO₄, Fe₂(SO₄)₃, AlNH₄(SO₄)₂ and Al₂(SO₄)₃], as a function of the number of water molecules, was shown in Fig. 5. It seems that more voids are created in those lattices from which more water molecules have been removed and hence they follow faster reaction kinetics to equilibrate the conductivity in hydrogen ambient. However, this is only an empirical observation.



Figure 4. Variation of electrical conductivity of $Al_2(SO_4)_3$, $AlNH_4(SO_4)_2$ and $FeSO_4$ with time after insertion of hydrogen (the conductivity of t=0 min is σ_{vacuum}).

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 is linear and it can be represented by the Arrhenius type expression:

$$\sigma = \sigma_0 \exp\left[\frac{-E_a}{KT}\right] \tag{13}$$

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



Figure 5. Time taken for equilibration of conductivity in hydrogen ambient for dehydrated salts (salts having different amount of water of crystallization).



Figure 6. Variation of electrical conductivity of $Al_2(SO_4)_3$, $AlNH_4(SO_4)_2$ and $FeSO_4$. with temperature in three environments (i.e., air, vacuum and hydrogen).

S.No.	Electrolyte material	Atmosphere	σ_0 (S.cm ⁻¹)	$E_{a}\left(eV ight)$
1.	A1 (SO)	Air	1.6 x 10 ⁻⁸	0.44
	$AI_2(5O_4)_3$	Vacuum	1.5 x 10 ⁻⁶	0.15
		Hydrogen	$1.0 \ge 10^{-5}$	0.27
2.		Air	3.8 x 10 ⁻⁴	0.45
	$AlNH_4(SO_4)_2$	Vacuum	3.1 x 10 ⁻⁵	0.34
		Hydrogen	5.8 x 10 ⁻⁶	0.04
3.	E-SO	Air	3.5 x 10 ⁻²	0.64
	FeSO ₄	Vacuum	0.66	
		Hydrogen	2.7 x 10 ⁻³	0.40

Table 3. Value of σ_0 and E_a of the dehydrated salts.

In Al₂(SO₄)₃, the σ vs. 1/T shows a deviation from Arrhenius behavior at T> 350 °C. In the thermal study of aluminum sulphate, it is reported that there is a phase transition (amorphous to crystalline) around this temperature. The non ionic conductivity (i.e. in air and vacuum) increases with a faster rate at temperature >350 °C while in hydrogen ambient the conductivity (ionic in nature) starts decreasing. The possible reason is that the crystalline nature is not suitable for the ionic conductivity enhancement.

In AlNH₄(SO₄)₂ there is only a linear region in the entire temperature range studied but in FeSO₄ the deviation from linear behavior starts at ~ 340 °C in air and hydrogen. This effect is more prominent in case of hydrogen ambient. It is reported that FeSO₄ has a dissociation temperature of ~ 480 °C. The present trend is possibly a reflection of a pre-dissociation effect. The dissociation seems to be assisted by hydrogen ambient.

Electrochemical emf measurement

For the electrochemical emf measurement, we use two types (symmetrical and asymmetrical) of concentration cell, using the dehydrated salt as an electrolyte:



The possible chemical reactions at the different electrodes are given below: In the symmetrical cell *"wet air/dehydrated salt/air cell"*

$$H_2 O \to 2H^+ + \frac{1}{2}O_2 + 2e^-$$

and

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

Similarly in the asymmetrical cell " H_2 / dehydrated salt / air" or "wet air / dehydrated salt / air"

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

and

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

Electrochemical emf generated in the two concentration cells is expressed as follows:

in symmetrical concentration cell

$$E = \frac{RT}{2F} \ln \left[\frac{p_{H_2O}(I)}{p_{H_2O}(II)} \right]$$
(14)

in asymmetrical concentration cell

$$E = E^{0} - \frac{RT}{2F} \ln \left[\frac{p_{H_2O}(I)}{p_{H_2O}(II)} \right]$$
(15)

where P_{H2} , P_{O2} , and P_{H2O} , are partial pressures of hydrogen, oxygen or water, respectively, R is the gas constant, F is the Faraday constant, and E° is the standard electrode potential.

The electrochemical emf generated for different cells with dehydrated salts as electrolyte $(Al_2(SO_4)_3, AlNH_4(SO_4)_2$ and FeSO₄) are given in Table 4. In this study a construction of symmetrical concentration cell was purposely assembled to check that the electrochemical emf developed in asymmetrical cells is genuinely due to the presence of higher activity of protonic species on one side. The symmetrical cell gives nearly zero potential as expected, since the electrochemical activity on the two sides is the same. However, the asymmetrical cell gives genuine electrochemical emf due to the activity of protonic species on the electrodes. This is an indication of possible motilities of gaseous ionic species in the electrolyte.

Table 4. Electrochemical emf of the dehydrated salts at 200 °C and 300 °C.

S. No.	Electrolyte Cell type		l type			
	materials	Wet air // Dry air		Hydrogen //	ydrogen //Air (p _{H20})	
		200 °C	300 °C	200 °C	300 °C	
1.	$Al_2(SO_4)_3$	12 mV	32 mV	457.1 mV	190 mV	
2.	$AlNH_4(SO_4)_2$	1.2 mV	8.5 mV	51.5 mV	30 mV	
3.	FeSO ₄	11.4 mV	23.1 mV	280 mV	180 mV	

Conclusion

Transference number, electrochemical emf measurement and electrical conductivity measurements (in the hydrogen ambient, the magnitude of the conductivity increases ~ three times with respect to air/vacuum) confirm that these dehydrated salts are primarily non ionic in air, but show a good protonic behavior in the hydrogen ambient. This study proposes an alternative set of materials (i.e., dehydrated salts) as possible electrolyte for the intermediate temperature fuel cell.

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