Space Charge Limited Conduction in Hydrated Salt

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Abstract- **Voltage assisted de-aquation has been studied in zinc potassium sulphate hexahydrate (ZPSH) Tutton salt pellets heated at a linear rate through the current versus time plot. The plots were obtained for different voltages of 1.5, 9, 20, 40 and 50 volts across the pellet. On comparing the amounts of charge flowing through the pellets it is seen that space charge effect is prominent above 20 V due to accumulation of H+ ions near the cathode.**

Keywords – ZPSH, Tutton salt, Protonic conduction, Voltage assisted de aquation

I. INTRODUCTION

On heating, hydrated salts loose water of hydration. Voltage assisted de aquation and TGA further provide information about de-aquation steps and also about the reduced dissociation energies of water groups inside such salts [1-5].

In voltage assisted de-aquation, apart from losing water, a hydrated salt also conducts electricity due of H+ and OH- ions. The water groups dissociated due to heat further create H+ and OH- ions which move to the respective electrodes and are collected there.

The H+ ions are more mobile than OH$^-$ ions and move quickly to the negative electrode. The OH$^-$ move to the positive electrode with lot of hindrance on its way. A layer of H atoms is first created on the cathode. The H atoms are bad conductor of electricity. The further approaching H$^+$ ions cannot thus give their charge to the cathode and this is the cause of creation of space charge region of H$^+$ ions close to the cathode. The OH- ions could diffuse slowly to the anode and complete the electric circuit. The moving OH- ions may come in contact with H+ ions and may lead to formation of H_2O again. These leave the sample through de aquation. A review on proton conductivity of materials with suitable applications is available as per Kreuer [6]. Yaroslavtsev [7] has also provided a review on proton conductivity of inorganic hydrates. In the present work it is found interesting to explore nature of conduction through protons in a hydrated salt.

II. EXPERIMENTAL

Herewith, we are presenting the results of voltage assisted de aquation in zinc potassium sulphate hexahydrate (ZPSH) which is a hydrated salt. The ZPSH material was made through growth of tiny crystals from saturated aqueous solution containing zinc sulphate and potassium sulphate in equimolar ratio. The crystals were picked up, dried to give fine powder. This powder was converted into pellets while taking equal amount of powder each time.

Quite a few equal size pellets of zinc potassium double sulphate hexahydrate (ZPSH) Tutton salt were made using hydraulic press and die arrangement. The pellets were coated with silver paint and then placed in the sample holder between platinum foils. There was an arrangement to heat a sample at the rate of 1^0C per minute. The current through the pellet was measured while the sample was heated from RT (25^0C) to 145^0C, the total time duration of measurement being 120 minutes.

A set of five different current versus time measurements were then conducted for d.c. voltages of 1.5, 9, 20, 40 and 50 volts across the pellet samples. We thus have five sets data for different d. c. voltages.

Table 1 shows current versus time data for voltage of 1.5 V across the sample. The corresponding graph is shown in Fig. 1a. Figs. 1b-1e further show four different graphs for applied voltages of 9, 20, 40 and 50 volts. Only the data obtained from 45 minutes to 120 minutes are shown in the Figs.1(a-e).

Table -1 Current through the pellet at different times, when heated at
1^0 C/minute, the voltage across being 1.5 Volt

S. No.	Time (min)	Current I(amp)
1	0	1.3E-08
2	5	1.2E-08
3	10	1.1E-08
4	15	9.4E-09
5	20	7.9E-09
6	25	5.9E-09
7	30	4.7E-09
8	35	3.2E-09
9	40	2.4E-09
10	45	1.8E-09
11	50	1.9E-09
12	52	2.4E-09
13	55	4.7E-09
14	57	5.3E-09
15	60	8.9E-09
16	62	2.5E-08
17	65	5.3E-07
18	67	7.1E-07
19	68	7.5E-07
20	70	7.1E-07

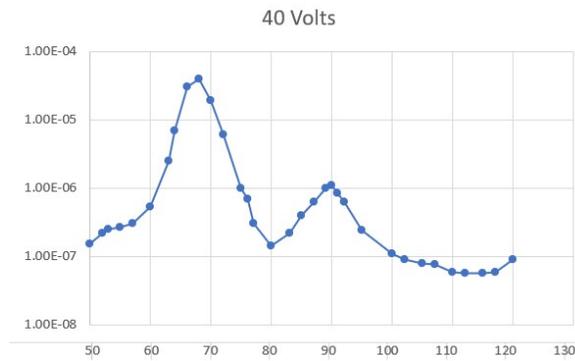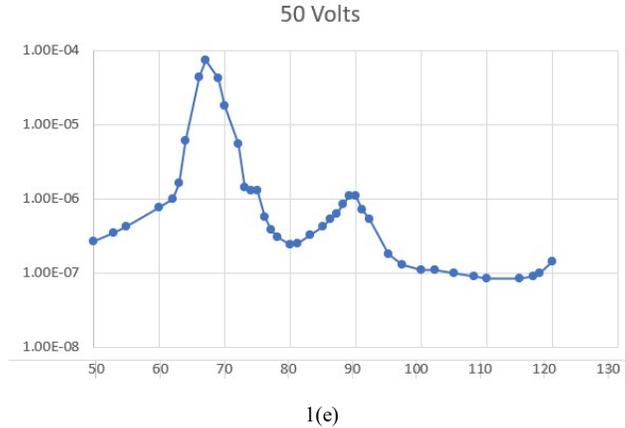| S. No.	Time (min)	Current I(amp)
21	71	5.6E-07
22	72	3.3E-07
23	73.5	2.5E-07
24	75	4.5E-08
25	77	4.0E-09
26	78	3.0E-09
27	80	2.9E-09
28	82	3.5E-09
29	85	6.7E-09
30	87	1.1E-08
31	90	1.6E-08
32	92	1.4E-08
33	95	8.9E-09
34	97	5.9E-09
35	100	3.5E-09
36	105	2.5E-09
37	107	1.6E-09
38	110	8.4E-10
39	112	7.9E-10
40	120	1.2E-09

1(a)

1(b)

1(c)

1(d)

1(e)
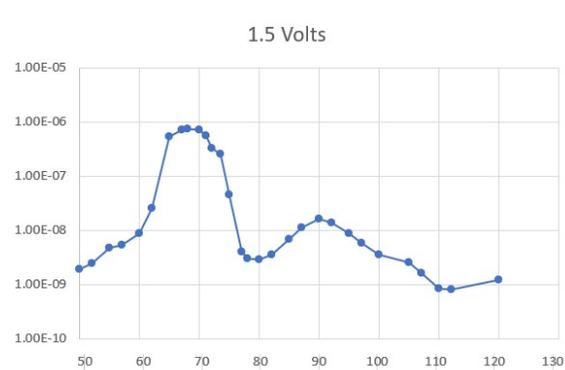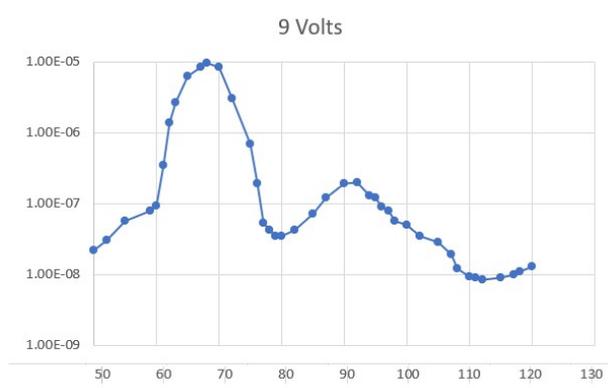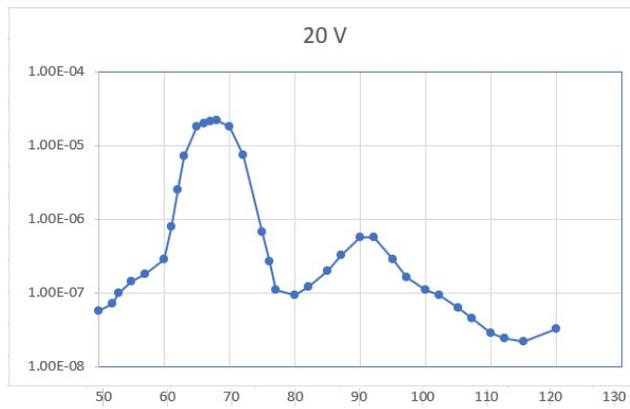
Figures 1.(a-e) Current versus time plot for ZPSH pellet heated at a linear rate for different applied voltages a)1.5 volts, b) 9 volts, c)20 volts, d)40 volts, and d) 50 volts

III. RESULTS

Important features of I(current) vs t(time) plots for heated ZPSH pellets while acted upon by different d. c. voltages are as under.

a. For all voltages the current decreased continuously from RT to about 70^0C. Such a current was only due to the surface conduction, no ionic conduction is involved.

b. Two broad peaks are observed in I vs t plot also representing I vs T plot. One of these peaks is around 90-91^{0}C and the other around 112-115^{0}C. These are attributed to equatorial and axial water groups respectively in the sample.

c. The amount of charge flowing for above peaks increases continuously as the voltage across the pellet is increased.

d. Further two humps are observed in all the I vs T plot around 78 ^{0}C and 127 ^{0}C in ZPSH salt, as a hydrated salt containing sodium may also be created within the system. It may be stated that sodium sulphate is always present in potassium sulphate of normal purity.

3.1. Charge Corresponding to Peaks –

In the I vs t plots for different voltages, the charge 'q' flowing for the first peak are evaluated taking into account semi-log nature of graph. We chose first peak as this was quite prominent. Table 2 gives the q values obtained for different voltage plots.

Table 2 The 'q' values for the first peak in I vs t plot

S. No.	Voltage across the pellet (Volt)	$q \times 10^4$ Coulomb
1	1.5	3.70
2	9	44.9
3	20	96.0
4	40	132
5	50	149

For calculating charge flowing through the peak, area under I vs t curve was counted from t=58 mins to 80 mins for all voltage runs. Hence the charge measured also represents the average current flow I_{avg} for the peak in question.

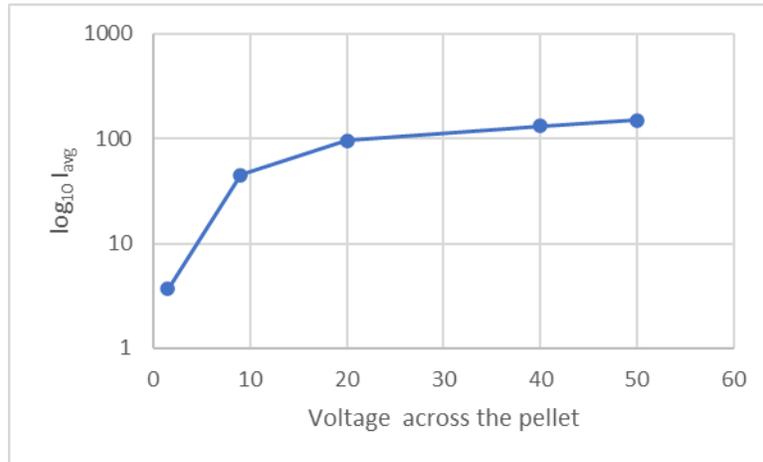The plot of log10 I_{avg} as a function of d. c. voltage across the pellet is shown in Fig. 2.

Figure 2. Plot of log_{10} I_{avg} versus applied voltage across the pellet, heating rate being 1^0C/min.

3.2 Space Charge Situation –

For a large voltage applied across the pellet, the number of H^+ ions reaching cathode would be quite large. All such protons are, however, not able to transfer their charge to the cathode, due to accumulation of neutral H atoms near the cathode. This perhaps checks the free flow of protons and a space charge region is created leading to a check on growth of charge flow through the pellet. An almost flat region in the log_{10} I_{avg} versus t plot from V=20 volts to V=50 volts is indicative of the creation of space charge in the pellet.

3.3 Nature of I vs V plot for saturation current –

3.3.1 Protonic conduction in a hydrated salt –

For voltages between V=20 and V=50 volts, I_{avg} versus V graph shows a very small positive slope(ε). The I_{avg} can thus be represented as

Thus log_{10} I_{avg} = εV + constant (y=mx+c form of equation of straight line)

log_e I_{avg} = 2.303(εV + constant)

= K_1V+K_2 (say)

Thus I_{avg}= $Ke^{\varepsilon V}$ (K also a constant)

= K(1+εV) as εV is also small

or, change in I_{avg} is proportional to change in V in space charge region.

The protonic conduction in hydrated salt is also influenced by OH^- ions.

3.3.2 Electronic conduction in a vacuum diode –

This is due to recombination between H+ and OH- ions. This law is however applicable only for voltages at saturation condition. The mutual repulsion of H+ ions here, is augmented by the attraction of OH- ions. In a vacuum diode, the space charge limited current [Lau, 2001], however, varies with applied d. c. voltage as

$$I \propto V^{3/2}$$

In such a conduction, only mutual repulsion occurs between electrons

IV. DISCUSSION

The results obtained for measurements done above 20 Volts in ZPSH salts point towards creation of space charge near the cathode. Such a space charge-controlled region in the system may be exploited for developing a thermal-controlled device using hydrated salts.

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