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Short Communication

Relative-Humidity/Temperature Relationships for Saturated Salt Solutions: Application to Lead/Acid Plate Curing

A. M. FOXWORTHY

CSIRO Division of Mineral Chemistry, P.O. Box 124, Port Melbourne, Vic. 3207 (Australia)

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Relative humidities above six saturated aqueous salt solutions in a sealed oven have been measured using an electronic temperature/humidity probe. The salt solutions have been chosen to span a wide range of temperatures (30 - 90 °C) and relative humidities (10 - 100%) in order to provide information relevant to the curing process of lead/acid battery plates. The results largely confirm and extend the combinations of temperature and humidity previously reported for these solutions by other investigators.

Introduction

The phase composition and physical characteristics of cured lead/acid battery plates exert a marked influence on the subsequent behaviour and performance of the plates during charge/discharge operations [1]. These properties are a function of the prevailing temperature and relative humidity (RH) conditions within the curing chamber. For example, high temperatures and humidities favour the formation of tetrabasic lead sulphate, $4PbO \cdot PbSO_4$, while lower temperatures and humidities promote the formation of tribasic lead sulphate, $3PbO \cdot PbSO_4 \cdot H_2O$. The relationship between plate composition and the temperature and the humidity of curing is, however, poorly understood. Furthermore, the effect of the curing parameters on the size and shape of the particles of each phase is equally ill defined, particularly with regard to crystal growth kinetics and particle connectivity, as well as plate permeability and porosity.

Studies undertaken in the CSIRO laboratories [2] have been aimed at determining the link between battery-plate performance during formation and cycling, and the temperature/humidity conditions prevalent during plate curing. These investigations have been conducted on hand-pasted plates cured in a sealed oven containing a chosen, saturated, aqueous salt solution to maintain a desired RH. For a given salt-solution/temperature relationship, occasional discrepancies have been observed between the measured RH values and those quoted in the literature. In other cases, the literature contained very few RH data for temperatures greater than 60 °C. The present

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work reports the RH of several salt solutions over the temperature range 30 - 90 °C.

Experimental

Relative humidities were measured in a humidity chamber (internal volume: 150 l) which was equipped with a fan to effect a good circulation of air, and a temperature controller to maintain temperatures from ambient to 150 ± 0.5 °C.

Measurements of humidity and temperature were made using a Vaisala Humidity and Temperature Probe, Model HMP32UT, attached to a Vaisala Humidity and Temperature Indicator, Model HM132 which, in turn, was connected to a chart recorder. The probe utilises a thin polymer film sensor, a Vaisala Humicap 5832 HM, to determine the humidity through changes in the capacitance of the sensor. This method has several advantages over more common practices that employ manometers or wet- and dry-bulb thermometers:

(i) the RH is read from a digital display external to the chamber, thus avoiding those difficulties associated with recording temperatures from thermometers hidden inside the sealed equipment;

(ii) no calculations are involved, unlike the manometer and the wet- and dry-bulb methods,

(iii) leaks cannot develop, as occurs with manometers [3].

The six salt solutions investigated in the present study are listed in Table 1. The temperature/humidity characteristics of the salts K_2SO_4 and KNO_3 have been well documented [3 - 8], but were included in order to provide "standards" for comparison between the methods used here and those reported in the literature. The other four salts were selected to provide a wide range of RH in the temperature range of interest to lead/acid battery manufacturers, namely, 30 - 90 °C. The humidities of these salts at temperatures greater than 60 °C are poorly characterised in the literature.

Saturated aqueous solutions of the salts were placed in recrystallising dishes (diameter: 19 cm) at the bottom of the oven and the internal fan was left running throughout the experiments. In some instances, equilibrium was not achieved for several hours because of the large volume of the oven and the slow response of the salt solutions to changes in temperature. Once equilibrium had been achieved, the values of RH and temperature were recorded and the temperature changed. When one RH value had been obtained at each temperature, the process was repeated until several corresponding readings for that temperature had been accumulated. A minimum of two RH determinations were conducted at each temperature.

Results and discussion

The RH for the six saturated aqueous salt solutions as a function of temperature are presented in Table 1. A comparison is made of the minimum, maximum, and average values for RH obtained in the present work with those found in the literature [3 - 9]. The results are displayed in

TABLE 1

Relative humidity (RH) above saturated aqueous salt solutions as a function of temperature

Salt	Literature [3 - 9]				Present study			
	Temp. (°C)	RH (%)			Temp. (°C)	RH (%)		
		min.	max.	avg.		min.	max.	avg.
K_2SO_4	30	96	98	96	33	96	99	98
	50	96	97	96	52	92	95	94
	60	95	96	96	62	92	94	93
	70	—	—	95*	73	91	93	92
	90	—	—	95*	92	89	93	91
$Pb(NO_3)_2$	30	—	—	96*	30	90	92	91
	40	—	—	95*	40	89	91	90
					50	87	88	88
					60	86	89	88
					70	90	91	91
					80	91	92	92
KNO_3	30	91	92	91	30	91	93	92
	40	88	89	88	40	86	89	88
	50	85	85	85	50	81	83	82
	60	82	82	82	60	78	84	81
	70	—	—	77*	70	73	77	75
	80	—	—	74*	80	69	72	71
	90	—	—	70*	90	65	69	67
$CuCl_2 \cdot 2H_2O$	30	67	89	78	32	84	85	85
	40	67	89	78	43	79	81	80
	50	—	—	86*	51	77	79	78
	60	—	—	84*	61	73	77	75
					71	70	73	71
					79	56	59	58
					89	46	53	50
$Mg(NO_3)_2 \cdot 6H_2O$	40	49	51	50	42	45	48	47
	50	46	46	46	51	39	40	40
	60	43	43	43	62	33	37	34
					71	29	33	31
					80	28	32	30
LiCl	30	11	12	12	31	11	13	12
	40	11	11	11	43	10	11	11
	50	11	11	11	52	9	8	9
	60	11	11	11	62	8	9	9
					70	9	10	9
					78	9	10	10
					90	9	10	10

*Only one literature value available for this salt and temperature combination.

graphical form in Fig. 1. The "error bars" in Fig. 1 represent the range of RH values experienced, with each plot point indicating the average of all readings taken at a given temperature. The small range of values obtained for repeated

measurements demonstrates that the capacitance method for determining RH provides adequate reproducibility.

In general, there is good agreement between the values of RH measured in the present study and those obtained for corresponding salts and temperatures in the literature (see, for example, Fig. 2). However, there are inconsistencies in the literature results (Table 1). For example, literature values for the RH of $CuCl_2 \cdot 2H_2O$ range from 67 to 89% at a temperature of 30 °C.

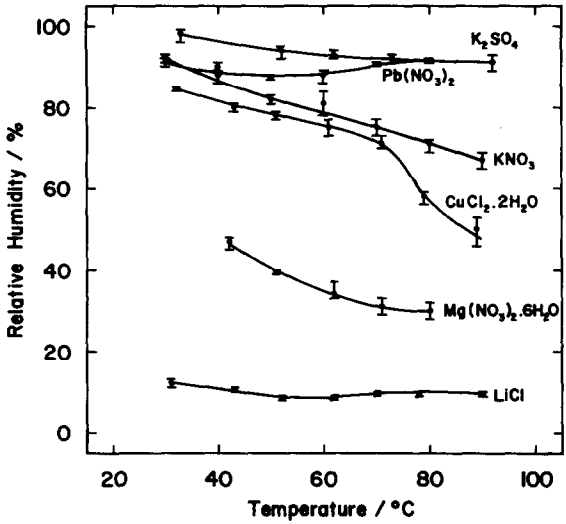

Fig. 1. Relative humidity as a function of temperature for given saturated aqueous salt solutions. Error bars indicate the range of humidity values obtained at each temperature.

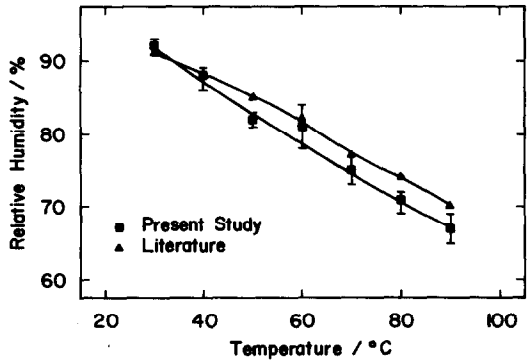

Fig. 2. Comparison of values of relative humiduty measured in the present study for KNO_3 with those obtained from literature. Error bars encompass range of humidity values obtained at each temperature from both sources.

The salts K_2SO_4 and $Pb(NO_3)_2$ provide uniformly high humidities over the range of temperatures examined (Fig. 1). Thus, these salts provide ideal conditions for the production of cured lead/acid battery plates containing tetrabasic lead sulphate. On the other hand, the slightly lower humidities obtained with salts such as KNO_3 and $CuCl_2 \cdot 2H_2O$ can be used to control the ratio of tetrabasic lead sulphate to tribasic lead sulphate. Other research at CSIRO [10] has established the phase boundary between these two basic lead sulphates so that a particular temperature for curing can be selected and the humidity then adjusted (using salt solutions) to produce plates with the desired ratio of these phases. Such a method allows battery manufacturers to tailor the chemistry of cured plates and, thereby, the subsequent charge/discharge performance of formed plates [1].

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