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Kinetics of lithium evaporation from solid solutions of Li_2O in NiO

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Measurements of the kinetics of evaporation of Li_2O from polycrystalline solid solutions of Li_2O in NiO have been performed under varying temperatures (1340 to 1665 K) and solution concentrations (0.25 to 19.5 at.% Li). By taking into account the changes in specific surface area during annealing of the preparations, an equation has been derived describing the kinetics of the evaporation process.

1. Introduction

Solid solutions of NiO–Li_2O are one of the most frequently studied model semiconducting systems of controlled electronic defect structure. In the majority of works concerned with this system, the experiments have been performed on samples with a stable equilibrium between ionic defects. Experiments under thermodynamic equilibrium of the solid solutions with the surrounding atmosphere are difficult owing to considerable evaporation of lithium from the samples.

Many applications of lithium oxide-doped nickel oxide require preparation of samples in the polycrystalline form. The methods of preparation and the properties of these solutions over a wide range of lithium concentrations have been the subject of recent studies carried out by the present authors [1-3]. This paper is a continuation of this series of studies.

Only one paper concerned with the kinetics of lithium evaporation from the solid solutions NiO–Li_2O has been found in the available literature [4]. In this, Iida reported studies on only one preparation of solid solution containing 2.89 wt% Li_2O (13.1 at.% Li). It has been found that evaporation of lithium follows a parabolic rate law and its activation energy is ~ 50 kcal mol^{-1}. It seemed of interest to extend these studies and to study the dependence of the rate of lithium evaporation on the initial LiO_2 concentration in the sample.

2. Experimental details

The synthesis of solid solutions of NiO–Li_2O was performed with the most usual method as described in [1]. Basic nickel carbonate is treated with solutions of lithium carbonate of appropriate concentrations, evaporated to dryness and the mixture thus obtained heated. Initial calcination was performed at 873 K for 1 h, after which the temperature was raised to 1273 K for a further hour. This temperature was selected as being optimal for preparation of the solid solutions, based on published data [5], and our own results [1].

After cooling, the preparations were ground in an agate mortar and washed with hot water in order to remove unreacted Li_2O. The amount of the latter was then determined photometrically.

After washing with water the preparations were again annealed at 1000°C for 2 h, cooled to room temperature, ground in a mortar and sieved using a mesh of 0.09 mm.

The preparations thus obtained were subjected to the following determinations:

(1) Determination of the lithium concentration in the solid solution. Samples of about 0.1 g were dissolved 1:1 in hydrochloric acid and the concentration of lithium in this solution was determined using a photometric method.

(2) The specific surface area of the preparations obtained was determined from the adsorption isotherm of krypton at liquid nitrogen temperature using the BET method. The results of (1) and (2) are summarized in Table I.

The kinetics of evaporation of Li_2O from the solid solution NiO–Li_2O was determined in the following way: an alundum boat containing about 1 g sample which formed a layer approximately 2mm thick, was placed for a specific time (0.5 to 12 h) in an electrically heated oven at temperatures of 1340, 1450, 1560 and 1665 K.

TABLE I Characteristics of initial preparations

Preparation no.	Conc. Li introduced (c_{int}) (at. % Li)	Conc. Li incorporated (c_0) (at. % Li)	Conc. Li washed (c_0) (at. % Li)	Conc. Li evaporated at first heating (c_{ev}) (at. % Li)	Specific surface area (S) ($m^2 g^{-1}$)
1	0.30	0.25	0.008	0.04	3.0
2	0.60	0.50	0.01	0.09	1.1
3	1.50	1.35	0.05	0.10	1.0
4	3.00	2.46	0.12	0.42	0.9
5	6.00	5.40	0.14	0.46	0.7
6	10.00	8.45	0.37	1.18	0.65
7	25.00	19.50	3.14	2.36	0.5

TABLE II Concentration of Li in solid solutions (at. %) with time

Preparation no.	Temperature (K)	Heating time (h)					
		0	0.5	1	3	6	12
1	1340	0.25	0.25	0.24	0.24	0.23	0.22
	1450	0.25	0.24	0.24	0.23	0.21	0.19
	1560	0.25	0.23	0.23	0.21	0.19	0.17
	1665	0.25	0.22	0.21	0.18	0.16	0.13
2	1340	0.50	0.49	0.49	0.48	0.46	0.45
	1450	0.50	0.47	0.46	0.42	0.39	0.36
	1560	0.50	0.47	0.44	0.38	0.32	0.27
	1665	0.50	0.37	0.31	0.25	0.22	0.19
3	1340	1.35	1.30	1.27	1.19	1.11	1.01
	1450	1.35	1.18	1.12	0.98	0.84	0.68
	1560	1.35	1.09	1.00	0.75	0.50	0.26
	1665	1.35	0.96	0.83	0.43	0.26	0.18
4	1340	2.46	2.34	2.29	2.14	1.99	1.78
	1450	2.46	2.13	1.91	1.57	1.36	1.05
	1560	2.46	2.06	1.82	1.43	0.98	0.59
	1665	2.46	1.47	1.19	0.57	0.32	0.24
5	1340	5.40	5.02	4.76	4.15	3.73	3.14
	1450	5.40	4.32	3.88	2.58	2.10	1.50
	1560	5.40	3.60	2.75	1.97	1.60	1.07
	1665	5.40	2.57	1.92	1.16	0.64	0.31
6	1340	8.45	7.37	6.75	5.50	4.70	3.80
	1450	8.45	6.75	6.05	4.55	3.65	2.35
	1560	8.45	5.70	4.75	3.30	2.15	1.30
	1665	8.45	5.00	3.70	1.80	1.10	0.50
7	1340	19.50	17.00	15.90	13.35	10.95	6.90
	1450	19.50	13.70	11.00	8.50	5.00	2.40
	1560	19.50	11.40	9.70	5.60	3.80	2.00
	1665	19.50	9.30	8.10	5.20	3.00	1.40

After cooling, the sample was ground, and weighed amounts were dissolved in hydrochloric acid. The lithium content in these solutions was determined using the photometric method. Changes in the specific surface area of the preparations after different periods of heating at different temperatures, were also determined.

3. Results of measurements and discussion

It follows from the data of Table I that the concentration of lithium incorporated into the solid solution (c_0) is related to the amount of lithium initially introduced into the sample (c_{int}) by the following equation:

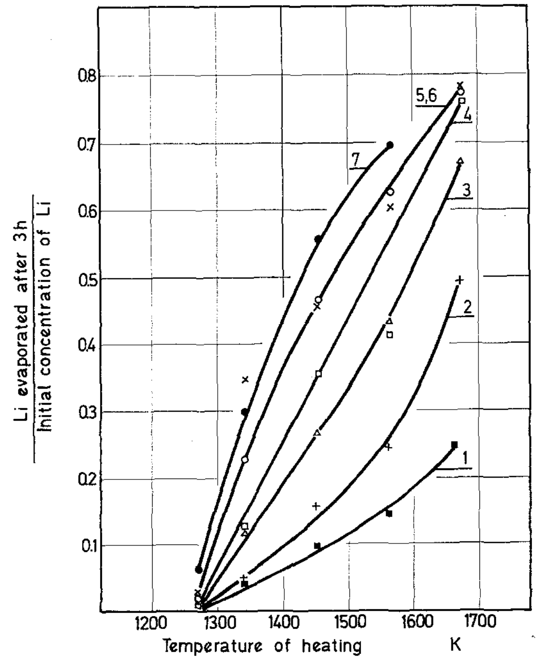

Figure 1 Dependence of the amount of Li_2O evaporated after 3 h on temperature.

$$c_0 = (0.858 \pm 0.012)c_{\text{init}}. \qquad (1)$$

This equation is analogous to that observed previously [1].

The amount of lithium evaporated from the solid solutions of NiO–Li_2O is given in Table II. Fig. 1 shows, for example, the temperature dependence of the amount of lithium evaporated from the samples after heating for 3 h. The numbers on the curves in this figure correspond to the numbers of the preparations.

A more extensive evaporation of lithium from dilute solid solutions is observed beginning at 1270 K. This temperature is decreased slightly with increasing lithium concentration in the solid solution. Loss of lithium during the heating of NiO–Li_2O solid solutions therefore increases with increase in the amount of lithium in the preparations.

It follows from the isothermal evaporation curves for lithium (cf. Table II) that the rate of evaporation at a given moment depends not only on the instantaneous concentration of the solid solution (c_t) but also on its initial concentration (c_0).

Let us consider, for example, the results obtained for the isothermal evaporation of lithium at 1560 K from two preparations

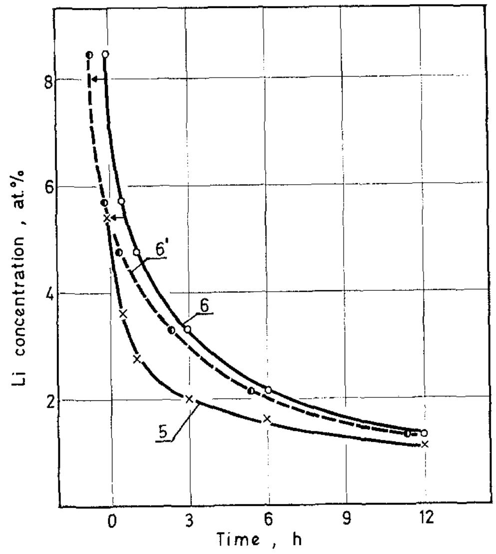

Figure 2 Isotherms of Li_2O evaporation at 1560 K for samples 5 (curve 5) and 6 (curve 6). Curve 6′ shows translation of curve 6 by the vector (− 37 min, 0).

containing 5.40 at. % Li (preparation no. 5) and 8.45 at. % Li (preparation no. 6). These isotherms are drawn in Fig. 2 with a continuous line. It can be seen that preparation no. 6 reaches a concentration of 5.40 at. % Li (the initial concentration of preparation no. 5) after 37 min. If the rate of lithium evaporation was dependent only on the instantaneous concentration, it should be possible to superimpose that part of curve 6, beginning from a point at 37 min, on to the initial section of curve 5, the curves coinciding within the limits of experimental error. This is, however, not observed and the rate of evaporation for preparation no. 5 at time $t = 0$ is higher than the evaporation rate over preparation no. 6 at time $t = 37$ min. This is due, in the author's opinion, to the differences in specific surface area of the preparations: 5(0 min, 1560 K) and 6(37 min, 1650 K) the first of them having the larger specific surface area.

In order to elucidate the effect of changes in specific surface area on the kinetics of evaporation, measurements of isothermal changes of specific area of selected preparations (nos. 2 and 5) during heating at temperatures of 1450 and 1560 K, were performed. The results obtained are given in Table III. As seen from this table, the surface area of these preparations in the initial period decreases rapidly, reaching a practically constant value (S_∞) after about 2 h. The values of S_∞ for the preparations in quest-

TABLE III Changes in specific surface area, S (m^2 g^{-1}) of preparations during heating

Preparation no.	Temperature (K)	Heating time (h)					
		0	0.5	1	2	5	10
2	1470	1.0	0.4	0.2	0.1	0.1	0.1
	1570	1.0	0.2	0.2	0.2	0.2	0.2
5	1470	0.7	0.5	0.2	0.1	0.1	0.1
	1570	0.7	0.3	0.2	0.2	0.2	0.2

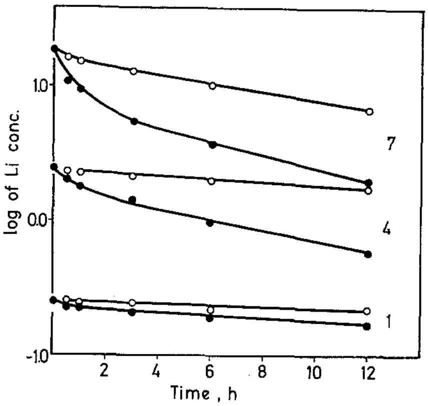

Figure 3 Dependence of log c_t on time for the preparations 1, 4 and 7; ○, 1340 K; ●, 1560 K.

ion increase with temperature. This apparent paradox can be readily explained; the specific surface area of solid solutions of NiO–Li_2O, obtained under the same conditions, decreases with increase in Li_2O concentration [1].

The equation, describing the rate of evaporation of lithium from the solid solutions, can be written as:

$$-\frac{dc}{dt} = k(T, c_0) \,.\, S(t, c_0) \,.\, f(c_t, c_0) \qquad (2)$$

where c = concentration, t = time, T = temperature, S = specific surface area, c_0 = initial concentration of Li_2O in the preparation, c_t = the concentration of Li_2O after time t and k = the rate constant of the evaporation process.

According to Iida [4], evaporation of lithium from the NiO–Li_2O solid solutions follows a parabolic rate law, i.e.

$$-\frac{dc}{dt} = k(c_0 - c_t)^{-1} \,. \qquad (3)$$

Taking the more general assumption

$$-\frac{dc}{dt} = k(c_0 - c_t)^{-n} \,, \qquad (4)$$

after solving Equation 4, we obtain

$$(c_0 - c_t)^{n+1} = (n + 1)kt \text{ for } n \neq -1 \,. \qquad (5)$$

The cases in which $n < 0$ can be excluded since, as indicated by the measurements performed, the rate of the process is a decreasing function of the heating time.

In order to check the hypothesis described by Equation 4 a plot of the function $\log(c_0 - c_t) = f(\log t)$ has been drawn. With exception of two solutions (preparations 1 and 2), the experimental points do not lie on a straight line. Thus the equation proposed by Iida does not adequately describe the experimental results in all the cases.

To find another equation which would better describe the evaporation process, the following facts were taken into account. During the course of preparation of polycrystalline samples of solid solutions of NiO–Li_2O in which the preparations are heated at a constant temperature, two simultaneous processes are taking place, (1) sintering of the preparation and (2) evaporation of lithium. Large changes in the specific surface area during the course of heating are observed only in the initial period, after which this parameter has a practically constant value independent of time. When considering lithium evaporation in these later stages of heating the sintering process may, therefore, be ignored. Therefore,

$$S(t, c_0) = S_\infty(c_0) \,. \qquad (6)$$

Let us assume that

$$f(c_t, c_0) = c_t^{\,n} \,. \qquad (7)$$

After solving Equation 2 we obtain

$$\ln c_t = \ln c_0 - k't \quad \text{for } n = 1 \qquad (8)$$

where $k' = k \,.\, S_\infty$, and

$$c_0^{1-n} - c_t^{1-n} = (1 - n)k't \quad \text{for } n \neq 1 \,. \qquad (9)$$

It was found that all the experimental data fit,

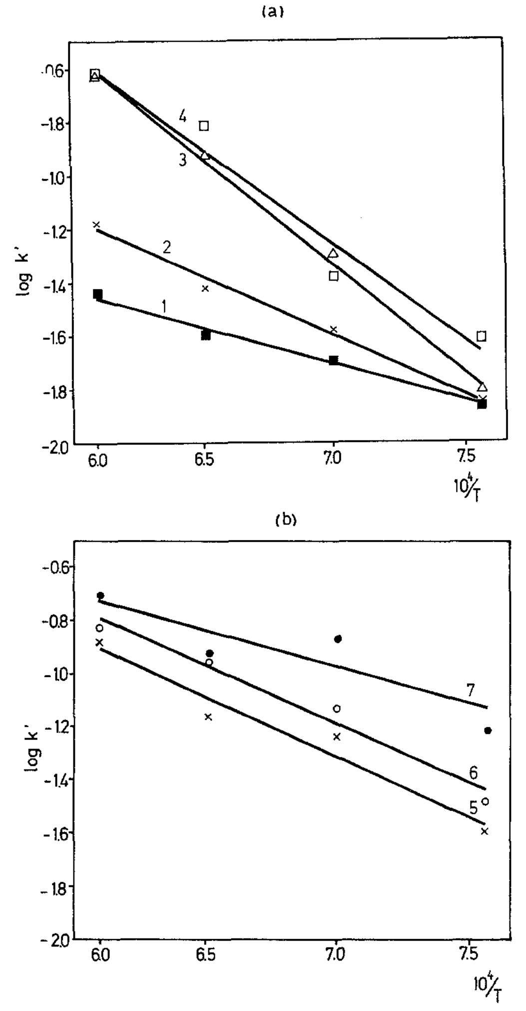

Figure 4 Dependence of log *k*' on $1/T$: (a) preparations 1 to 4; (b) preparations 5 to 7.

with sufficient accuracy, the straight lines in the log c_t versus $f(t)$ system of co-ordinates. This indicates that $n = 1$. This is illustrated in Fig. 3 where some of these functions are plotted.

The facts given can be interpreted in a simple way assuming that the rate of evaporation from the solid solution is proportional to the vapour pressure of Li_2O over this solution. If, at the same time, the Raoult law is obeyed, this rate is proportional to the concentration of the solid solutions. The rate of evaporation should then be the 1st order process with respect to lithium concentration in the solid solution.

The calculated values of *k*' are shown in Fig. 4a and b for the co-ordinate system log $k' = f(1/T)$. The Arrhenius dependence was plotted using the least square method and the values of the activation energies of evaporation, *E*, were then calculated. It was assumed for these calculations that values of S_∞ for particular preparations are independent of temperature. The results obtained (Fig. 5) indicate that the values of the activation energy change non-monotonically with increase in lithium concentration. For the diluted solutions, the activation energy of the process under consideration increases, reaching a maximum value of 37 kcal mol^{-1} at a concentration of about 1.3 at. % Li, above which it decreases.

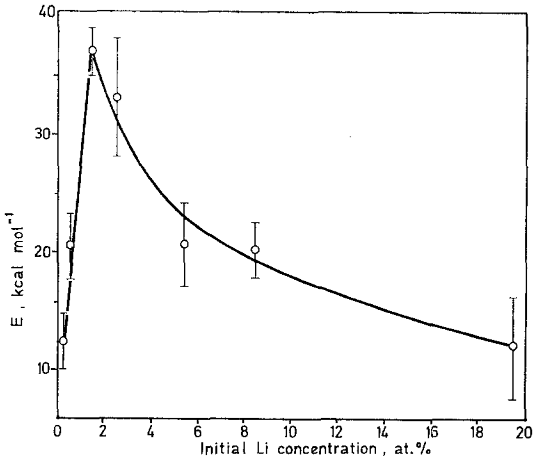

Figure 5 Dependence of activation energy of Li_2O evaporation of initial Li concentration (c^o) in NiO–Li_2O solid solutions.

Finally, we would like to draw attention to two facts. The first pertains to large differences between the values of the activation energy reported by Iida and those of the present work. The values of the activation energy obtained here are smaller than the value of 50 kcal mol^{-1} determined by Iida [4] for a solid solution containing 13.1 at. % Li. The value interpolated from the present results to this concentration is 16.3 kcal mol^{-1}. This is due to the fact that the kinetic equations used to calculate the values of the activation energies are different in the two works.

The second fact is concerned with non-monotonic changes of the activation energy with change in the lithium concentration in the NiO–Li_2O solid solutions. The non-monotonic changes of some other physico-chemical properties of these solutions with increase in lithium concentration have been observed in our previous works. They were interpreted by assuming two different mechanisms of lithium incorporation. The problem is discussed in detail in [6].

References

1. J. DEREŃ and M. RĘKAS, *Roczniki Chem. Ann. Soc. Chim. Polonorum* **46** (1972) 1411.
2. J. DEREŃ, J. NOWOTNY and M. RĘKAS, *ibid* **46** (1972) 1495.
3. J. DEREŃ, M. RĘKAS and G. RÓG, *ibid* **46** (1972) 1837.
4. Y. IIDA, *J. Amer. Ceram. Soc.* **43** (1960) 171.
5. *Idem, ibid* **43** (1960) 117.
6. A. BIELAŃSKI and J. DEREŃ, Proceedings of the Symposium on Electronic Phenomena in Chemisorption and Catalysis on Semiconductors, 1968 (De Gruyter, Berlin, 1969) p. 149.

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