Temperature Dependence of the Formation of NiO-Li_2O Solid Solution

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Since Verwey[1] extensively studied the semiconductivity of a solid solution of lithium oxide in nickel oxide, many investigators[2,3,4] have studied the physical or catalytic properties of the solid solution. In the previous papers[1,2,3,4] the solid solution of NiO-Li_2O was formed by heating the mixture of nickel oxide and lithium carbonate. Unfortunately, the dissolved lithium oxide was not determined chemically and was thought to be the same as the added lithium oxide. It is expected that the amount of free lithium oxide is high when the sample is heated at a low temperature and the amount of evaporated lithium oxide is high when the sample is heated at a high temperature in the process of the NiO-Li_2O solid solution formation. Accordingly, it is desiarble to determine the amount of the dissolved lithium oxide.

The mixture of nickel oxide and 5 or 10 at. % of lithium was heated and studied in the previous papers[1,4]. In the present experiment about 18 at. % of lithium equivalent to 4.15 wt. % of lithium oxide was mixed. Since the dissolved lithium oxide became constant after a heating period of 3 hr. at 800°C, the mixture of nickel oxide and lithium carbonate which was equivalent to 4.15 wt. % of lithium oxide was heated for 3 hr. at various temperatures. Chemical analysis of lithium oxide was carried out by a flame photometry[5]. Nickel oxide is not soluble in cold dilute acetic acid but lithium carbonate or free lithium oxide is soluble in it. The amount of lithium oxide dissolved in nickel oxide or free oxide was determined by the extraction method and the result is shown in Table I.

Table I shows that the amount of lithium oxide dissolved in nickel oxide is very small when the sample is heated below 600°C and increases with an increase in the heating temperature up to 800°C, but decreases above 1000°C. On the other hand, the amount of free lithium decreases with an increase in the temperature. It is seen that there is a relatively large amount of free lithium oxide present when the sample is heated at high temperatures of 1400 and 1500°C. The amount of lithium oxide evaporated increases remarkably with an increase in the temperature. Table I shows that the mixture heated at 800°C loses one half of the lithium oxide added and the mixtures heated at 1400 and 1500°C have only one tenth of the lithium oxide added. High temperatures are not suitable for the formation

TABLE I. CHEMICAL ANALYSIS AND ELECTRICAL RESISTANCE OF THE MIXTURE HEATED AT VARIOUS TEMPERATURES

Heating temp. (°C)	Free Li_2O (wt. %)	Dissolved Li_2O (wt. %)	Evaporated Li_2O (wt. %)	Electrical resistance (Ω cm.)
unheated	4.15	0	0	3.3×10^{6}
200	4.15	0	0	3.3×10^{6}
300	4.15	0	0	1.2×10^{6}
400	4.15	0	0	4.8×10^{5}
500	4.15	0	0	1.8×10^{4}
600	4.00	0.07	0.08	3.5×10^{2}
800	0.60	1.39	2.16	8.0×10
1000	0.32	1.34	2.49	8.2×10
1100	0.31	1.21	2.63	8.8×10
1200	0.26	0.84	3.05	1.3×10^{2}
1300	0.18	0.78	3.19	1.8×10^{2}
1400	0.11	0.34	3.70	9.2×10^{2}
1500	0.10	0.22	3.83	1.1×10^{2}

1) E. J. Verwey et al., *Philips Res. Rep.*, **5**, 173 (1950).
2) A. Cimino et al., *Z. phys. Chem. N. F.*, **16**, 101 (1958).
3) G. Parravano, *J. Am. Chem. Soc.*, **75**, 1452 (1953).
4) P. Fensham, ibid., **76**, 969 (1954).
5) T. Takeuchi et al., *Rep. Government Ind. Res. Inst. Nagoya (Nagoya Kogyo Gijitsu Shikenjo Hokoku)*, **6**, 719 (1957).

of the solid solution of lithium oxide in nickel oxide, and a temperature range of 800 to 1000°C is suitable.

Since an amount of lithium oxide less than 0.01 wt. % is not found by the flame photometry, the amount of lithium oxide dissolved in nickel oxide below 600°C could not be determined exactly. The electrical resistance of nickel oxide has been known to be sensitive to the foreign atoms incorporated with the lattice[1]. In order to find the temperature at which lithium oxide starts to dissolve in nickel oxide, the electrical resistance of the mixtures heated at various temperatures was measured at room temperature by a method similar to that described by Griffith[6]. The electrical resistance of the mixtures decreases remarkably with an increase in the temperature up to 800°C, and increases with a temperature above 1000°C. It is clearly seen from Table I that the electrical resistance of the mixture heated at 300°C is smaller than that of the pure nickel oxide. As the pure nickel oxide was prepared from ignition of nickel sulfate at 900°C in air for 10 hrs., its electrical resistance is not thought to vary when the oxide is heated below 900°C in air. It is found that NiO-Li_2O solid solution starts to be formed about 300°C.

In order to confirm the fact, electrical resistance of pure nickel oxide and of the mixture were measured at a heating rate of 100°C/hr. from room temperature to 600°C. Fig. 1 clearly shows that the electrical resistance of the mixture becomes lower about 300°C than that of the pure nickel oxide. It is concluded that lithiuum oxide starts to dissolve in nickel oxide at about 300°C.

Bevan and coworkers[7] have suggested that diffusion in ionic compound only becomes appreciable above 0.5 T_m, where T_m is the melting point absolute. Since the melting point of nickel oxide is about 2000°C, the temperature of 300°C is equivalent to 0.25 T_m. It is found that the diffusion of lithium oxide in nickel oxide can clearly be observed by this suitable method even at 0.25 T_m.

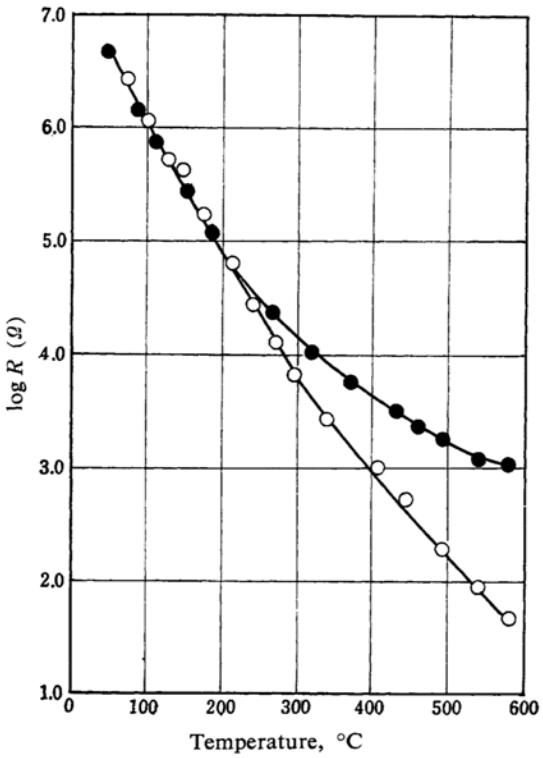

Fig. 1. Electrical resistance of pure nickel oxide (●) and the mixture of nickel oxide and lithium carbonate (○) under heating. A heating rate is 100°C/hr.

6) R. H. Griffith, *Disc. Faraday Soc.*, **8**, 258 (1950).
7) D. J. M. Bevan et al., *J. Chem. Soc.*, **1948** 1729.

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