A Note on the Solid Chemisty of the NiO-Li_2O Solid Solution

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Verwey[1] found that an oxide contains a higher or lower valency in its crystal when foreign atoms with, respectively, a lower or a higher valence than the cation of oxide are dissolved in the oxide. From a consideration of the formation of a higher or lower valency of the cations, he successfully explained the electrical conductivity of oxides incorporating foreign atoms with a different valence in terms of the cation of the oxide. This finding is known as the valency control principle. According to the principle, nickel oxide should have x atoms of Ni^{3+} ions to satisfy the electrical neutrality of the crystal when x atoms of Li^+ are dissolved in nickel oxide. The high electrical conductivity of the NiO-Li_2O solution is attributed to the formation of Ni^{3+}. Accordingly, the molecular formula of nickel oxide containing lithium oxide may be expressed by $Ni_{1-2x}{}^{2+}\ Li_x{}^{+}\ Ni_x{}^{3+}\ O$. However, it seems to be questionable that the number of Ni^{3+} ions is the same as that of Li^+ ions dissolved. Johnston and Heikes[2] did not refer to Mn^{3+} in their report on the

1) E. J. W. Verwey, P, W. Haayman, F. G. Romeyn and G. W. Van Oosterhout, *Philips Res. Rep.*, **5**, 173 (1950).

2) W. D. Johnston and R. R. Heikes, *J. Am. Chem. Soc.*, **78**, 3255 (1956).

MnO-Li_2O system. There has also been no report dealing with the relation between Li^+ and Ni^{3+} in the NiO-Li_2O solid solution.

The present study has been undertaken to clarify the question and to measure the solubility limit of lithium oxide in nickel oxide. In addition, from these data the ionic radius of Ni^{3+} has been determined.

Experimental

Nickel oxide was prepared by heating high purity nickel sulfate at 800°C. Mixtures of nickel oxide and lithium carbonate were pressed into tablets heated at various temperatures in air. To prevent the loss of lithium oxide by evaporation, the tablets in a platinum boat were covered by a powdered mixture of lithium carbonate and nickel oxide during the heating.

Free lithium oxide and dissolved lithium oxide were determined by a flame photometer in the way described in a previous paper.[3] The chemical analysis of Ni^{3+} was made according to the directions of Verwey.[1] The X-ray powder diffraction patterns were recorded by a diffractometer with a copper target. The lattice parameter of nickel oxide was determined as a function of dissolved lithium oxide by measuring the spacings of the (420) and (422) peaks.

Results and Discussion

It is not yet known how much lithium can be dissolved in nickel oxide when a mixture of lithium carbonate and nickel oxide is heated in air at high temperatures. To determine the temperature dependency of the solubility of lithium oxide in nickel oxide, a mixture of 90 at.% of nickel oxide and 10 at.% of lithium carbonate was heated in air for 3 hr. Figure 1 shows that the amount of lithium oxide dissolved in nickel oxide decreases with an increase in the heating temperature above 800°C. This decrease is attributed to the extensive evaporation of lithium oxide from the NiO-Li_2O solid solution[4] and to the evaporation of the unreacted lithium oxide. Accordingly, it is found that the temperature of 800°C is most suitable for lithium oxide to dissolve in nickel oxide. It has been reported[3] that the amount of lithium oxide dissolved in nickel oxide becomes essentially constant in a heating period of 3 hr. Mixtures of various ratios of lithium carbonate and nickel oxide were heated in air at 800°C for 3 hr. and then air-quenched.

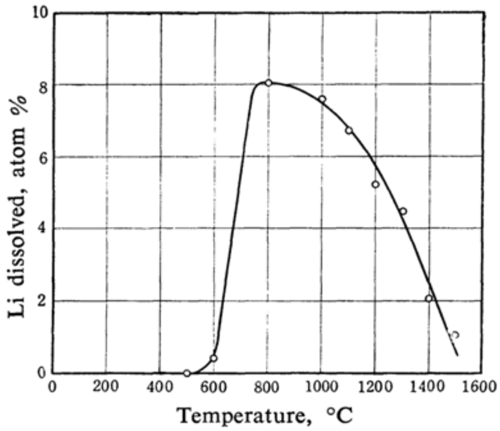

Fig. 1. Relation between the amount of dissolved lithium and heating temperatures.

It may be seen from Fig. 2 that the amount of lithium oxide dissolved in nickel oxide is always lower by a constant ratio than that of additive lithium oxide. Figure 2 shows that the amount of lithium oxide dissolved is constant above 25 at.%. It has, therefore, been concluded that the solubility of lithium oxide in nickel oxide is 25 at.% at 800°C.

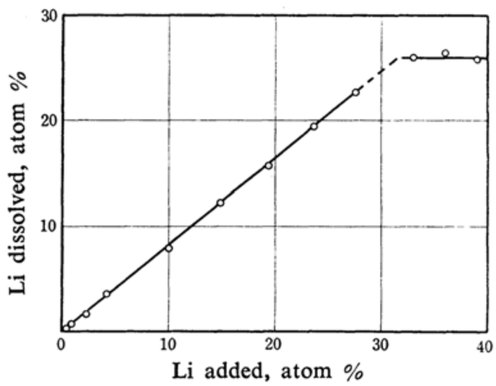

Fig. 2. Relation between the dissolved lithium and added lithium when NiO-Li_2O mixture is heated at 800°C for 3 hr.

The relation between the amount of lithium oxide dissolved and the Ni^{3+} formed in nickel oxide is shown in Fig. 3. The amount of Ni^{3+} ions is essentially the same as that of the dissolved lithium oxide within the solubility of lithium oxide. It is certified that the valency control principle established by Verwey[1] is applicable for the case of the NiO-Li_2O solid solution. Accordingly, the NiO-Li_2O solid solution can reasonably be expressed by the chemical formula of $Ni_{1-2x}^{2+} \cdot Li_x^+ Ni_x^{3+} O$. The X-ray pattern of the NiO-Li_2O solid solution exhibits a broad peak as is shown in Fig. 4, as the amount of lithium oxide dissolved increases. The broad peak results from the deformation of the crystal of the NiO-Li_2O solid solution or from

3) Y. Iida, *J. Am. Ceram. Soc.*, **43**, 117 (1960).

4) Y. Iida, ibid., **43**, 171 (1960).

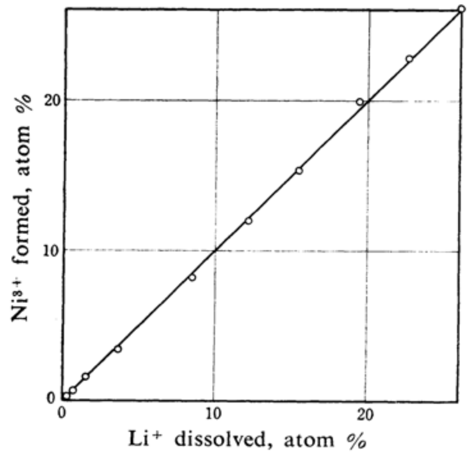

Fig. 3. Relation between the dissolved Li^+ and Ni^{3+} formed in NiO-Li$_2$O solid solution.

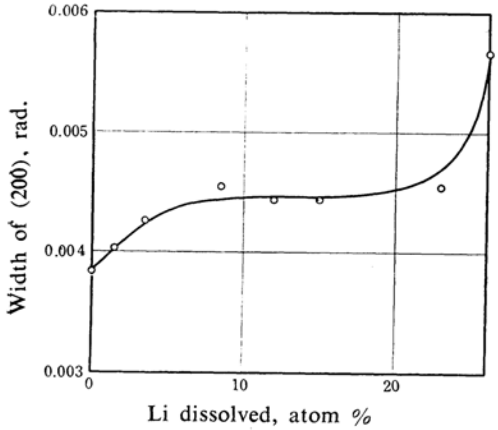

Fig. 4. Width of (200) X-ray peak of NiO-Li$_2$O solid solution as a function of lithium dissolved.

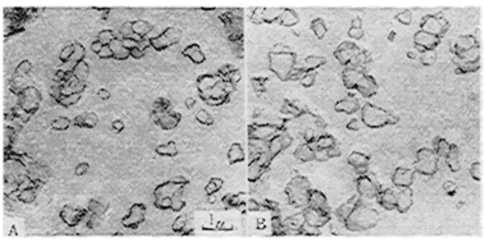

Fig. 5. Electron micrographs of pure NiO (A) and NiO-Li$_2$O (25 atom %) solid solution (B).

a decrease in its crystal size. The electron microscope photographs shown in Fig. 5 show that the particle size of the NiO-Li$_2$O solid solution does not vary with an increase in the amount of dissolved Li^+. Therefore, it is reasonable to assume that the crystal lattice of the original NiO is somewhat deformed when the nickel is replaced by lithium in the lattice.

Fensham[5] reported the lattice parameter of the NiO-Li$_2$O solid solution as a function of the Li^+ ions added. However, the amount of Li^+ ions dissolved is smaller than that of Li^+ ions added, as Fig. 2 shows. It is necessary to plot the Li^{1+} ions dissolved against the lattice parameter of the NiO-Li$_2$O solid solution. Figure 6 shows that the lattice parameter of nickel(II) oxide decreases linearly with an increase in the amount of lithium oxide dissolved. As the amount of Ni^{3+} ions

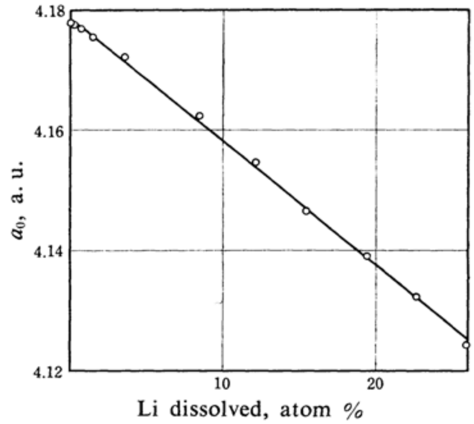

Fig. 6. Lattice parameter of NiO as a function of lithium dissolved.

is the same as that of Li^+ ions dissolved, the variation in lattice parameter can be expressed by Vegard's law as follows:

$$\Delta a_0 = 2(\Delta r_1 + \Delta r_2) \cdot x$$

where Δa_0 is the change in the lattice parameter,

Δr_1 is the difference between the ionic radii of Ni^{2+} and Ni^{3+},

Δr_2 is the difference between the ionic radii of Ni^{2+} and Li^+, and

x is the atomic % of the Li^+ ions dissolved.

There is no literature about the ionic radius of Ni^{3+}. The ionic radius of Ni^{3+} can, however, be calculated by the above equation. According to Ahrens,[6] the ionic radii of Ni^{2+} and Li^+ are 0.69 and 0.68 a. u. respectively. Therefore, the ionic radius of Ni^{3+} is found to be 0.60 a. u., which is quite reasonable in view of the fact that the ionic radius decreases with an increase in its positive valency.

Summary

In the NiO-Li$_2$O solid solution, it has been certified by a chemical analysis that the

5) P. J. Fensham, *J. Am. Chem. Soc.*, **76**, 969 (1954).
6) L. H. Ahrens, *Geochim. et Cosmochim. Acta*, **2**, 155 (1952).

amount of Ni^{3+} formed in the solid solution was the same as that of Li^+ dissolved. The NiO-Li_2O solution can be expressed by a molecular formula, Ni_{1-2x}^{2+} Li_x^+ Ni_x^{3+} O. The solubility limit of lithium to nickel oxide is 25 atomic per cent at 800°C, which is an optimum temperature for the formation of the solid solution.

The lattice parameter of nickel oxide decreases with the increase in the amount of lithium dissolved. From Vegard's law, the ionic radius of Ni^{3+} has been calculated to be 0.60 a. u.

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