JOURNAL OF MATERIALS SCIENCE 9 (1974) 1401–1408

Equilibrium relationships in the systems Li–Co–O and Li–Ni–O

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A knowledge of equilibrium relationships in the systems Li–Co–O and Li–Ni–O was of interest because of the possibility of using Li-doped oxides as electrode materials in the fused carbonate fuel cell. Equilibrium relationships in air in the former system were investigated using a thermobalance and an isobaric ternary phase diagram was constructed which shows that Co_3O_4 co-exists with a CoO rich solid solution phase and an $Li_2O.Co_2O_3$ rich solid solution phase at 860° C.

Because of the difficulty of obtaining complete reaction, equilibrium in the system Li–Ni–O was investigated primarily by X-ray examination of fired specimens. It was found that after leaching out unreacted Li_2CO_3, all the mixtures lay along the join NiO–$LiNiO_2$ in the ternary phase diagram, indicating that in the presence of Li_2O oxidation of NiO was occurring.

Results were presented to show the effects of composition and heat treatment on the electrical conductivities of selected mixtures.

1. Introduction

As described in a previous paper [1] the work was undertaken to explore the possibility of using conducting oxide electrodes in fused carbonate fuel cells. In addition to possessing the required electrical characteristics, the electrodes had to be of high porosity and surface area, while resisting disintegration in the fused carbonate. A knowledge of equilibrium relationships in the systems Li–Co–O and Li–Ni–O was of interest because of the practice of lithia-doping to increase the electrical conductivity of cobalt and nickel oxides, and also because lithium carbonate was one of the constituents of the fused salt electrolyte so that solution of lithia in the electrodes would be likely to occur in service.

Lithiated-CoO containing less than 1.0 at. % Li has been prepared by several workers. Johnson *et al.* [2], however, produced cobalt oxide containing larger amounts of lithia by pelleting mixtures of CoO and Li_2O_2 under argon and firing in sealed containers above 900° C. On quenching from the firing temperature, cubic (NaCl-type) oxides of the general formula $Li_xCo_{1-2x}{}^{2+}Co_x{}^{3+}O$, or $Li_xCo_{1-x}O$, (corresponding to solid solutions of $Li^+Co^{3+}O_2$ in CoO) were obtained with values of x up to 0.2. On slow cooling from the firing temperature $LiCoO_2$, which has the structure of $CsCl_2I$, was found to be present and on the basis of these results a partial phase diagram for the system CoO–$LiCoO_2$ was constructed showing the solubility of the $LiCoO_2$ in CoO decreasing with falling temperature.

Considerably more work has been carried out on lithiated nickel oxide. Goodenough *et al.* [3] prepared solid solutions of the form $Li_xNi_{1-2x}{}^{2+}Ni_x{}^{3+}O_2$ in which $0 \leqslant x \leqslant 0.48$. Solutions in which $x \leqslant 0.3$ were made by firing mixtures of NiO and Li_2CO_3 at 800° C in air, and solutions in which x approached 0.4 by heating NiO with molten LiOH at 600° C. In preparing solutions in which x exceeded 0.4, Li_2O_2 was incorporated into the mixtures which were fired to 800° C in air.

When $x \leqslant 0.38$ the crystal structure was found to be cubic, an eight-fold increase in unit cell volume occurring between $x = 0.30$ and $x = 0.38$ due to partial ordering of the cations. A rhombohedral phase was obtained with values of $x > 0.38$ and it was suggested that a continuous

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series of solid solutions existed between this composition and the composition $LiNiO_2$.

Toussaint [4], who confirmed that pure NiO has a rhombohedral structure at room temperature, transforming to cubic at 210°C, prepared solid solutions of the general form $Li_xNi_{1-x}O$ by firing mixtures of NiO and Li_2O_2 at 1000°C in sealed crucibles. These were found to be cubic at room temperature when $x > 0.12$ and remained cubic to $x = 0.35$. With $x = 0.39$, the maximum value reached, small amounts of $LiNiO_2$, which has the $CsCl_2I$ structure, were found to be present.

2. Starting materials

Nickel oxide (NiO) and cobalt oxide (Co_3O_4) were prepared as described previously [1]. Lithia was added to these oxides as reagent grade Li_2CO_3.

3. The system Li–Co–O

Equilibrium relationships in air in this system were established using a thermobalance to follow weight changes at equilibrium in pre-reacted mixtures of the oxides as a function of temperature. The oxide mixtures were prepared by firing pelleted mixtures of Li_2CO_3 and Co_3O_4 for 3 h at 800°C in air. After air-quenching, the pellets were crushed and unreacted alkali was dissolved from the powder using cold, dilute acetic acid. The residues were then washed and dried and samples were brought into solution and analysed quantitatively for lithia using a flame photometer. The phases present in the mixtures after leaching were identified from X-ray powder photographs.

Fig. 1 shows the relation between the lithia contents of the mixtures after firing and removal of unreacted alkali and that present as carbonate in the initial mixtures before firing. It will be seen that the percentage of reacted Li_2O in the mixtures is always considerably less than that added as carbonate initially and appears to be approaching a limit at about 15.3 % Li_2O, which is the lithia content of the compound $LiCoO_2$, ($Li_2O.Co_2O_3$). X-ray analysis showed that all of the mixtures except A and F consisted of Co_3O_4 and $LiCoO_2$, the measured unit cell parameters of the latter compound being $a = 2.8152$ Å and $c = 14.050$ Å, in good agreement with those obtained by Johnson *et al.* [2]. In mixture A only Co_3O_4 was detected and in mixture F only $LiCoO_2$, possibly because, in each of these mixtures the quantity of the second phase present was too small to be detected, or alternatively that there is slight mutual solid solubility of the two compounds in each other.

The results of the equilibrium studies on the pre-reacted mixtures using the thermobalance are shown in Fig. 2. The at. % of oxygen in the mixtures were calculated from the observed weight losses at equilibrium and the initial oxygen contents of the pre-reacted mixtures,

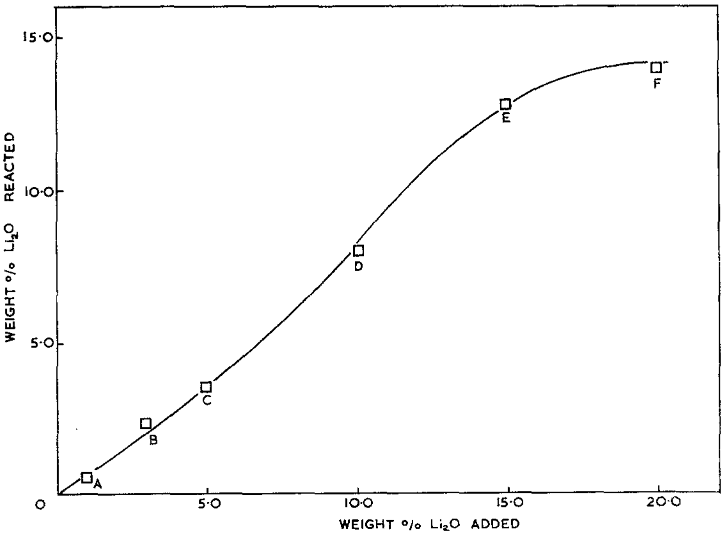

Figure 1 The relationship between the wt% Li_2O present in unreacted mixtures of Co_3O_4 and Li_2CO_3, and the wt% Li_2O found to have reacted with the cobalt oxide after firing at 800°C for 3 h.

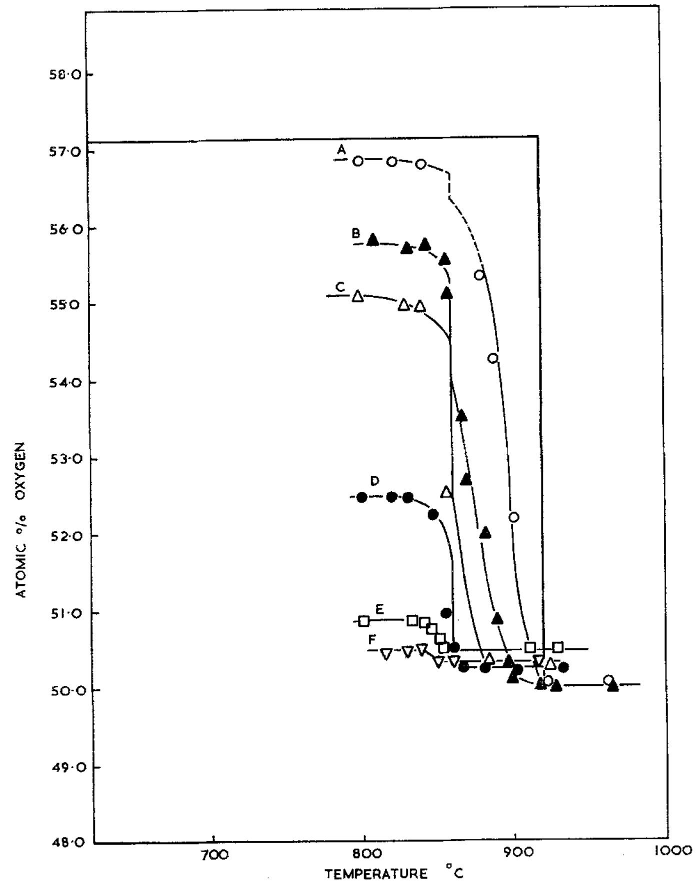

Figure 2 Equilibrium curves for pre-reacted cobalt and lithium oxide mixtures in air at 1 atm pressure. Plotted as at. % oxygen in the mixtures versus temperature.
Cation compositions of the mixtures in at. %

	Co	*Li*
A.	97.4	2.6
B.	89.1	10.9
C.	83.6	16.4
D.	65.4	34.6
E.	55.1	44.9
F.	52.6	47.4

The equilibrium curve for cobalt oxide alone is also shown.

which were calculated on the assumption that the latter, as indicated by the X-ray studies, consisted of Co_3O_4 and $LiCoO_2$ in proportions determined by the analysed Li_2O contents.

For the equilibrium studies each mixture was first held at 930°C in air on the thermobalance until it had reached equilibrium with the atmosphere. It was then brought to equilibrium at progressively lower temperatures. All the samples were found to return to their initial pre-reacted weights showing that loss of lithia during this operation had been negligible.

The equilibrium curve for cobalt oxide alone, which was established during the earlier work [1], has been included in Fig. 2 for comparison. In this sample the transformation from Co_3O_4 to CoO occurred at constant temperature as required by the phase rule and is indicated by a vertical step on the curve at 918.5°C. With mixtures of lithium and cobalt oxides on the other hand oxidation on cooling occurred over a range of temperatures although several of the curves also show a vertical step at 860°C. The existence of this step was established by the thermobalance in the case of mixtures B, C and D, and is suggested on curve A. The occurrence of these steps shows that, at 860°C in these mixtures, three condensed phases must co-exist with the gas phase and will form a tie triangle in the ternary diagram. Similarly, where the equilibrium curves slope, not more than two condensed phases will co-exist with the gas phase.

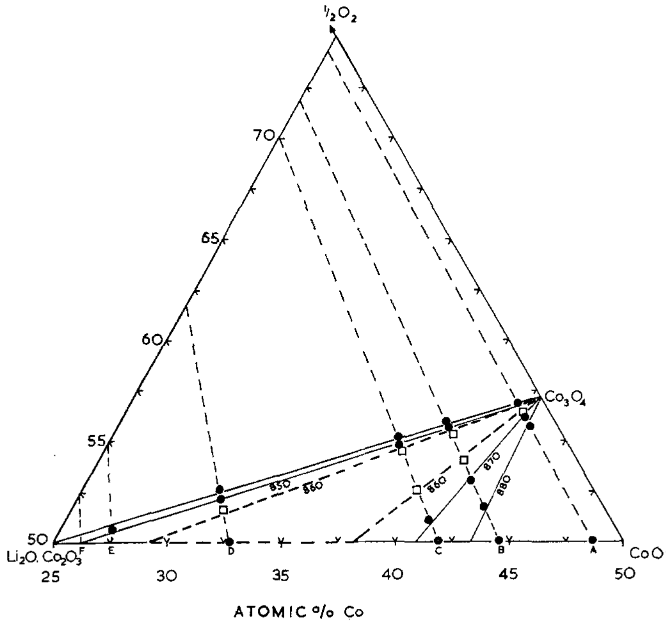

Figure 3 Part of the ternary equilibrium diagram of the system Li–Co–O in air at 1 atm. pressure. The isotherms were established from the equilibrium curves of Fig. 1.

The isobaric ternary diagram of the system at 0.21 atm oxygen pressure, constructed from the equilibrium curves of Fig. 2, is shown in Fig. 3. The compositions of the fully-oxidized mixtures which, as shown above, consisted of Co_3O_4 and $LiCoO_2$, and represented the stable state of the system at low temperatures in air, lie along the line joining Co_3O_4 to $Li_2O.Co_2O_3$. The dashed straight lines sloping downwards from left to right represent the reaction paths along which the composition of the experimental mixtures would change with change in oxygen content, and the plotted points on these reaction paths represent compositions reached at various temperatures on the equilibrium curves. The isotherms (straight lines with temperatures alongside) were constructed by joining the compositions reached at the temperatures indicated. In areas where two condensed phases co-exist, these are also conjugation lines joining the compositions of the two phases which co-exist in equilibrium with each other and with the gas phase at that temperature.

The two 860°C isotherms, which are shown dashed and were established from the compositions at the top and bottom of the vertical steps on the equilibrium curves, also form the boundaries of a tie triangle linking the compositions of the Co_3O_4 spinel, the CoO–$LiCoO_2$ phase (with the NaCl structure) and the $LiCoO_2$–CoO phase (with the $CsCl_2I$ structure) which co-exist with the gas phase at this temperature.

Confirmation of the phase relationships indicated in Fig. 3 was obtained by microscopic examination of polished sections after various heat-treatments in air. Thus pellets of mixture C after holding at 1000°C for 2 h were found to be single-phase after quenching from that temperature, but became two-phase (Co_3O_4 and $LiCoO_2$) when subsequently held at 800°C until the weight had become constant. Similarly, mixture D was found to consist of three phases after holding at 1000°C for 2 h and then at 850°C for long enough to bring its composition within the boundaries of the tie triangle. Owing to lack of contrast between the phases in this system it was not possible to obtain micrographs suitable for reproduction although features of the microstructures could be observed visibly as described in Section 5.

4. The system Li–Ni–O

In this system, unlike the system Li–Co–O, oxidation to a spinel phase did not occur in air at temperatures covered by the investigation. The compositions of the fired mixtures, after leaching out unreacted Li_2CO_3, therefore, all lay along the join NiO–$LiNiO_2$ in Fig. 4 and did not change

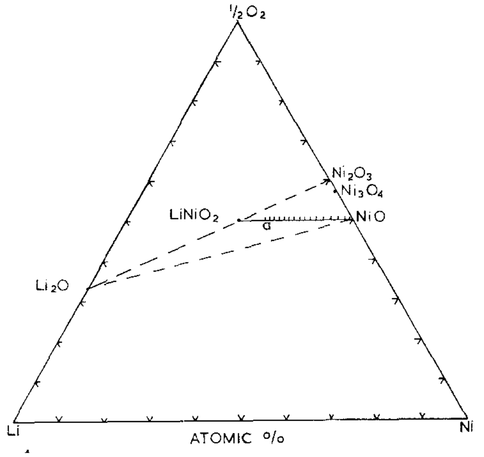

Figure 4 Ternary diagram of system Li–Ni–O showing join NiO–LiNiO$_2$. Compositions of experimental mixtures lay on the line NiO–Li$_2$O before firing and on the line NiO–LiNiO$_2$ after firing in air. Point a is the limit of the range of the Li$_x$Ni$_{1-x}$O solid solutions at 800°C.

with temperature.

Work on the system was consequently confined to the preparation of a series of compositions for the electrical conductivity measurements. For this purpose mixtures of Li$_2$CO$_3$ and NiO containing the equivalent of up to 20% Li$_2$O by weight were pelleted and fired at 800°C in air for 3 h, after which they were air-quenched, crushed, leached with acetic acid and analysed for Li$_2$O using the flame photometer. Fig. 5 shows that the maximum take-up of Li$_2$O by the NiO occurred with 10% Li$_2$O in the original mixture and was only 4.25% by weight. (The Li$_2$O content of LiNiO$_2$ is 15.25% by weight.) The Li$_2$O take-up then decreased with increasing Li$_2$CO$_3$ in the mixture.

X-rays showed that all the fired mixtures contained unreacted NiO in addition to the cubic Li$_x$Ni$_{1-x}$O solid solution phase. The lattice parameter of the latter decreased with increasing Li$_2$O in the mixture, being 4.163, 4.137, 4.116 and 4.112 Å in mixtures G, H, I and J respectively. After refiring these mixtures at 950°C for 5 h, however, only the Li$_x$Ni$_{1-x}$O phase was detected and its lattice parameter in the four mixtures had increased to 4.170, 4.150, 4.134 and 4.138 Å, confirming that solution of NiO in it had occurred.

It can be seen from the equation

$$\tfrac{1}{2}x\mathrm{Li_2CO_3} + (1-x)\,\mathrm{NiO} + 1/4x\mathrm{O_2} = \mathrm{Li}_x{}^{+}\mathrm{Ni}_{1-2x}{}^{2+}\mathrm{Ni}_x{}^{3+}\mathrm{O} + \tfrac{1}{2}x\mathrm{CO_2}$$

(and also from Fig. 4), that the incorporation of Li$_2$O into NiO involves oxidation of Ni^{2+} to Ni^{3+}. The most probable cause of the decrease in lithia take-up with high Li$_2$CO$_3$ contents, and of the retention of unreacted NiO after the

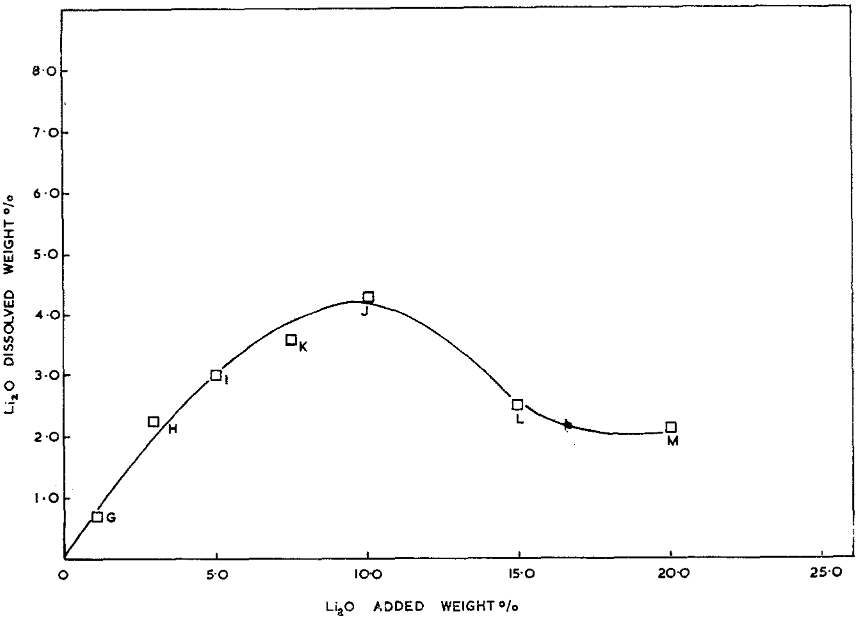

Figure 5 The relationship between the wt% Li$_2$O present in unreacted mixtures of NiO and Li$_2$CO$_3$, and the wt% Li$_2$O found to have dissolved in the NiO after firing at 800°C in air for 3 h.

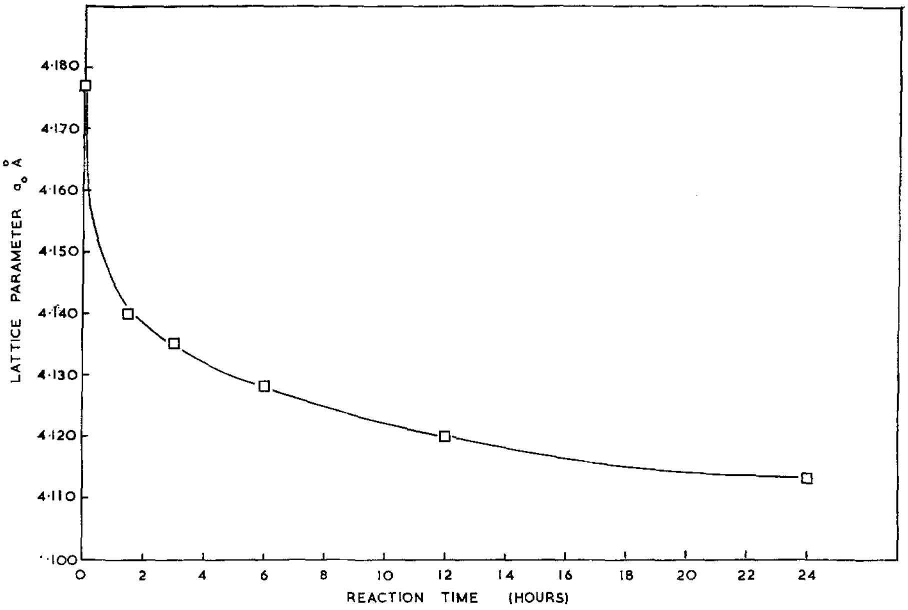

Figure 6 Variation with total firing time at 800°C of lattice parameter of $Li_xNi_{1-x}O$ phase in a mixture of NiO and Li_2CO_3 containing initially 7% Li_2O by weight.

initial firing, was that penetration of atmospheric oxygen into the pellets had been obstructed by the presence of liquid carbonate in the voids between the particles.

To test this hypothesis a sample of NiO was reacted by firing at 800°C with three successive additions of Li_2CO_3 equivalent to increments of 7, 10 and 10% Li_2O by weight in the composition of the mixture, thus avoiding a large single addition of the carbonate. The firing times after these additions were respectively 24, 12 and 18 h, but, during the 24 h firing period after the first addition had been made, the mixture was ground, sampled and re-pelleted a number of times without further additions of carbonate. Fig. 6 shows how the lattice parameter of the $Li_xNi_{1-x}O$ phase varied with the total firing time during this period and it will be seen that it had fallen from 4.177 Å, the value for NiO, to 4.113 Å after 24 h firing and appeared to be approaching constancy.

This conclusion was confirmed by the finding that, when the 24 h sample was treated with acetic acid to remove unreacted Li_2CO_3, no effervescence occurred, showing that no unreacted alkali was present. Some unreacted NiO was, however, present in all the samples.

After the second and third additions of carbonate and the two subsequent firings, the rhombohedral $LiNiO_2$ phase was found to be present in both the samples and the lattice parameter of the cubic $Li_xNi_{1-x}O$ phase had decreased to 4.107 and 4.109 Å respectively. These values are in good agreement with the value found by Toussaint [4] at the limit of this phase when x had its maximum value of 0.39. The present results thus confirm the latter's findings, although some unreacted NiO was again found to be present. They also provide an explanation for the fact that attempts by other authors to prepare $LiNiO_2$ from stoichiometric mixtures of Li_2CO_3 and NiO have been unsuccessful.

No microstructural work was carried out on this system since the methods used produced porous agglomerates which were unsuitable for the preparation of polished sections.

5. Electrical conductivity measurements

The electrical resistance of fired pellets of the Li_2O-cobalt oxide and Li_2O-nickel oxide mixtures was measured between 20 and 1000°C, using a potential probe technique as described previously [1]. Because of the lower resistance, however, a four-probe technique, which automatically compensated for the resistance of the leads, was used instead of the two-probe technique used previously. Prior to testing, all the

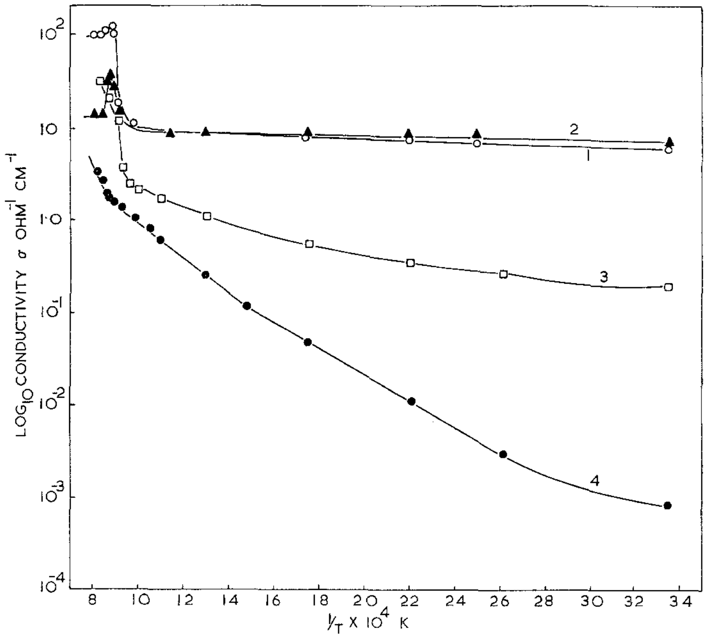

Figure 7 Plots of log conductivity versus reciprocal temperature of lithia-cobalt oxide mixtures in air. *Cation compositions of mixtures in at. %*

	Co	*Li*
1.	97.4	'2.6
2.	83.6	16.4
3.	65.4	34.6
4.	52.6	47.4

pellets were fired at 800°C for 2 h in air to produce bodies of comparable porosity (about 40%).

Fig. 7 shows the results of the resistance measurements on four Li_2O-cobalt oxide mixtures (A, C, D and F of Fig. 3). The resistances were measured at progressively decreasing temperatures from 1000°C downwards and before each measurement was made the temperature was held constant for 12 h.

With both 1 and 2, which would consist of the $Li_xCo_{1-x}O$ phase at 1000°C, as oxidation occurred on cooling, a sharp rise of conductivity occurred as x increased to its maximum value in this phase and Co_3O_4 separated. Then as the reaction paths of the two mixtures crossed the three-phase tie triangle in Fig. 3, corresponding to oxidation of the Li-saturated $Li_xCo_{1-x}O$ phase to the Co-saturated $LiCoO_2$ phase and Co_3O_4, a sharp fall in conductivity occurred. Assuming the limiting compositions indicated for these two phases in Fig. 3, this reaction, which, at constant oxygen pressure, would proceed to completion isothermally, can be written

$$14.5(Li_{0.24}Co_{0.52}^{2+}Co_{0.24}^{3+}O) + O_2$$
$$= 8.5(Li_{0.41}Co_{0.18}^{2+}Co_{0.41}^{3+}O) + 2Co_3O_4\,.$$

The fall in conductivity accompanying this reaction suggests that the Co-saturated $LiCoO_2$ phase had the lowest conductivity of the three solid phases involved. An explanation for the very marked effect of this phase was suggested by the microstructures which showed that it tended to occur between the spinel grains. On further cooling to about 800°C its composition would change progressively from that indicated on the right hand side of the above equation to the stoichiometric composition $LiCoO_2$ with separation of further spinel, giving rise possibly to the progressive change of slope of the two curves at the bottom of the vertical steps. (It should be noted that in general the temperatures indicated for the various transitions in Fig. 7 are rather lower than those indicated by Fig. 3 due to the fact that super-cooling occurred.)

On further cooling there was only a very slight fall in the conductivity of both 1 and 2 down to room temperature. The reason for this small temperature-dependence was not established.

The behaviour of mixtures 3 and 4 can also be explained largely on the basis of the phase changes occurring during cooling in air. Thus with 3, which would consist of a mixture of the

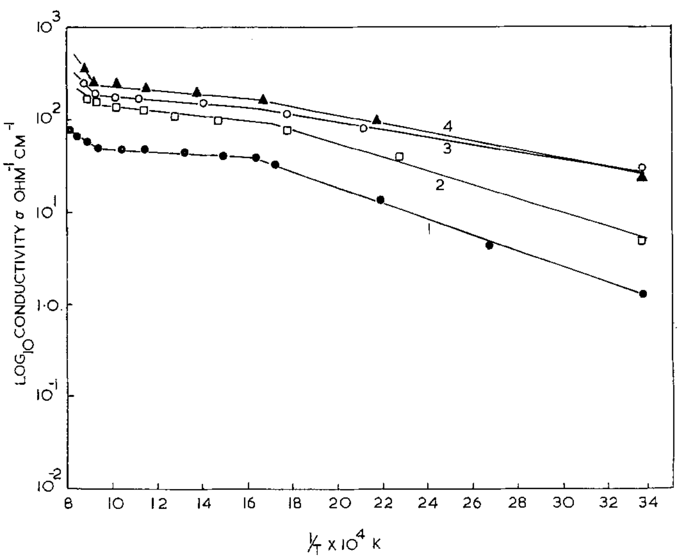

Figure 8 Plots of log conductivity versus reciprocal temperature of lithia-nickel oxide mixtures in air. *Cation compositions of mixtures in at. %*

	Ni	*Li*
1.	96.6	3.4
2.	89.9	10.1
3.	86.6	13.4
4.	81.9	18.1

Li-saturated $Li_xCo_{1-x}O$ phase and the Co-saturated $LiCoO_2$ phase between 1000 and 850°C, and would change isothermally to a mixture of the latter and Co_3O_4 at 850°C, the conductivity first fell progressively and then (slightly below 850°C) vertically, the vertical step being followed by a progressive decrease in slope as before.

On the other hand with 4, which would consist of the $LiCoO_2$ phase containing excess Co, a progressive change to stoichiometric $LiCoO_2$ (plus a small amount of spinel) would occur from some temperature below 850°C down to 800°C, and no vertical step occurs on the curve. The marked decrease in conductivity with increasing Li_2O content observed with 3 and 4 at low temperatures can probably be attributed to low conductivity of the $LiCoO_2$ phase, the content of which, at low temperatures, would increase with increasing Li_2O content.

Fig. 8 shows the results of similar measurements on four Li_2O-nickel oxide pellets whose compositions all lay within the homogeneity range of the $Li_xNi_{1-x}O$ solid solutions at 800°C. (It is not known whether the range would decrease sufficiently on cooling to cause separation of $LiNiO_2$ although this phase was not detected by X-rays in samples fired at 800°C and furnace-cooled.) All four curves consist of three approximately straight portions, a "knee" occurring at 790°C and a second break at 317 to 337°C. The form of the curves is thus very similar to that of the curve for NiO established previously [1], the temperatures of the breaks being similar, although the conductivities are much higher and increase with Li_2O content.

The slopes of the curves above the knee appear to increase with increasing Li_2O content but the corresponding energies of activation fall in the range 0.32 to 0.70 eV, which is of the same order as that observed with NiO (0.47 eV [1]). Below the knee the slope was very small, being similar to that observed on curves 1 and 2 of Fig. 7 and corresponding to an apparent energy of activation of 0.05 eV. The reason for this small slope was again not established.

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Received 9 October 1973 and accepted 17 April 1974.