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Short communication

On Li_2O evaporation from $Li_xNi_{1-x}O$ solid solution

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Abstract

Lithium oxide evaporation from $Li_xNi_{1-x}O$ with $x = 0.2$ and 0.3 at 800°C was investigated by XRD measurements. The results indicated that the mechanism of lithium loss depends on the nominal lithium content of the solid solution. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

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This short note follows the recent work of Sata [1] on Li_2O evaporation from $Li_xNi_{1-x}O$ solid solution. Sata investigated lithium oxide vaporization from $Li_xNi_{1-x}O$ with $x = 0.1$–0.4 at temperatures in the range 400–700°C. He found that log–log plots of evaporated Li_2O vs time consist of two or three straight lines with different slopes. The vaporization stopped at third stage, leaving some Li_2O behind. The x-values in the samples decreased linearly from the surface to the interior along the specimen thickness. Sata hypothesised that the formation of Li_2O_2 from Li_2O decomposed from the solid solution and its diffusion in the specimen may be related to the rate-determining step in the vaporization. At higher temperatures ($T > 1000$°C), instead, the evaporation of lithium oxide from $Li_xNi_{1-x}O$ is governed by the parabolic law [2]. The diffusion of lithium ions to the surface of the solid solution is the rate-determining step in the evaporation.

In this communication we have evaluated the way of lithium loss at 800°C by reviewing the data reported in Ref. [3] related to thermal treatment for times up to 341 h of $Li_xNi_{1-x}O$ solid solutions with nominal $x = 0.2$ and 0.3, obtained from solid-state reaction of Ni and Li_2CO_3 powders. From the values of lithium atomic fraction x in $Li_xNi_{1-x}O$, calculated from XRD measurements and reported in Tables 1 ($x = 0.2$) and 2 ($x = 0.3$) of Ref. [3], we have calculated the evaporated lithium atomic fraction x_{ev} from the relationship [4]:

$$x_{ev} = (x_0 - x_t)/(1 - x_t) \tag{1}$$

where x_0 and x_t are lithium atomic fraction in the solid solution at the beginning and after t h of the vaporization process. Figs. 1 and 2 show log–log plots of x_{ev} vs time for nominal $x = 0.2$ and 0.3, respectively. The specimen with $x = 0.2$, as can be seen in Fig. 1, shows a trend of Li_2O vaporization like that obtained by Sata. Above 178 h the vaporization stopped: the values of x in $Li_xNi_{1-x}O$ after 178 and 289 h, indeed, were 0.176 and 0.173, respectively. The log–log plot of the sample with $x = 0.3$, instead, is almost linear with slope 0.5, as shown in Fig. 2: this means that the Li_2O evaporation is diffusion controlled and is governed by the parabolic law.

Regarding the distribution of lithium ions in $Li_xNi_{1-x}O$, information can be obtained by the Rietveld refinement procedure, based on the fit between calculated and observed XRD patterns. The goodness of fit (GoF), obtained by the refinement performed with the single-phase model, is correlated to the homogeneity of the solid solution: the greater the difference from unity is the GoF parameter, the more non-homogeneous is the solid solution. If we plot the difference of GoF values of $Li_xNi_{1-x}O$ with $x = 0.2$ and 0.3 as a function of log time, as reported in Fig. 3, we can note the different behaviour of these compositions. For short times of thermal treatment, the solid solution with $x = 0.2$ is more homogeneous than that with $x = 0.3$ ($\Delta GoF > 0$), while for longer times the solid solution with $x = 0.2$ is less homogeneous than the other ($\Delta GoF < 0$). The large peak and the inversion of ΔGoF, shown in Fig. 3, are related to the different mechanism of lithium loss. The initial homogenization of sample with $x = 0.2$ was

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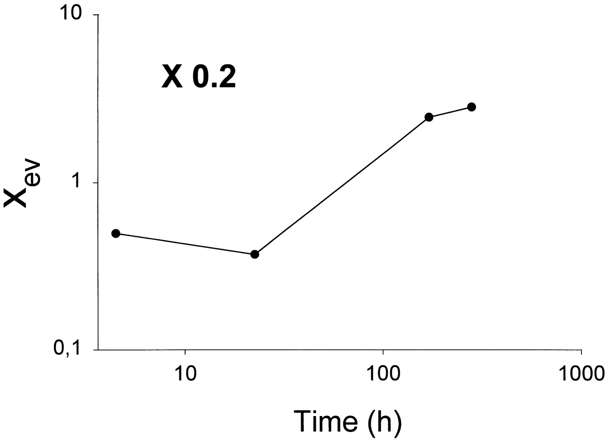

Fig. 1. Log–log plot of evaporated lithium atomic fraction vs thermal treatment time for the solid solution with nominal $x=0.2$.

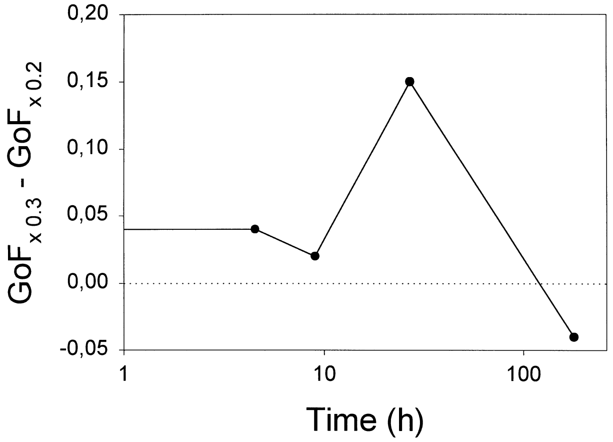

Fig. 3. ΔGoF of samples with $x=0.2$ and 0.3 as a function of log time.

attained by grain boundary diffusion of lithium ions, as, for short times of thermal treatment up to 27 h, $Li_xNi_{1-x}O$ particles were small, as shown in Fig. 2 of Ref. [3]. The dependence of lithium gradient along $Li_xNi_{1-x}O$ particles with nominal $x=0.3$ on the logarithm of thermal treatment time is reported in Fig. 4. Lithium gradient is expressed as the difference of the maximum (x_{max}) and the minimum (x_{min}) lithium atomic fractions present in the solid solution, obtained by the Rietveld refinement performed with the multi-phase model. After 4.5 h of thermal treatment lithium ion concentration in the solid solution decreased going from outer to inner part of the grain, being not the complete homogenization process of the solid solution [5]. From 4.5 to 9 h of annealing, lithium gradient decreased both by lithium oxide evaporation from the grain surface and by lithium ion migration towards the bulk. After 9 h of thermal treatment, the solid solution was nearly homogeneous ($x_{max}-x_{min} < 0.01$). Above 9 h of thermal treatment, instead, the amount of lithium increased from external to internal part of Li-doped NiO particles. From 9 to 27 h of isothermal treatment, lithium gradient increased by lithium oxide loss from the surface of the particles. Then, from 27 h to the end of the thermal treatment, lithium gradient decreased by diffusion of lithium ions from the bulk to the surface of the grains. This result is the opposite to that obtained by Sata (lithium amount decreasing from the surface to the interior along the specimen thickness).

The different behaviour of specimens with $x=0.2$ and 0.3 could be explained by the absence/presence of defects. At 800°C the lattice diffusion of lithium and oxygen ions from the bulk to the surface is very low, so lithium loss should occur by mechanism proposed by Sata, as revealed for the sample with $x=0.2$. But lithium ion diffusion in Li-doped NiO can be enhanced by the presence of vacancies. It is known that the $Li_xNi_{1-x}O$ lattice constant linearly decreases with lithium content of the solid solution [6]. The lattice contraction can be attributed to the transformation of a Ni^{2+} (larger) ion into a Ni^{3+} (smaller) ion for each Li^+ ion that enters the lattice. Literature data [7] reported that the

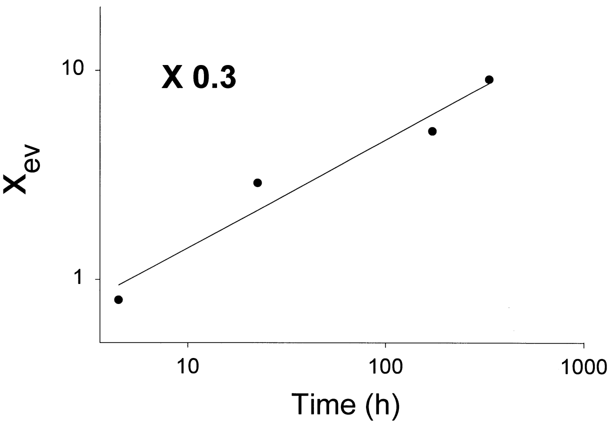

Fig. 2. Log–log plot of evaporated lithium atomic fraction vs thermal treatment time for the solid solution with nominal $x=0.3$.

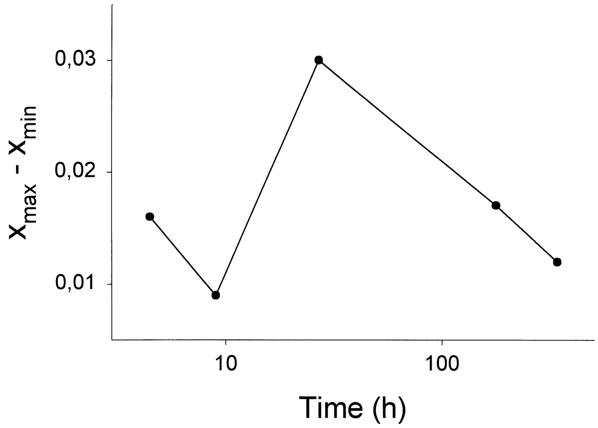

Fig. 4. Dependence of lithium gradient, expressed as $x_{max}-x_{min}$, on the logarithm of time for the solid solution with nominal $x=0.3$.

dependence of lattice constant on x deviates from linearity for $x > 0.2$: the value of the lattice constant is higher than that expected from the extrapolation of linearity. This can be explained considering that substitutional lithium doping of NiO, besides oxidizing Ni^{2+} as:

$$x/2Li_2O + (1-x)NiO + x/4O_2 \rightarrow Li_xNi^{2+}_{1-2x}Ni^{3+}_xO \tag{2}$$

can occur, analogously to lithium doping of MgO [8], by the formation of oxygen vacancies as:

$$Li_2O \rightarrow 2Li'_{Ni} + V''_O + O_O \tag{3}$$

where Li'_{Ni} is substitutional Li in Ni site and V''_O is the oxygen vacancy. In the same way of Li-doped MgO, it is possible the occurrence of defect associates as $(V''_OLi'_{Ni})$ and $(Li'_{Ni}V''_OLi'_{Ni})$ which can support lattice diffusion of lithium ions to the surface.

Summarizing, the result of this work indicates that the mechanism of lithium loss depends not only on temperature, but also, especially for temperatures lower than 1000°C, on the nominal lithium content of the solid solution.

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