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**PREPARATION AND CHARACTERIZATION OF DENSE NiO-BASE
CERAMICS (NICKEL OXIDE AND LITHIUM SUBSTITUTED
NICKEL OXIDE)**

by

C. GEEL, R. MORLOTTI and S. PIZZINI

1969



**Joint Nuclear Research Center
Petten Establishment - Netherlands**

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It is shown that for pure nickel oxide the physico-chemical properties, as density and excess oxygen content, are strongly influenced by the manufacturing process, mainly by the preliminary treatment of the powder.

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ABSTRACT

Preparation and quality control methods for nickel oxide base ceramics are described.

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KEYWORDS

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PREPARATION AND CHARACTERIZATION OF DENSE NiO-BASE
CERAMICS (NICKEL OXIDE AND LITHIUM SUBSTITUTED
NICKEL OXIDE) *)

C.Geel, R.Morlotti and S.Pizzini

Nickel oxide, both pure and doped with alkali, is a very interesting material for the chemical industry (as a catalyser and for electrochemical applications as an electrode in batteries) and possibly in the electronics industry.

This note deals with the manufacture of dense ceramic bodies of controlled lithium content, from very pure NiO to highly doped (> 40 a/o lithium) products.

Two different goals have been achieved:

- a) the shaping of pure, dense and crack-free bars or pellets of NiO as well as of lithium doped NiO by standard ceramic methods (low temperature pressing followed by high temperature sintering);
- b) the achievement of products of controlled quality.

In Table I the results of a first series of experiments are reported for products (rather coarsely grained powders) coming from different sources, namely:

- a) as a commercially available product (better than 99 % pure);
- b) from decomposition and annealing at 1200 °C for 24 hrs., of nickel oxalate precipitated from an aqueous solution of nickel nitrate by an oxalic acid solution.

The powders were pressed without binder in conventional steel dies at room temperature and sintered according to the specifications of Table I.

*) Manuscript received on 15 July, 1969.

Table I

Relevant parameters for the preparation of NiO bars from the decomposition of the oxalate.

Forming- pressure t / cm ²	Sintering temperature °C	Density as* pressed g / cm ³	Density as* sintered g / cm ³	Origin
11	1200	5.08	4.90	market
7	-	4.86	4.19	
3.5	-	4.57	4.10	
10.5	1400	5.06	5.18	market
7	-	4.98	4.94	
3.5	-	4.64	4.74	
10.5	1600	5.09	5.49	market
7.0	-	4.93	4.34	
3.5	-	4.56	5.08	
10.5	1200	4.99	5.12	from Nickel oxalate
7.0	-	4.85	5.26	
3.5	-	4.19	5.21	
11.5	1400	4.92	5.10	idem
7.0	-	4.73	4.86	
3.5	-	4.11	4.26	
11.5	1600	4.94	5.92	idem
7.0	-	4.75	5.87	
3.5	-	4.19	5.39	

(*) The theoretical density of NiO is 6.806

These results show that only at high temperatures a reasonable densification does occur and that the pressure of forming has a certain influence on density. To improve the density of the products, it was decided to try pressing with more active powders as suggested in References 1-5.

Such powders were produced by lowering the decomposition temperature of the oxalate and making the annealing time shorter, to avoid agglomeration and densification of the fine grains. From Table II it is possible to see that nickel oxalate decomposed at 300 °C, 450 °C or 600 °C densifies much better than before to a maximum of about 92 % of theoretical density.

The products were pressed at 7 t/cm² and sintered at 1600 °C.

It is apparent that the density is independent of the decomposition temperature. The result is in contradiction to the work of Brown⁶, who found the optimum in densification with powders decomposed at 450 °C. The reason for this is that the exothermic reaction taking place during decomposition, causes a temperature rise, which varies with the different experimental conditions. To avoid these difficulties, nickel oxalate was first decomposed very slowly (for 20 hrs.) at 280 °C, and afterwards brought to 300 °C - 450 °C or 600 °C and held there for half an hour. These products, pressed at 7 t/cm² and sintered at 1600 °C, gave the densities mentioned in Table III.

All the NiO products obtained by the decomposition of nickel-oxalate at these low temperatures however, show a very dark colour and much deviation from stoichiometry. For this reason other starting compounds have been used, as reported in Table IV. The temperature of sintering is 1600 °C as before.

Table II

Density of the sintered bars as a function of the decomposition temperature of the oxalate.

Decomposition temp. °C	Density g / cm ³	Relative density
600	6.26	91.9 %
450	6.24	91.6 %
300	6.25	91.8 %

Table III

Influence of the annealing temperature on the density of NiO (from oxalate).

Decomposition temperature °C	Annealing temperature (°C)	Density g / cm ³	Relative density
280	600	6.08	89.5 %
	450	6.23	91.5 %
	300	6.56	95.1 %

Table IV

Relevant parameters for the preparation of sintered bars from different starting products.

Decomposition compound	Decomposition temperature (°C)	Forming pressure t / cm ²	Density g / cm ³	Relative density
Ni-oxalate	300 *	3.5	6.24	91.7 %
		10.5	6.27	92.2 %
Ni-sulfate	900	3.5	6.34	93.2 %
		10.5	6.38	93.8 %
Ni-nitrate	600	3.5	6.30	92.6 %
		10.5	6.24	91.7 %

(*) without preliminary heating at 280 °C

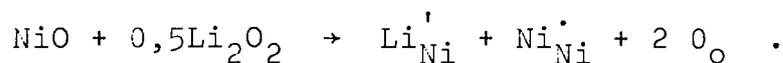
This Table is a summary of the results dealing with the preparation of NiO and shows that the most dense products were obtained when starting from nickel sulfate.

As far as the purity and stoichiometry of the samples is concerned, at the higher decomposition temperatures the more stoichiometric products were obtained, whereas the purity depends very much on the purity of the starting products and on the care with which each step of the manufacturing procedure is performed.

As an example, Table V gives impurity content values for a sample obtained from the decomposition of the oxalate. The oxalate has been obtained by precipitation from a solution of many-times recrystallized "reagent grade" $\text{Ni}(\text{NiO}_3)$

Lithium doped NiO

Lithium doped nickel oxide, with a maximum value of the substituted lithium of 40,26 a/o (atomic percent), was successfully obtained by using lithium peroxide instead of lithium carbonate⁹⁻¹⁰ as the lithium dopant. Lithium peroxide, in fact, provides the stoichiometric amount of oxygen needed for the substitution of nickel with lithium according to the reaction



The preparation of the solid solutions consists of the preliminary mixing of nickel oxide powder (from the sulfate) with lithium peroxide, followed by pressing and sintering.

The mixing was done by ball milling the weighed components in an agate mortar with nickel balls.

Table V

Impurity concentration in a sample of
NiO (from the oxalate decomposition).

Impurity content, ppm						
Cr	Fe	Al	Co	Li	Na	K
44±4	<60	105±3	<1	18.6±1	<3	<38

This procedure avoids the contamination of the final product observed in some preliminary runs when milling with corundum balls in a corundum mortar.

Shaping into bars or pellets 13 mm in diameter was carried out by pressing the powder in a double piston steel die at about 7 ton/cm², slowly releasing the pressure to about 1 ton/cm² or less, removing the die and eventually completely releasing the pressure to extract the bar.

Sintering is carried out at relatively low temperatures (950 - 1000 °C) in a closed Pt crucible to prevent excessive losses of lithium¹¹⁻¹² (probably due to hydrothermal decomposition of the non-reacted lithium oxide to the highly volatile LiOH)¹³. This also avoids loss of oxygen caused by thermal decomposition of the solid solution.

The highest lithium concentrations (40,26 a/o lithium) were obtained when starting with a mixture having about a 50 a/o lithium, sintering for about 12 hrs. at 950 °C cooling down the samples (which, when structurally analysed appeared biphasic with a total Ni³⁺ content of about 34 a/o), grinding, pressing and resintering at the same temperature for about 30 hrs. The final product contains more than 40 a/o substituted lithium (40,26 a/o Ni³⁺). X-ray spectra indicate the presence of a solid solution and a LiNiO₂ phase.

Lithium concentrations were determined by flame emission spectrophotometry. The substituted lithium was determined from the Ni³⁺ concentration, measured by a modified Bunsen and Rapp method¹⁴ in which the sample is dissolved (in an evacuated bulb) in concentrated HCl in the presence of KI. The free iodine is titrated with a thiosulfate solution and the end point detected by the dead stop method using Pt micro-electrodes and at a polarization voltage of 25 mV.

Dummy runs carried out on NiCl_2 -KI solutions having the same nickel concentrations as the lithium-doped samples, demonstrated that the lowest Ni^{3+} concentration which could be detected with the dead-stop method (with an error lower than 5%) was from samples as low in lithium content as 0,1 a/o.

For the lowest doped grades, the end point should be detected by a conventional colorimetric method.

Some results are given in Table VI, where it is apparent that a non-negligible difference exists between the lithium content in the mixture before and after sintering. This difference increases as the lithium content increases and can be attributed to the lithium losses during the initial step of the sintering process. We suppose that the undissolved Li_2O reacts with water vapor, according to the reaction



In Fig. 1 the values of the substituted lithium are reported vs the Ni^{3+} content for different samples. It appears that the values are practically coincident except at the higher concentrations (near the limit of the homogeneity range) where however, an appropriate thermal treatment was found to remove the observed deviations (see above).

In Fig. 2 are reported the results of another set of measurements (done in cooperation with the Analytical Chemistry Service of CCR EURATOM - ISPRA) which show that the measurement of the X-ray lattice $^{15-16}$ spacing is also a good means of assessing the substituted lithium level.

Table VI

Concentration of substituted lithium (and Ni^{3+})
as a function of the composition of the
initial mixture.

Initial Mixture		After sintering			
		iodometric (Ni^{3+})		spectrofotometric (total Li)	
at %	wt %	at %	wt %	at %	wt %
0.56	0.0522	0.604	0.0572	0.56	0.0523
1.0	0.0938	0.578	0.054	0.536	0.05
2.0	0.180	2.06	0.191	1.98	0.186
3.0	0.285	3.05	0.289	2.68	0.273
4.0	0.382	4.12	0.394	4.08	0.39
5.0	0.482	4.80	0.461	4.82	0.464
6.23	0.615	5.61	0.542	5.10	0.492
9.6	0.978	7.98	0.784	7.88	0.773
14.45	1.54	11.38	1.243	9.53	1.025
19.2	2.155	14.65	1.56	14.65	1.51
19.2	2.155	16.85	1.92	16.60	1.89

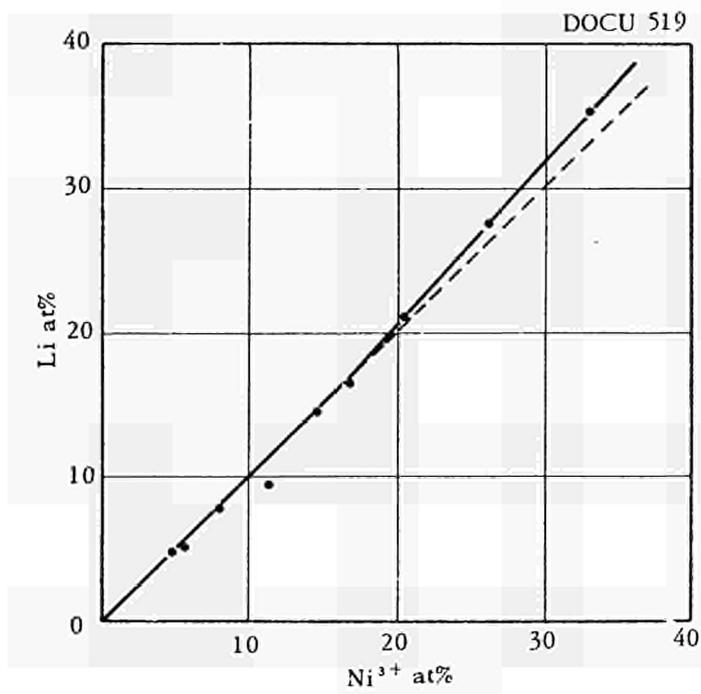


Fig. 1 Plot of the experimental values of the atomic ratios of Li (from photometric analysis) and Ni³⁺ (from electrochemical analysis, see text).

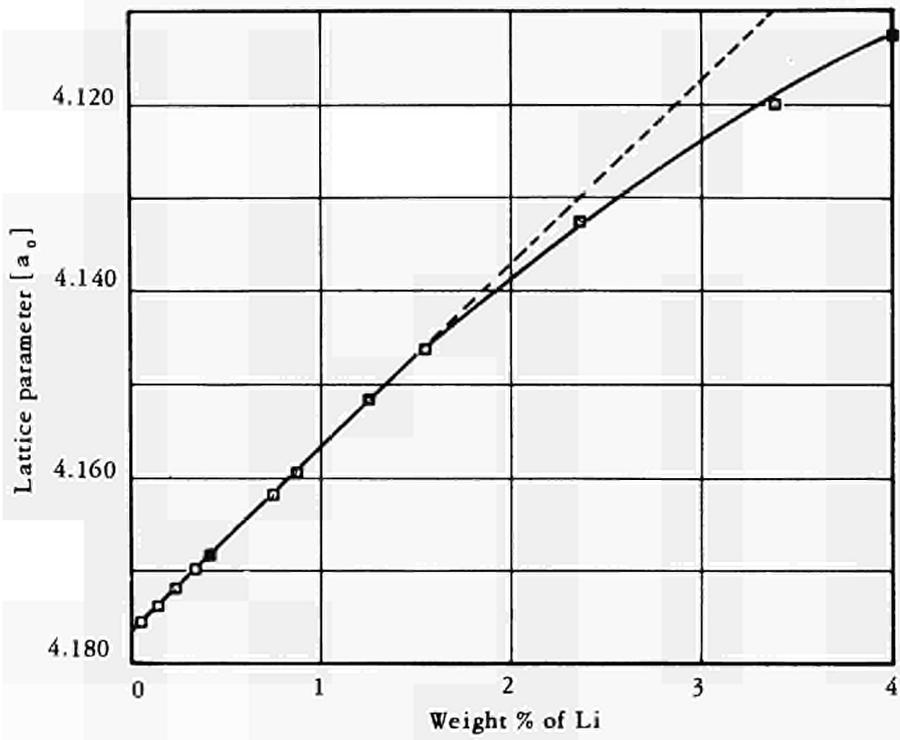


Fig. 2 Lattice spacing of the solid solutions NiO-Li₂O as a function of lithium content.

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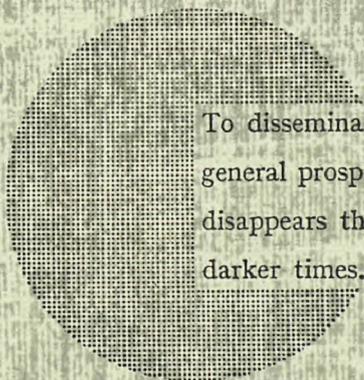
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Alfred Nobel

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