

A NDP FACILITY TO PERFORM NON-DESTRUCTIVE SURFACE ANALYSIS

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Abstract

During 1994, the Chilean Nuclear Energy Commission, CCHEN, decided to built an NDP experimental facility using one the neutron beam tubes of the La Reina MTR type reactor. This work shows one of the many possible uses of this technique. At the CCHEN, a small group was interested in lithium ceramic compounds. They need to know the properties of some sintered oxides with the purpose of seeing how the distribution of the Li inlayed in the homogeneous powder would be affected after the high compression that will receive to make very thin pellets (less than 1 mm thick). Several pellets were analyzed, for different Li concentrations and different compressions during the sintering process of the powder. Some spectra and its respective depth profiles are shown here.

This work is the history of those pellets. They made theirs pellets and the NDP technique told them how homogenous the samples were.

1. INTRODUCTION

Neutron depth profiling, NDP, is a method of near surface analysis for isotopes that undergo neutron-induced positive Q-value charged particle reactions and is commonly used to perform non-destructive analysis of almost all condensed materials. The technique is used to determine the atomic concentration and distribution of these particles as a function of depth. As a product of each nuclear reaction, a recoil nucleus will always be produced. After emerging from the surface of the sample, this reaction products will be properly counted and measured their energies. Depending on the target specific isotope, the proton, the alpha particle and recoil nucleus will have a characteristic energy [1]. Lithium, for instance, has the following absorption reaction:



Table I shows all isotopes undergoing neutron-induced positive Q-value charged particle reactions.

Of all the elements listed in Table I, ${}^6\text{Li}$, ${}^{10}\text{B}$ and ${}^{14}\text{N}$ are particularly appropriate for the NDP technique due to both, its large neutron capture cross sections and relatively large isotopic abundance.

NDP technique can probe non-destructively the first microns of almost any condensed matter. Depth profiles of all materials containing the isotopes listed above can be obtained after a proper deconvolution of its own spectra or by the unfolding of the response function of the measured data; nevertheless those materials not containing such an isotopes could be doped with anyone of them [2].

The most relevant characteristics of NDP as an analytic technique are:

- It is nondestructive.
- The isotopic concentrations are determined quantitatively.
- Profiling's measurements can be performed in essentially all solid materials.
- It is able to perform profiles across interfacial boundaries.
- There is little interference; neutron has that property.

TABLE I. REACTIONS USED BY NDP TECHNIQUE

Reacting Element	Reaction	% Abundance or (at/mCi)*	Energy of the Emitted Particles (keV)			Cross-Section (Barns)
			p or α	Recoil Nucl.	γ	
He	$^3\text{He}(n,p)^3\text{H}$	0.00014	572	191		5333
Li	$^6\text{Li}(n,\alpha)^3\text{H}$	7.5	2055	2727		940
Be*	$^7\text{Be}(n,p)^7\text{Li}$	(2.5E14)	1438	207		48000
B	$^{10}\text{B}(n,\alpha,\gamma)^7\text{Li}$	19.9	1472	839	478	3837
B	$^{10}\text{B}(n,\alpha)^7\text{Li}$		1776	1013		3837
N	$^{14}\text{N}(n,p)^{14}\text{C}$	99.6	584	42		1.83
O	$^{17}\text{O}(n,\alpha)\text{C}^{14}$	0.038	1413	404		0.24
Na*	$^{22}\text{Na}(n,p)^{22}\text{en}$	(4.4E15)	2247	103		31000
S	$^{33}\text{S}(n,\alpha)^{30}\text{Si}$	0.75	3081	411		0.19
Cl	$^{35}\text{Cl}(n,p)^{35}\text{S}$	75.8	598	17		0.49
K	$^{40}\text{K}(n,p)^{40}\text{Ar}$	0.012	2231	56		4.4
Ni*	$^{59}\text{Ni}(n,\alpha)^{56}\text{Fe}$	(1.3E20)	4757	340		12.3

(*) Radioactive species.

The uses of this technique are increasing with time. Hundreds of purely scientific, material science or technological development publications backs up this extensive utilization. Some of the most frequent applications of this non-destructive surface analysis are:

- Implantation
- Pre- and post-irradiation damage
- Interfacial profiling
- Stress by compression.

2. DESCRIPTION OF THE EXPERIMENTAL FACILITY

2.1. The neutron beam

The neutron source of this instrument is a MTR pool type nuclear reactor with a nominal power of 5 (MW). The NDP facility is located on the experimental hall of the La Reina reactor, at the Beam Port N° 4. It is a radial neutron beam tube, with two SS collimators and two cylindrical filters. One is a silicon filter located just behind of the primary collimator at the entrance of the neutrons, and the other is a bismuth filter inside the outer collimator which let out a “pencil beam” of 11 (mm) diameter with a thermal flux of 4.1×10^6 (n/cm²/s) monitored by a LND 3305 fission chamber.

2.2. Experimental chamber

It is an aluminum cylinder of 324 (mm) high, 305 (mm) diameter and 8.5 (mm) thick with two fixed circular aluminum windows that allows the inlet and the outlet of the neutrons. It contains a double mechanical goniometer supporting both, sample and two α -spectroscopy detectors. Vacuum is essential.

2.3. Electronic detection system

It is a conventional system:

- 1 Rack NIM BIN
- 3 Preamplifiers
- 3 Amplifiers
- 1 Dual high tension source, for the detectors
- 1 Bias Supply 0 → 5 (kV), for the fission chamber and
- 1 Reference pulse generator.

2.4. Acquisition data system

It is also a conventional system. The analog signals coming from the amplifiers are compiled through a digital multiplexer router to a time card and a multichannel card unit PCA II.

3. DESCRIPTION OF THE STUDY PERFORMED

The study consisted in to verify know how well distributed was lithium inlayed in some oxide compounds. The final idea was to produce ceramic electrodes for secondary lithium batteries. NDP was the proper instrument for that study.

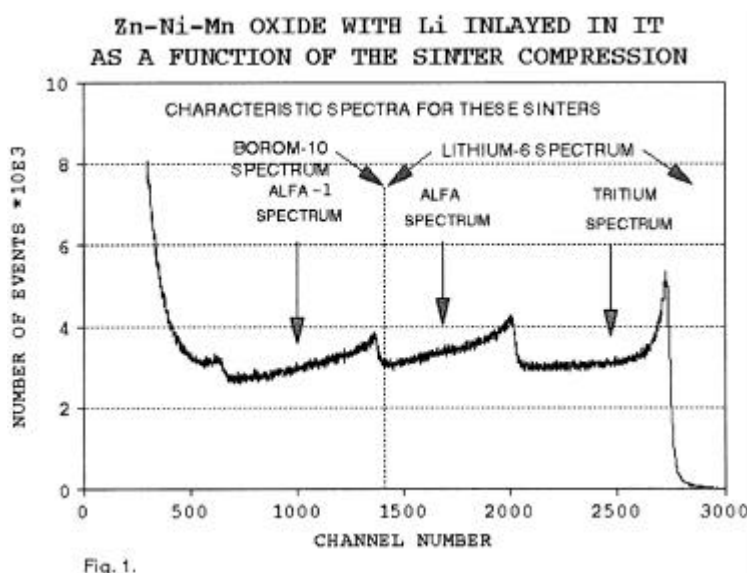
3.1. Preparation of the sample

Samples consist in a powder of zinc-nickel-manganese oxide, homogeneously mixed with natural lithium, compressed in a cylindrical press and then furnaceed in order to make a sintering of, approximately, 1 (mm) thick. Three different kind of oxides were used:

- Sample 1: $\text{Zn}_{0.10}\text{Ni}_{0.90}\text{Mn}_2\text{O}_4 + 0.6 \text{ Li moles/mol}$, with a pellet density of $\rho = 5.1727 \text{ (g/cm}^3\text{)}$
- Sample 2: $\text{Zn}_{0.25}\text{Ni}_{0.75}\text{Mn}_2\text{O}_4 + 0.6 \text{ Li moles/mol}$, with a pellet density of $\rho = 5.1437 \text{ (g/cm}^3\text{)}$
- Sample 1: $\text{Zn}_{0.75}\text{Ni}_{0.25}\text{Mn}_2\text{O}_4 + 0.6 \text{ Li moles/mol}$, with a pellet density of $\rho = 5.1908 \text{ (g/cm}^3\text{)}$.

3.2. NDP measurements

After the sintering process, the samples were neutron irradiated in the experimental chamber, one by one, thus obtaining each characteristic lithium-6 spectrum (See Fig. 1). The spectrum shown in this figure, is the one used to obtain the profile of Sample # 2.



**Zn-Ni-Mn OXIDE WITH Li INLAYED IN IT
AS A FUNCTION OF THE SINTER COMPRESSION**

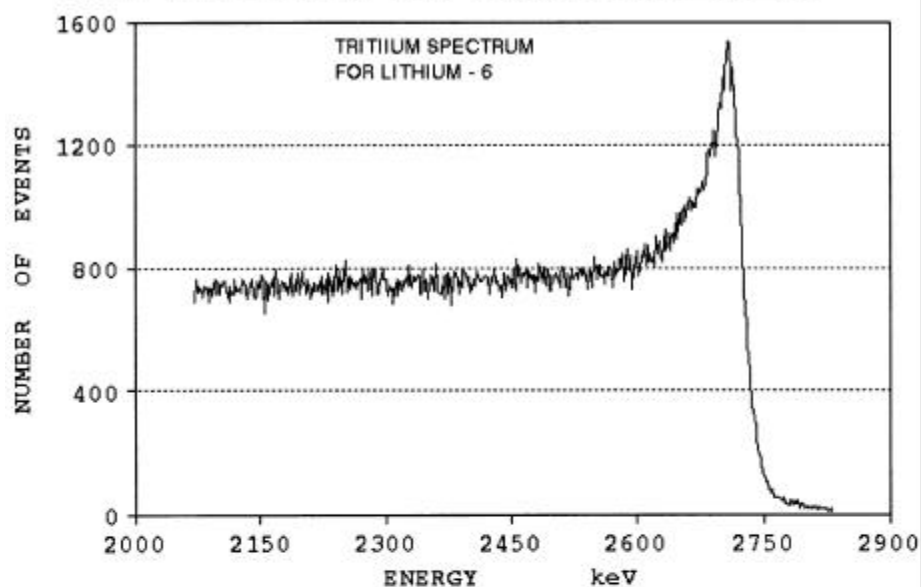


Fig. 2.A

**Zn-Ni-Mn OXIDE WITH Li INLAYED IN IT
AS A FUNCTION OF THE SINTER COMPRESSION**

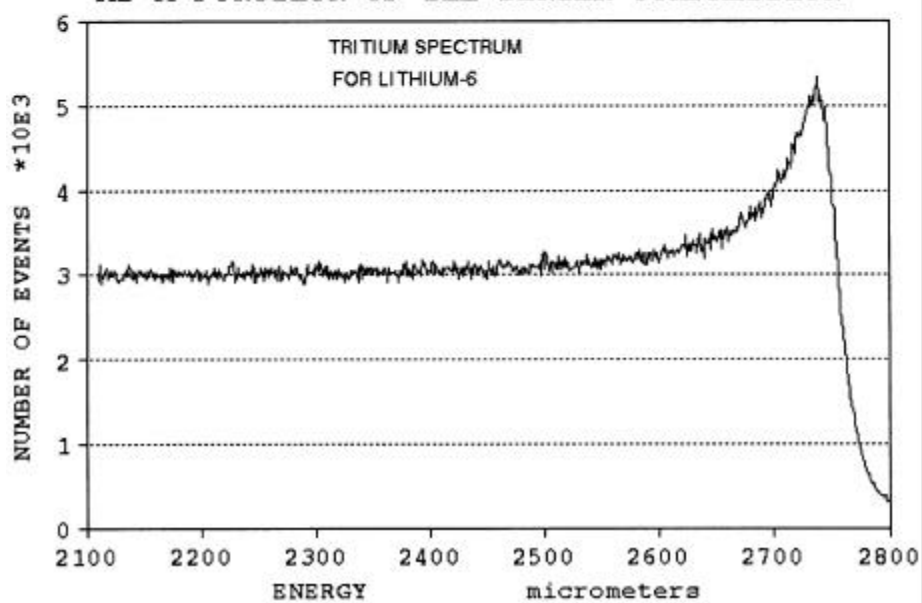
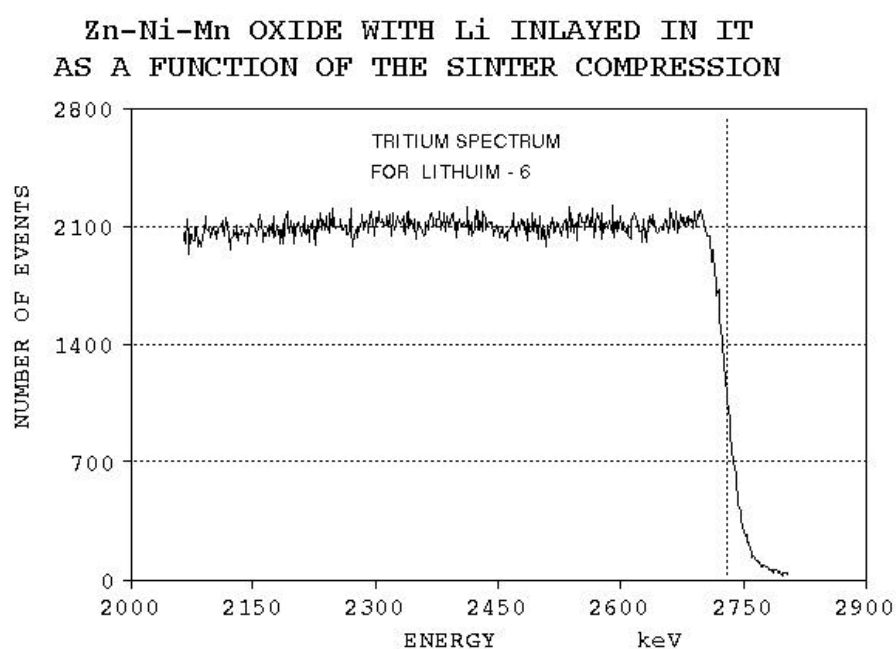


Fig. 3.A

Figure 1 shows the complete spectrum corresponding to all the absorption reactions that might be produced by neutrons inside the sintered oxide. The irradiation time was 25 hours with a dead time of 2.5%. It can be seen that the compound was able to embody a notorious amount of boron during the sintering process (?).

It also shows the lithium-6 spectrum, which has two picks: the tritium (^3H) and the alpha (^4He). For thick samples is better to use the tritium spectrum (less mass + higher energy \rightarrow more penetration power), but results are about similar.

Figures 2.A, 3.A, and 4.A show the tritium spectrum, for samples 1, 2 and 3, respectively, of the ^6Li , whose abundance in natural lithium is a 7.5%.



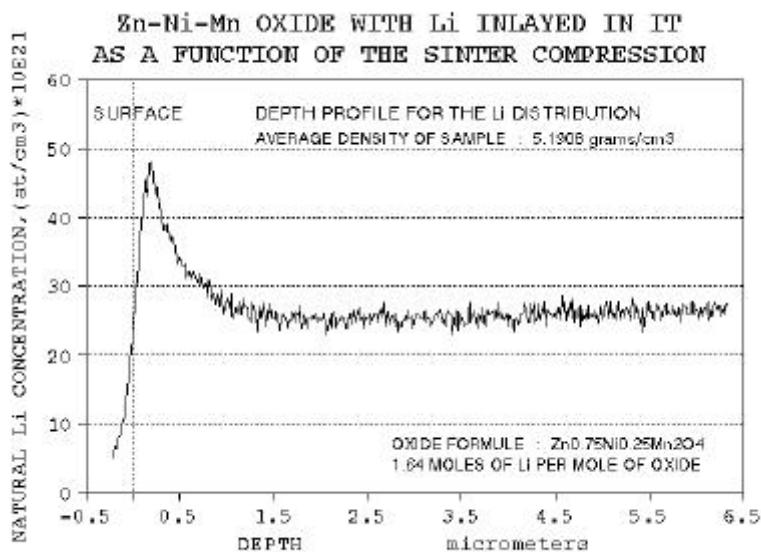
3.3. Results

Once obtained the tritium spectrum of each the samples, data were physically and mathematically processed to become a depth profile.

Figures 2.B to 4.B shows the resulting depth profiles of samples # 1 to # 3, respectively obtained from its corresponding spectra. This figures will show that samples surfaces are not clearly defined zones. Each surfacee spreads out in a zone of about 0.5 (μm) wide, between ± 0.25 (μm).

3.3.1. First attempt

Figure 2.B shows an abrupt decreasing of the Li distribution from the maximum at the surface, down to the 50% within the first 2.0 (μm). It can be appraised a certain stability in the atomic distribution, with a little tendency to grow up as depth increases. For this specific sample, the lithium molar proportion was 1.64 mole of Li per mole of oxide; a pellet density of 5.19 (g/cm^3) and an oxide



composition of $\text{Zn}_{0.75}\text{Ni}_{0.25}\text{Mn}_2\text{O}_4$. A simple stoichiometric calculation gives a lithium atomic concentration of 2.46×10^{23} (at/cm³), and the final experimental atomic concentration, as shown by the depth profile, is $(2.73 \pm 0.11) \times 10^{23}$ (at/cm³), which is about a 10% higher.

Sintering has not an homogeneous distribution of the Li atomic density from its very surface. Therefore, it must be improved.

3.3.2. Second attempt

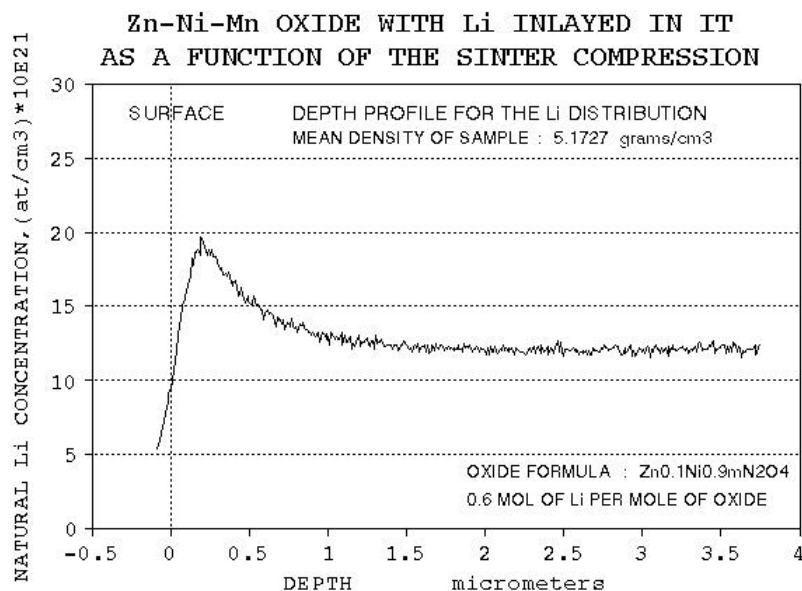
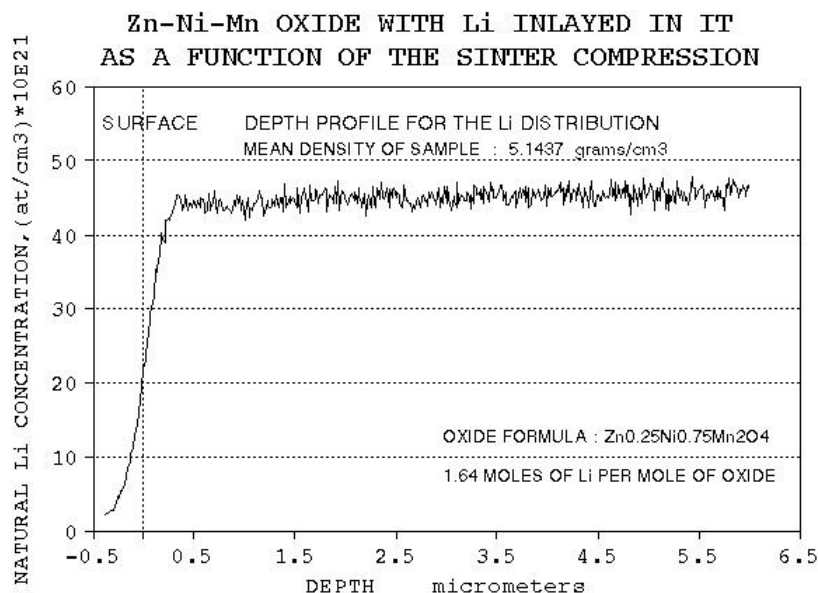


Figure 3.B shows a less abrupt decreasing of the Li distribution from its maximum at the surface, down to about the 60% at 1.5 (μm) depth. In this attempt, the stability of the Li atomic

density is quite good. This profile confirms the possibility of an improvement. Nevertheless, the compression's first impact ought to become smoothened.

3.3.3. Third attempt



Here, the homogeneity of the Li distribution is almost achieved and it is practically unbeatable. The uncertainty of the surface is still about 0.5 (μm) but the atomic density of the inlayed lithium is very much close to 2.8×10^{23} (atoms/ cm^3) with an average fluctuation of $\pm 4.2\%$.

4. CONCLUSIONS

There was a common pattern amongst the Li concentration distribution. Approximately within the first 0.5 μm inside the uncertain surface, the Li concentration increases abruptly up to about the 60% of the final concentration and decreased to that value as shown. This increase in the concentration was related to the impact of the piston during the compression of the powder. There was an annealing, but that process could have not produce such kind of diffusion of the superficial Li atoms into that kind of material.

These mixed oxides are used as guests for the lithium, in solid state as much as in solutions, for secondary lithium battery electrodes [3].

NDP, as an analytic technique, has shown to be direct and useful to study the behavior of surfaces and interfaces of almost any solid matrix. Chilean facility (unique in the southern hemisphere), together with the analytical methods developed, offers profiles with a very good resolution and sensibility as well as a reasonable irradiation times as compared with other facilities. The development of a coincidence spectrometry [4], in order to enhance the resolution and the measurement times, is being carried out.

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