

## SYNTHESIS OF LiNiO<sub>2</sub> CRYSTALS FROM MOLTEN SALT ELECTROLYSIS

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### ABSTRACT

Transition metal compounds like oxides, sulphides, nitrides, carbides, silicides etc are finding extensive importance in the electrical and electronic devices. LiNiO<sub>2</sub> has greater potential demand in advanced battery research. LiNiO<sub>2</sub> has been identified as one of the most effective cathode materials in rocking chair battery.

Though these compounds could be synthesized by solid state reaction like precursor, sol-gel, co-precipitation etc, they can be conveniently deposited in a fine crystalline form by molten salt electrolysis, employing suitable melts and electrodes.

LiNiO<sub>2</sub> was deposited on Ni anode from a melt of LiOH-NaOH at 1023 - 1123 K. The cell set-up, mainly the Ni cell with the Ni electrodes, melt composition and pretreatment, the favourable operating temperature and current density for the deposition of this transition metal oxides in fine crystalline form etc, have been presented in this paper.

The properties of these oxides mainly the chemical composition, XRD data etc, have also been studied and reported.

**Key word : LiNiO<sub>2</sub> electrodeposition- Solid state compound-XRD comparison**

### INTRODUCTION

LiNiO<sub>2</sub>, as a transition metal oxide with a layered structure, finds application as a promising cathode material / intercalation compound for 4 V secondary Li battery called Li ion, rocking chair, sea-saw battery because Li ion shuttles or rocks between electrodes composed of intercalation compounds during charge discharge cycles. LiNiO<sub>2</sub> is more attractive because of its less toxic nature and high discharge capacity viz. 150 mAh/g compared with LiCoO<sub>2</sub> (120 mAh/g) and the adequate availability of its natural resource with favourable cost, but high temperature treatment during the course of preparation leads to the decomposition of LiNiO<sub>2</sub> to compositional varieties of Li<sub>1-x</sub>Ni<sub>1+x</sub>O<sub>2</sub> (x > 0) with partially disordered cation distribution which affect its electrochemical performance, viz. working voltage, rechargeable capacity [1-7].

The difficulty in obtaining stoichiometric LiNiO<sub>2</sub> may be attributed to the closeness of the ionic radii of Ni<sup>3+</sup> (0.6 Å) and Li<sup>+</sup> (0.7 Å) which would be favourable to some randomness in distribution. Thus displacement of Ni and Li ions occur easily without dimensional mismatch compared to LiCoO<sub>2</sub>. In view of this, the preparation of battery active LiNiO<sub>2</sub> needs special attention. [8-9]

The technique of solid state reaction has been widely followed in preparing this compound. Different methods of preparation [9-20] of LiNiO<sub>2</sub> are given in the Table-I. An attempt has been made to synthesize LiNiO<sub>2</sub> by molten salt electrolysis as well as solid state reaction and some of their characteristics have been compared in this paper.

**TABLE-1 METHODS OF PREPARATION OF LiNiO<sub>2</sub>**

Solid phase synthesis [9-18]	Heating mixture of Ni compound and Li compound at 773-1173 K in presence of O <sub>2</sub> with several pelletising and powdering steps  Source for Li : LiOH, LiNO <sub>3</sub> , Li <sub>2</sub> CO <sub>3</sub> , Li <sub>2</sub> O Source for Ni : Ni powder, NiO, Ni(NO <sub>3</sub> ) <sub>2</sub> , Ni(OH) <sub>2</sub> , NiCO <sub>3</sub> , NiOOH.
Precursor method	Aq. Solution of Ni(NO <sub>3</sub> ) <sub>2</sub> and LiOH mixed, dried to slurry and heated to 1073 K
Alcoholate method [19]	Ni carboxylate viz acetate /formate heated in ethylene glycol/glycerol to alcoholate-mixed and heated with Li alcoholate
Electrochemical [20]	Electrochemical insertion of Li into amorphous NiO based at room temperature.

### EXPERIMENTAL

The experimental cell, as shown in Fig -1, consisted of a thick walled Ni crucible of 90 mm O.D, 60mm I.D, 70mm depth as the container for the molten electrolyte. The crucible was kept inside a pit type tubular furnace with temperature control for maintaining the predetermined

operating temperature. The electrodes, namely anode and cathode were made of 10-mm dia Ni rod and immersed into the melt to the required depth from a top electrode holding arrangement. Provision has been made for the removal of any fumes evolved during melting the electrolyte and electrolysis, by means of suction arrangement.

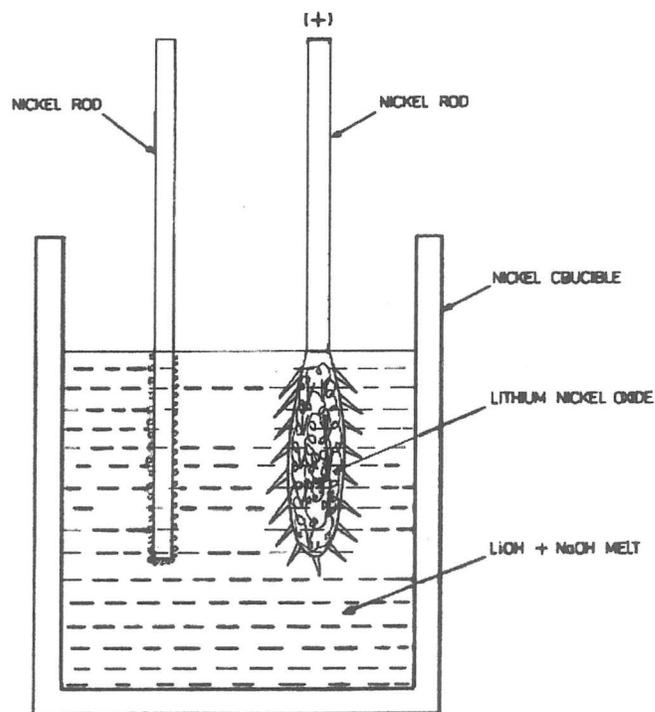


FIG.1 EXPERIMENTAL CELL : LiNiO<sub>2</sub>

As the loss of LiOH in the form of vapour by volatilisation could be reduced by adding NaOH, electrolysis was carried out with a mixture of LiOH : NaOH as the electrolyte. For facilitating Nickel to be present in the higher oxidation state, the melt was saturated with O<sub>2</sub> gas for 1h prior to the electrolysis. Experiments were conducted at different anodic current densities for studying the nature of the product deposited at the anode. The experimental data is given in Table 2.

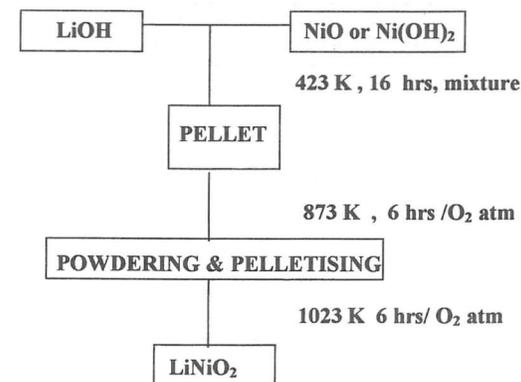
TABLE 2. EXPERIMENTAL DATA OF LiNiO<sub>2</sub>

ELECTROLYTE	OPERATING TEMPERATURE K	O <sub>2</sub> GAS SATURATION 3 cc / sec	ANODE CURRENT DENSITY A/ cm <sup>2</sup>	RESULTS
LiOH	1123	Nil	5-10	No deposit, volatilisation of LiOH
NaOH : LiOH (1 : 1)	873	1 hr	2-5	Deposition, no LiNiO <sub>2</sub> phase
"	973	"	7.0	"
"	1083	"	3-4	Deposition with LiNiO <sub>2</sub> Phase
"	1123	"	3-4	"
"	1023	Nil	2.7	Deposition with 2 phases ( LiNiO <sub>2</sub> & Li <sub>2</sub> Ni <sub>8</sub> O <sub>10</sub> )
KOH : LiOH	1023	1 hr	4.0	Deposition, no LiNiO <sub>2</sub> Phase

**LiNiO<sub>2</sub> FROM SOLID STATE REACTION**

For a comparative study, LiNiO<sub>2</sub> was synthesized by solid state reaction. Six samples of LiNiO<sub>2</sub> with different Li / Ni ratio were prepared by precursor method. Two compounds namely, NiO and Ni(OH)<sub>2</sub> were selected as the sources for Ni and LiOH.H<sub>2</sub>O for Li. The procedure adopted for the solid state reaction is given in the Flow Chart -1.

FLOW CHART 1. STEPS FOR THE PREPARATION OF LiNiO<sub>2</sub>

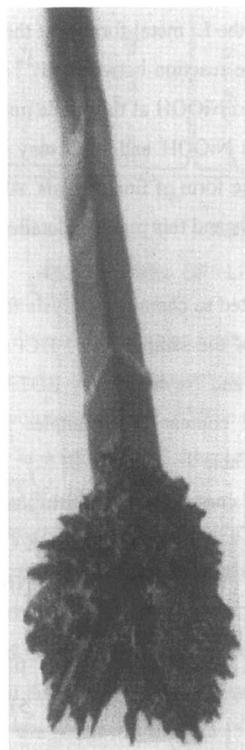


**RESULT AND DISCUSSION**

**NATURE OF DEPOSIT**

LiNiO<sub>2</sub> (Lithium Nickelate III) was formed as crystalline deposit as shown in Fig 2, by molten salt electrolysis. The deposit was found to be less adherent and collected from the anode by scraping onto a glass plate by a steel strip and thoroughly washed with methanol for the removal of free alkali.

**CRYSTALLINE DEPOSIT**

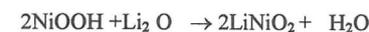
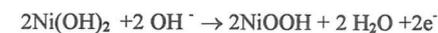
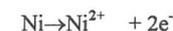


**Fig 2. LiNiO<sub>2</sub> DEPOSIT**

The anodic deposit of the above experiments was shiny black needle shaped crystals of 0.2 to 0.5 thick with metallic lustre. Microscopic examination of some of the products revealed formation of lustrous black crystals which appeared to be octahedral while the product from solid state reaction were found to be dark gray in color without any crystal formation.

**MECHANISM OF FORMATION**

The electrode reaction in the molten salt method is represented by



At the high operating temperature, the Li metal formed at the cathode gets dissolved in the melt, making it highly basic with Li<sub>2</sub>O. The reaction between Ni<sup>2+</sup> and OH<sup>-</sup> ion results in the formation of Ni(OH)<sub>2</sub> which may get oxidised to NiOOH at the anode under the severe condition of electrolysis. The acid – base reaction between NiOOH and Li<sub>2</sub>O may result in the formation of LiNiO<sub>2</sub> which gets deposited on the anode in the form of fine crystals. Above mentioned scheme is a probable mechanism of formations of LiNiO<sub>2</sub> and this requires detailed study.

**CHEMICAL ANALYSIS**

The deposited samples were subjected to chemical analysis for the estimation of Li and Ni content after dissolving a known quantity of the sample in 1:1 HCl acid and after dilution Li content was determined by flame photometry and Ni content by EDTA Titration with murexide indicator at pH 10. The average Li and Ni content of 6 samples from each of molten salt electrolysis and solid state reaction in given in Table 3.

**TABLE 3. Percentage of Lithium and Nickel content in the synthesized samples.**

SAMPLES FROM	PERCENTAGE OF	
	LITHIUM	NICKEL
Molten salt electrolysis	5.2 ± 0.7	62.3 ± 4
Solid state reaction	6.1 ± 0.7	51.0 ± 4
LiNiO <sub>2</sub> (Stoichiometric)	7.2	60

**XRD STUDIES**

The structural and micro crystalline behavior of different samples of LiNiO<sub>2</sub> obtained from fused salt deposition were studied by X ray diffraction data technique using Cu K<sub>α</sub> radiation in Jeol X-ray Diffractometer. The diffractogram for LiNiO<sub>2</sub>, of one the samples from molten salt is given in Fig .3

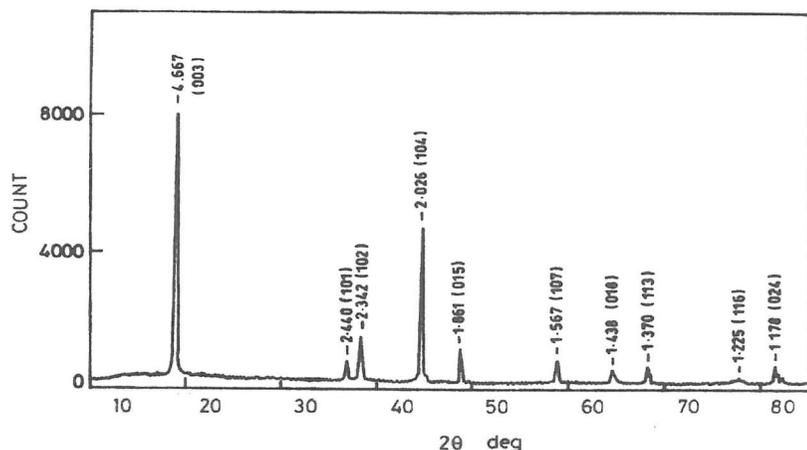


Fig.3 XRD PATTERN OF LiNiO<sub>2</sub>

Using the XRD data of the samples from molten salt electrolysis, the lattice parameters of unit cell, volume and density were computed and found to be of hexagonal structure with a =2.881 Å, c = 14.104 Å, volume=101.382 Å<sup>3</sup>. The hexagonal cell contains three formula weight and the calculated density is 4.9g/cc and these values are in close agreement with reported values ( JCPDS NO: 90063 ) of LiNiO<sub>2</sub>.

The lattice ratio c/a was found to be 4.89Å which was in close agreement with the reported [5] standard 4.9 Å which indicated that the oxygen ions in the structure with hexagonal setting very nearly close packed.

It was observed that the diffraction peaks of the molten salt samples were higher and sharper when compared with diffraction peaks obtained for LiNiO<sub>2</sub> prepared by solid state reaction. The present study agrees to the reported values in [5] at temperature range (1073-1173K) and this suggested the reaction was accelerated and crystallization produced at this temperature range.

All the samples produced by solid state reaction were also subjected to XRD studies. The data revealed the presence of LiNiO<sub>2</sub> phase in samples corresponding to the experiment with

Li / Ni ratio of 1.3:1 and other samples yielded mixed phases. From the XRD values the ratio of integrated intensity of the prominent peaks i.e. I( 003), I(104) of LiNiO<sub>2</sub> samples synthesized from both methods were compared and given Table 4.

**TABLE 4. COMPARISON OF INTEGRATED INTENSITIES:**

SAMPLE CODE	2θ	d <sub>obs</sub>	I/I <sub>o</sub>	I	INTENSITY RATIO I(003) /I (104)
1	19.10	4.643	100	882	0.997
2	19.00	4.667	92	909	0.917
3	19.00	4.667	100	2784	1.358
4	19.10	4.643	100	3500	1.020

1,2 from solid state reaction

3,4 from molten salt

It was also observed that intensity values of samples from molten salt electrolysis were found to be 3 to4 times greater than that of solid state reaction, indicating the formation of crystalline phase with defined lattice parameters.

For all samples prepared in this study the strongest line was observed as being the (003) line and to estimate the degree of contamination of a rock salt domain in a solid state matrix a simple method was adopted. It was to measure the integrated intensity ratio of the (0,0,3) to the (1,0,4) . Line. The displacement between Ni<sup>3+</sup> ions at octahedral 3 (a) sites and Li<sup>+</sup> ions at 3(b) sites in the space group R 3 m weakens the intensity of the (0,0,3) line, while such a displacement does not affect the intensity of the (1,0,4) line [6] . The integrated intensity ratio of (0,0,3) to (1,0,4) lines of LiNiO<sub>2</sub> used in the present study is given in Table 4. As discussed earlier the intensity ratio for LiNiO<sub>2</sub> prepared from solid state reaction is less than 1 while samples prepared by molten salt the values are above 1 i.e.,1.358 and 1.02. The samples with intensity ratios below 1.0 are considered to be inactive in non-aqueous lithium cells [6]. Hence, the samples prepared from molten salt electrolysis will be a better cathode in lithium rechargeable batteries.

## CONCLUSION

LiNiO<sub>2</sub>, as a promising cathode material for the advanced Li ion battery can be conveniently synthesized from molten salt electrolysis. The problem faced in preparing stoichiometric LiNiO<sub>2</sub> by solid state reaction may be circumvented in the molten salt technique as the material is obtained in fine crystalline form with stabilized structure. The duration required for the synthesis of this compound is greatly reduced to few hours as against the time consuming conventional methods of preparation.

## ACKNOWLEDGEMENT

The authors are very grateful to the Department of Science and Technology (DST), New Delhi for the financial support for this work.

## REFERENCE

1. Shuji Yamada, Masashi Fujiwara and Motoya Kanda  
*J.Power sources* 54 (1995)209
2. J.M.Tarascon and D.Guyomard  
*Electrochimica Acta* 38, 9(1993) 1221
3. J.R. Dahn, U.Von Sacken and C.A.Michel  
*Solid state ionics* 44(1990) 87
4. J.N.Reimers, J.R. Dahn and U.Von Sacken  
*J.Electrochem.Soc.*140(1993)2752
5. Tsutomu Ohzuku Atsushi Ueda, Masatoshi Nagayama  
*J.Electrochem. soc* 140, 7 (1993) 1862
6. Tsutomu Ohzuku, Atsushi Ueda, Masatoshi Nagayama, Yasunobu Iwakoshi and Hideki Komori  
*Electrochimica Acta* 38, 9,(1993)1159.
7. T. Nohma, H.Kurokawa, M.Uehara, M.Tahakashi, K.Nishio, and T.Saito  
*J.Power sources* 54 (1995)522
8. L.D. Dyer, B.S.Bori, and G.P. Smith  
*J.Amm. Chem Soc.* 76, 1499 (1954)
9. Bongers P.F., Thesis,  
*University of Leiden* (1957)
10. Welf Bronger, Heribert Bade and Wilhelm Klemm  
*Z.Anorg. Allgem.Chem.*,333(4-6), 188 – 200 (1964) (Ger)

11. Migon, N. Henri. Courtois, Zinne, Michel, Gleitzer, Charles  
*Rev. Chim. Miner* 1976, 13 (1), 1-8 (Fr)
- 12 N.B Khodyasher, S.A. Onorin V.VVolkhin  
*Pre. Politekh. Inst.Prem. USSR Khim.Technol.Neorg. Sorbentov* 1979,28-31 (Russ) Ed.By Volkhin V.V
13. E.Antolini  
*Mater. Sci.Lett*,12 (1993) 1947
14. Koho.  
*J.P.*, 60,115,165 (85,115,165) *Cl.Hol.M4186*, 21 June 1985
15. Lacerf, Andro,Broussely,Michel,Gabano, Jeanpaul  
*Eur-Pat.Appl.Ep345, & 07, 9Cl.HolM4/58* 13 Dec 1969.
- 16.G.Compet,B. Morel, M.Bourrel, J.M. Chabagno,D. Ferry, R.Garie, C. Onet, C. Geoffry, J.J.Videan. et.al.  
*Mat.Sci. Engg. B1991, B 8(4) 303-8 (Eng) 7*
17. Arai, Haijime, Okade, Shigeto Ohtsuka, Hideaki, Ichimure, Masahiro (Interdiscipli. Res.Lab.NTT.Ibaraki, Japan 319 –11)  
*Proc. Electro. Chem. Soc.1993, 93-23. (Proceeding of the symp. on new sealed rechargeable Batteries and Supercapacitors. 1993) 452-60 (Eng).*
18. Hagegawa, Masak, Bito, Yasuhiko, Oto, Shiji, Murai, Hiroyuki, Toyoguchi, Yasinori, Eur.Pat.  
*Appl.EP 573040 (Cl.HolM4/48), 08 Dec 1993*  
*Appl. 92 / 143, 280, 04 june 12 pp.*
19. Yoshio Masayuki, Noguchi Hideyuki, JPN Kokai Tokkyo Koho  
*JP 06, 203, 834,(94,203,834) (Cl. Ho1 M4/58), 22 July 1994, Appl. 92 / 362, 087 31 Dec 1992, 5pp*
20. Yamada, Shujji, Fujiwara, Masashi, Kanda, Motoya  
*J.Power.Sources* 1995, 54 (2), 209-13 (Eng)
21. Kurasawa, Tatsuhiko Tamaka, Takao Acitruka Mahoto, C.Delmas, I.Saadwne and A.Rougier  
*J.Power. Sources* 43-44 (1993) 595

Received, May 21, 1999  
Accepted, Septembre 3, 1999