

## ON THE EFFECTS OF Al & B SUBSTITUTION IN LiNiO<sub>2</sub>

**P. Kalyani, N. Kalaiselvi N. Muniyandi**  
Advanced Batteries Division,  
Central Electrochemical Research Institute,  
Karaikudi 630 006, India.

### Introduction:

LiNiO<sub>2</sub> despite its high energy density and charge retention features suffers from phase inhomogeneity and capacity fading due to crystallographic phase transitions upon charge/discharge cycling. Substitution in LiNiO<sub>2</sub> reduces these detriments leading to superior electrochemical behavior. Hence interest is inclined towards the simultaneous substitution of Al<sup>1</sup> and B<sup>2</sup> in LiNiO<sub>2</sub>, with a view to have compounds with improved structural stability, cyclability and charge retention. Hence a series of oxides with formula LiNi<sub>0.7</sub>Al<sub>0.3-x</sub>B<sub>x</sub>O<sub>2</sub> (x=0, 0.1, 0.2 & 0.3) were synthesized and characterized by PXRD, CV and charge/discharge studies. The present study is confined with 70% of Ni, as this level is established to have a better capacity retention, cycling efficiency and without cation mixing.<sup>3</sup>

### Experimental:

The oxide samples were synthesized in air by nitrate-urea solution combustion method following a firing schedule, which is given in table-1.

### Results and discussion:

It is evident from table-1 that with the increasing B content the temperature and dwelling time for phase pure compound formation is found to decrease. Thus boron substitution facilitates the phase formation at a lower temperature. "c/a" value for the substituted compounds were in the range of 4.97-5.01, an indication of the preservation of 2D character in these samples. This also shows that both Al and B have got substituted at the Ni sites without affecting the layered structure, despite their ionic size difference. Compounds cycled between 3.6 and 4.4V at a scan rate of 0.1mV/sec (fig. 1) indicate that as the boron content increases the anodic current decreases and only a broad maximum at 4.1 – 4.3V is observed. On the contrary, the cathodic peak current at lower voltage region starts diminishing and the peak at higher voltage increases as a function of boron content. But for these samples, a significant shift in the reduction peak towards higher voltages is observed, thus decreasing the voltage difference between the oxidation & reduction, indicating high Li<sup>+</sup> reversibility. Charge/discharge cycling performed at a current density of 0.1mA/cm<sup>2</sup> shows that samples with 10 & 20% of boron perform well when compared with the remaining two. This is further supported by the I<sub>(003)</sub>/I<sub>(104)</sub> value which is ca. 1.3 for these two samples only. Physical characteristics like specific surface area, density etc., of these compounds will also be discussed.

### References:

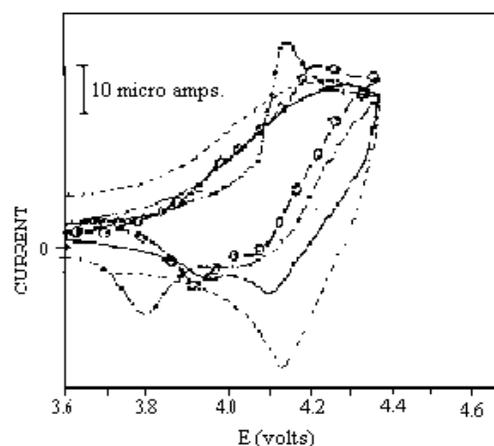
1. T. Ohzuku, A. Ueda, and M. Kouguchi, *J. Electrochem. Soc.*, **142**, 4033 (1995).
2. M. Mizutani, and T. Fukunaga, Jpn, Kokai Tokyo Koho Jp 05,325,971 (93,325,971) (Cl. H01M4/58), Dec 10, 1993.
3. C. Delmas, I. Saadoune, and A. Rougier, *J. Power Sources* **43/44**, 595 (1993).

### Acknowledgements:

The authors thank Dr. M. Raghavan & Dr. N. G. Renganathan for useful discussion. P. K. thanks CSIR, New Delhi, for the financial assistance.

x	Temp/time ° C / h r s	I <sub>(003)</sub> /I <sub>(104)</sub>	"a" "c" (Å)	c/a
0.0	750 32	1.11	2.85 14.15	4.97
0.1	750 24	1.25	2.85 14.12	4.95
0.2	700 3	1.27	2.84 14.16	4.98
0.3	600 3	1.18	2.83 14.18	5.01

**Table- 1. Optimum preparation conditions & crystal parameters of LiNi<sub>0.7</sub>Al<sub>0.3-x</sub>B<sub>x</sub>O<sub>2</sub>.**



**Fig.2. CV of the compounds at 0.1mV/sec**

--- x = 0.3; — x = 0.2; o-o-o x = 0.1;  
- · - · x = 0.0