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On the Effects of Simultaneous Substitution of Al^{3+} and B^{3+} in $LiNiO_2$ Cathodes

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A series of solid solutions of the formula $LiNi_{0.7}Al_xB_yO_2$ with $x + y = 0.3$, has been synthesized by adopting urea-nitrate solution combustion route. Two diamagnetic cations from the same non-transition metal group *viz.*, Al^{+3} and B^{+3} have been substituted simultaneously in to the crystal lattice of $LiNiO_2$ with a view to realize the combined advantages such as over-charge protection and longer cycle life respectively. The synthesized cathode materials were characterized in the light of diffraction (XRD), spectroscopic (Fourier transform infrared, FTIR) and electrochemical (CV and charge/discharge) analyses. It is manifested from XRD that the observed correlation between the amount of boron substituted and the requirement of heat-treating conditions such as heating time and temperature implied that the B^{+3} dopant plays a dual role, both as a dopant and as a flux. The dwelling time and the treating temperature required for the formation of phase pure $LiNi_{0.7}Al_xB_yO_2$ compounds, either with a comparatively higher amount of boron with respect to Al or with the presence of maximum amount of B to the extent of 30% without Al were found to decrease as a function of boron content. The results of the XRD and FTIR studies established the complete mixing of Al and B with Ni, especially at the various levels and combinations of dopants attempted in the present study. The stabilization of Ni in the +3 state and the existence of enhanced two-dimensional structure without any cation mixing have been achieved through this novel attempt of simultaneous substitution of diamagnetic cations *viz.*, Al^{3+} and B^{3+} in the layered $LiNiO_2$ matrix, as evidenced from the CV studies. The effect and the extent of substitution of Ni with Al and B on the structural and electrochemical performance of $LiNi_{0.7}Al_xB_yO_2$ are discussed elaborately in this communication.
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Over two decades pioneering research has been devoted to optimize 4 V cathode materials for lithium batteries. Alkali transition metal oxides like $LiMn_2O_4$[1] or $LiCoO_2$,[2] which undergo topotactic redox reactions (for battery rechargeablility) are the proven choice. Since $LiCoO_2$ is currently used in commercial electronic devices, strong interest has been dedicated to the nickel analog *viz.*, $LiNiO_2$, which is relatively less expensive with a higher discharge capacity than the former.[3] Even before the advent of $LiCoO_2$, Dyer *et al.*[4] as early as 1954, proposed a route to synthesize $LiNiO_2$ and analyzed its crystal structure in detail. But unlike $LiCoO_2$, the latter requires controlled preparation conditions to obtain the compound possessing stabilized layered configuration in view of realizing better battery activity. Attempts to prepare the compound under normal conditions resulted in the formation of an electrochemically inactive compound, namely $Li_2Ni_8O_{10}$.[5] This is because of the difficulties involved in stabilizing nickel in the +3 oxidation state and the incomplete formation of the layered structure, which results in the increased lithium-nickel disorder that deteriorates the cathodic performance ultimately. These intricacies of $LiNiO_2$ impose serious limitations to its wider acceptance for commercial utilization in the energy sector.

The problems associated with any cathode oxide material can generally be addressed by two ways, *i.e.*, the introduction of a suitable dopant into the crystal structure at an optimized level and the adoption of suitable methodology to synthesize phase pure compounds. Making the crystal structure pliant by substituting the transition metal ion with other cations toward the improvement of the crystal structure stabilization, cyclability, thermal stability in the charged state, and the suppression of the irreversible crystallographic phase transition during cycling[6] has become a reality especially in recent years. Several transition and nontransition metal dopants like Mg,[7] Al,[8-10] Co,[11] Mn,[12] and Ti[7] have been attempted with a view to minimize the irreversible phase transition of $LiNiO_2$ upon cycling and to improve the two-dimensional (2D) characteristics or otherwise to improve the safety factor. Among the dopants, aluminum has been of profound interest with respect to both $LiCoO_2$[9] and $LiNiO_2$[8-10] cathodes, due to its low atomic mass and cost. *Ex situ* powder X-ray diffraction (PXRD) studies by Alcántara *et al.*[13] have shown that $LiAlO_2$ mixes completely with $LiNiO_2$ to form a series of solid solutions of composition, $LiNi_{1-y}Al_yO_2$ $(0 < y < 0.7)$. Ohzuku *et al.*[8] have shown that a 2D-hexagonal phase is preserved over the entire range of Li content during charge/discharge in $Li_xNi_{0.75}Al_{0.25}O_2$ $(x = 0 < x < 0.7)$. Hence, Al^{+3} substitution favors the stabilization of Ni in the +3 oxidation state and enhances the existence of dual dimensionality of the layered structure which leads to the suppression of phase transition during electrochemical cycling. Because Al cannot be oxidized or reduced beyond a +3 state, the maximum amount of intercalated or deintercalated lithium can also be limited, depending upon the Al content. Hence, partial substitution of Al for Ni prevents the cell from overcharge and hence improves cell safety.[8,14] Further, advantages of partial substitution of Al in to the crystal structure of $LiCoO_2$ has been reported by Ceder *et al.*[15,16] in their *ab initio* studies, that an increase in cell voltage could be achieved by Al substitution by forcing more electronic exchange between lithium and the oxygen network. Similarly, there have been few other reports on the electrochemical behavior of boron-doped $LiCoO_2$,[17,18] $LiNiO_2$,[19] and $LiMn_2O_4$.[20] Also, it is established that batteries using B-substituted $LiCoO_2$ as active cathode material have improved charge/discharge cycle performance and long life.[17]

As a novel attempt, simultaneous substitution of two cations belonging to the same nontransition metal group such as Al^{+3} and B^{+3} has been carried out in the present study. Despite the basic difference in their ionic radii values (Ni^{3+}:0.56 Å, Al^{3+}:0.51 Å, and B^{3+}:0.24 Å), these cations with +3 as the only oxidation state, have been selected as dopants, basically with a view to examine the combined effect of Al and B substituents on the structural and electrochemical properties of $LiNiO_2$. In this regard, a series of solid solutions with the general formula $LiNi_{0.7}Al_xB_yO_2$ $(x + y = 0.3)$ with varying amounts x and y ranging from 0.0 to 0.3 have been synthesized by urea-nitrate combustion method and the results evaluated through *ex situ* PXRD, Fourier transform infrared (FTIR), cyclic voltammetry (CV), etc., are furnished in the present communication. Again, the preference for the 70% of Ni in $LiNi_{0.7}Al_xB_yO_2$ compounds originated from a similar observation made by Subba Rao *et al.*[21] in $LiNi_{0.7}Co_{0.3}O_2$, wherein the usage of 70% of Ni with Al dopant has been established to have improved charge retention

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Table I. Optimum preparation conditions and crystal parameters of $LiNi_{0.7}Al_xB_yO_2$.

Compound	Temp/D.T.[a] °C/h		Lattice constants a (Å)	Lattice constants c (Å)	Lattice constants Unit cell volume $(Å)^3$	$I_{(003)}/I_{(104)}$	c/a
$LiNi_{0.7}Al_{0.3}O_2$	750	32	2.849	14.152	99.512	1.11	4.967
$LiNi_{0.7}Al_{0.2}B_{0.1}O_2$	750	24	2.848	14.116	99.156	1.25	4.956
$LiNi_{0.7}Al_{0.1}B_{0.2}O_2$	700	3	2.840	14.162	98.919	1.27	4.987
$LiNi_{0.7}B_{0.3}O_2$	600	3	2.832	14.180	98.487	1.18	5.007
$LiNiO_2$ (O_2 atm)	750	21	2.902	14.212	103.611	1.23	4.894

[a] D.T. is Dwelling time.

and cycling efficiency. This paper highlights the electrochemical behavior of $LiNiO_2$ simultaneously substituted with B and Al, synthesized by the urea-nitrate combustion method.

Experimental

Synthesis.—The substituted nickel oxides of the general formula $LiNi_{0.7}Al_xB_yO_2$ ($x = 0.3$, 0.2, 0.1, 0.0, and $y = 0.3 - x$) have been synthesized by solution combustion[22,23] using urea as a fuel to aid the combustion process. Calculated amounts of boric acid, nitrates of lithium, nickel, aluminum, and urea were dissolved in hot distilled water to give a homogenous solution. The amount of urea was calculated based on the procedure given in Ref. 22. The mixture was heated slowly to 400°C for about 30 min. Note that the process of slow heating ensures slow and uniform combustion of the mixture, which resulted in the formation of black foam. On the other hand, recovery of the final product from the crucible itself was very difficult in the case of rapid heating process. The foam thus obtained was then crushed and the powdered sample was subjected to a firing sequence in purging air at a temperature of 600-750°C for about 3 to 32 h as given in Table I. Similarly, $LiNiO_2$ has been synthesized by treating the urea-nitrate mixture in flowing oxygen at 750°C for 21 h, solely to compare the characterization results of the doped derivatives.

Instruments.—Phase characterization was done by powder X-ray diffraction (XRD) technique using a JEOL-JDX 8030 X-ray diffractometer using Ni filtered Cu-Kα radiation ($\lambda = 1.5406$ Å) in the 2θ range of 10-80° and at a scan rate of 0.1°/s. FTIR spectra were recorded with Perkin Elmer Paragon-500 FTIR spectrophotometer using KBr pellets in the region 400 to 2000 cm^{-1}. Density of the powders was determined by the method based on Archimedes' principle using a xylene medium. Surface morphology of the particles was examined from the scanning electron micrographs obtained from Hitachi S-3000 H scanning electron microscope (SEM) and the particle size of the oxide materials was determined using a Malvern easy particle sizer. Surface area of the synthesized powders was determined by the Brunauer-Emmett-Teller (BET) adsorption method using low temperature nitrogen adsorption (Quanta Chrome Nova 1000, US).

Electrochemical performance was evaluated by assembling cathode-limited 2016 lithium coin cells. Cathodes were fabricated by slurrying the cathode powders with 10% graphite and 2% poly(vinylidene fluoride) PVdF as binder in N-methyl 2-pyrrolidone (NMP) as solvent and coating the mixture over Al foil (serves as current collector). After drying at 110°C overnight, the discs were pressed in a hydraulic press with a pressure of about 10-15 Kg/cm^2 for perfect adherence of the coated material over the surface of the current collector. Discs of 1.6 cm diam were punched out and typical cathodes were found to have an average active material coverage of about 7-10 mg per disc. Electrolyte consisted of 1 M $LiAsF_6$ in equal volumes of ethylene carbonate (EC) and dimethyl carbonate (DMC) and the separator used was polypropylene fabric. Charge/discharge studies were performed using an in-house cell-testing unit. Cyclic voltammograms were recorded using Autolab software controlled by a personal computer.

Results and Discussion

Effect of B addition vs. formation temperature and dwelling time.—The effect of addition of boron on the temperature of formation of the oxide compounds is obvious from the Table I. With the increasing B content, the formation temperature as well as the dwelling time were found to decrease gradually, *i.e.*, the compound containing Al as the dopant required a temperature of at least 750°C and a dwelling time of 32 h, whereas the compound containing B as the only dopant required a minimum temperature of 600°C and a heat-treating period of 3 h. However the compounds containing both Al and B as dopants required a temperature and a dwelling time which were observed to be in-between those of monosubstituted nickel oxides, *i.e.*, $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$ and $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$ compounds required a temperature of 700-750°C and a dwelling time ranging from 3-24 h, depending upon the B content. Among the simultaneously substituted compounds also, the firing temperature and the dwelling time were found to vary inversely with the amount of boron, *i.e.*, higher B content over Al favors lesser reaction time and temperature. Ultimately, these observations led to an assumption that B may perhaps play a dual role, both as a dopant and as a flux, *i.e.*, the presence of boron may find its participation helpful in reducing the firing temperature and time. The optimum preparation conditions of the monosubstituted (Al or B) and the bisubstituted (Al and B) nickel oxides along with the parent $LiNiO_2$ compound (for comparison) are furnished in Table I.

Phase analysis.—Figure 1 a-e represents the PXRD profiles of the oxide samples heat-treated under the conditions mentioned in Table I. The inset gives the PXRD profile of the sample $LiNi_{0.7}B_{0.3}O_2$, heat-treated at 750°C for 2 h to study the effect of boron substitution and the effect of temperature on phase formation. The characteristic peak at $2\theta = 19°$ was absent, thus emphasizing the necessity of heating the sample at a temperature below 750°C. Therefore, attempts were made to synthesize $LiNi_{0.7}B_{0.3}O_2$ compound at temperatures such as 700 and 600°C for about 3 h. Among the two trials, the compound obtained from a firing temperature of 600°C alone was found to be phase pure and crystalline in nature. Thus the XRD results are in support of substantiating the fact that boron gets doped into the $LiNiO_2$ matrix and the same has played a vital role in reducing the firing temperature and time. All the XRD peaks of $LiNi_{0.7}Al_xB_yO_2$ powders were indexed assuming a rhombohedral structure (sp gr: $R\text{-}3m\text{-}D^5_{3d}$). The splitting of the (108) and (110) peaks observed invariably for all the doped derivatives are quite obvious from Fig. 1, which is in favor of the Li-cation ordering, an indication of better cathodic activity of the synthesized compounds. The crystal constants, $I_{(003)}/I_{(104)}$, c/a values and cell vol-

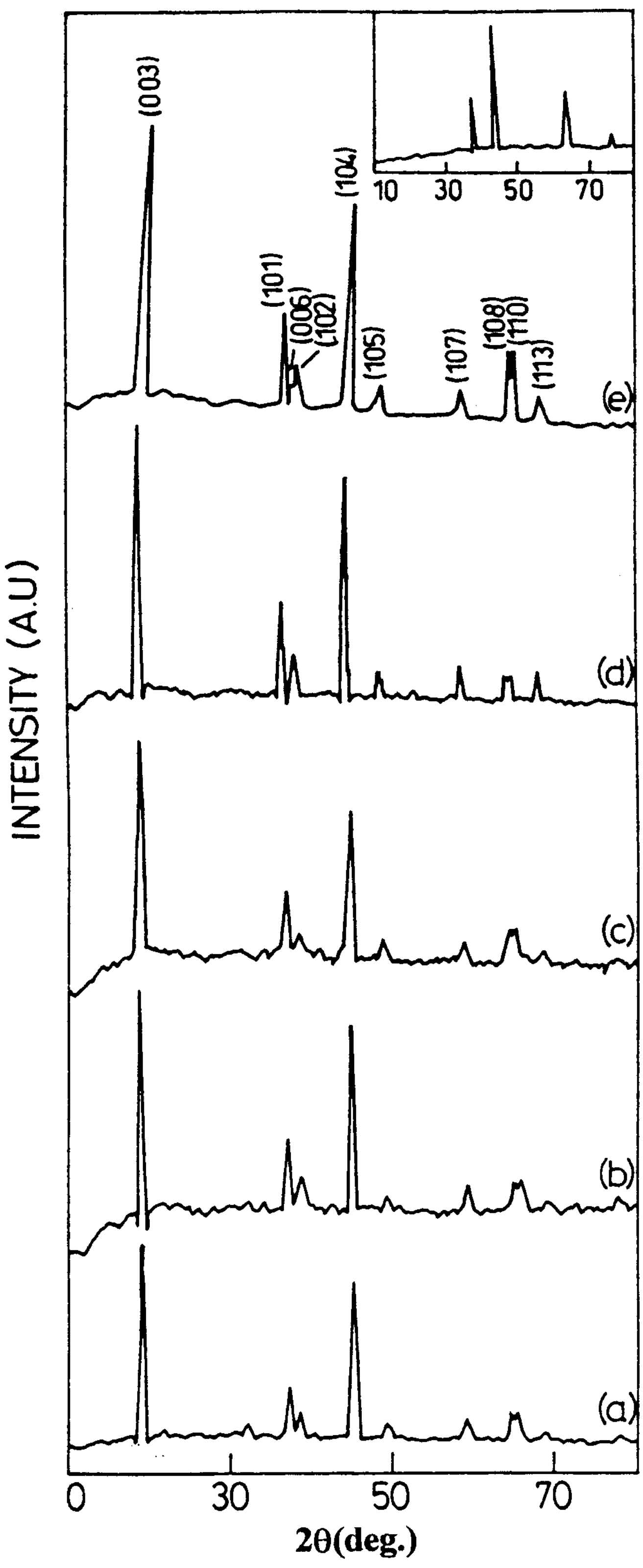

Figure 1. PXRD patterns of the substituted nickel oxide cathodes. (a) $LiNi_{0.7}B_{0.3}O_2$, (b) $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$, (c) $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$, (d) $LiNi_{0.7}Al_{0.3}O_2$, and (e) $LiNiO_2$. Inset: XRD of $LiNi_{0.7}B_{0.3}O_2$ heated at 750°C for 2 h.

ume were determined by an iterative least squares refinement method using the indexed h, k, l values and are included in Table I.

A low extent of substitution of larger cations by B is expected to result in the contraction of unit cell parameters.[18] Interestingly, in the present study also, a decreasing trend in a value has been observed with the increasing B content. The degree of trigonal distortion of the cubic lattice, normally expressed as the c/a ratio was also found to be reduced for the doped derivatives of $LiNiO_2$. These reduced unit cell parameters may also be viewed as an impact of location of dopants in the compound *i.e.*, if the B atoms are located in crystallographic sites exactly the same as that occupied by the constituent atoms in the stoichiometric $LiNiO_2$, reduction in cell volume may be expected. Boron when substituted isomorphically for Ni in the $3a$ octahedral $(-3m)$ sites of the NiO_2 layers may lead to significant changes in the very appearance and the intensity of the diffraction lines. However, it is also reported in the literature[18] that the low scattering power (and the low proportion) of B may not be helpful in finding the exact location of these atoms by XRD. Therefore, we do not attribute the observed change in the appearance as well as the intensity of the diffraction peaks solely to the entire occupation of all the substituted B atoms in to the octahedral $(-3m)$ sites of the $LiNiO_2$ crystal lattice.

On the other hand, the c value was found to decrease initially up to 10% of B content and thereafter an increase in the c values has been noticed with the increasing B content. This may be due to the combined effect of the smaller radius of boron that could not effectively influence the surrounding oxygen spheres to result in a smaller lattice constant value throughout the series in a linear fashion and the possible tetrahedral $3m$ site occupancy of part of the boron doped in the $LiNiO_2$ crystal lattice. Also, the overall effect of the substitution with Al and B may be a probable reason for the difference in the trend observed with the simultaneous doping of Al and B with an increasing B content and a lesser Al content. The c/a ratio, which is a qualitative measure of the stabilization of Ni^{+3} and the 2D layered structure[24] of the compounds has been found to vary between 5.007-4.956, substantiating the structural stability of the synthesized compounds. Similarly, the values of $I_{(003)}/I_{(104)}$ ratio vary between 1.11 (for $LiNi_{0.7}Al_{0.3}O_2$) to 1.27 (for $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$), a qualitative measure for the better battery activity of the compounds.[24] Also, the unit cell volumes calculated for the compounds indicate volume shrinkage as the B content increased.

It has been reported that the presence of extra nickel as impurity in the form of electrochemically inactive Ni^{2+} in the $3b$ Li sites of $LiNiO_2$, is responsible for the reduced electrochemical performance of the same. Delmas *et al.*[25] have ascribed the capacity fading to the possible formation of electrochemically inactive region in the cathode material, resulting from the oxidation of pre-existing Ni^{2+} ions in the lithium layer. In this context, it is quite interesting that the extra nickel in the lithium plane can partially be solved by B substitution. Further, in the recent investigations of Alcántara *et al.*,[18] it is reported that the presence of a B dopant in the $LiCoO_2$ compound favored lattice adaptation to a super lattice structure of lithium ions. Similarly, it is believed that the presence of boron in the tetrahedral sites of $LiNiO_2$ (an analog of $LiCoO_2$) makes the structure more flexible with respect to lithium ordering. In other words, the boron dopant may displace Ni^{2+} to $3a$ sites, leading to an increased Ni^{3+} content in the boron-doped nickel oxides, thus enhancing the electrochemical activity. This has further been substantiated by the observations of Kemp and Cox,[26] who have reported the presence of relatively increased amount of Ni^{3+} ions in the $3a$ sites of $LiNiO_2$ resulted from the germanium doping. Hence the boron substitution in the present series of compounds favors this kind of stabilization of Ni^{+3} in the $3a$ sites, forcing away the Ni^{2+} that was originally present in the $3b$ lithium sites, thus resulting in the stabilized 2D layer structure ultimately. This is further evidenced by the higher $I_{(003)}/I_{(104)}$ ratio values of 1.25 and 1.27, calculated for the 10 and 20% of boron, respectively. Hence the substitution is facilitated even at a moderate temperature of about 600-700°C despite the difference in the ionic sizes of Ni^{3+}(0.56 Å), Al^{3+}(0.51 Å) and B^{3+}(0.24 Å), thus establishing the solubility of Al^{3+} and B^{3+}.

The effect of Al cannot be explained completely by XRD, because it is already reported that the aluminum ions do not perturb the layered structure of the compound.[13,16,27] However, based on the reported results of ^{27}Al magic angle spinning nuclear magnetic resonance,[13] a possible occupancy of aluminum ions in the octahedral sites $(3a)$ and a smaller amount of Al in the tetrahedral $6c$ sites are expected to occur in the present case also. Though it seems to be uncertain to describe the exact location of Al from XRD, it is further understood from the forthcoming characterization studies such as FTIR and CV that the possible occupancy of interstitial $6c$ sites by a lesser fraction of Al cannot be neglected. Also, it is worthwhile to remember that the interstitial tetrahedral site occupancy of Al, if any, could lead to negative effect only with respect to lithium diffusion in the aluminum-substituted solid solutions.[13] This is reflected in the charge/discharge studies, wherein a 20% reduction in capacity, observed for the $LiNi_{0.7}Al_{0.3}O_2$ compound over 25 cycles, is apparently due to the hindered lithium diffusion.

Since boric acid has a lower melting point (170°C), it is highly probable for the formation of Li—B—O glass like compounds in the final products. The formation of such type of material would definitely impart hardness and the crystallinity of the products would be affected, despite the fact that glasses do not have long-range crystallographic order. Since the products are soft and fluffy and are of high crystalline in nature, we preclude the possibility of glass formation in the final oxides.

Local structure by FTIR analysis.—The presence of B and Al as dopants in the $LiNiO_2$ lattice can be identified from the IR spectral bands observed for the $LiNi_{0.7}Al_xB_yO_2$ solid solutions. Figure 2 a-e shows the FTIR spectrum of the substituted and the unsubstituted nickelate compounds synthesized under the heat-treating condition as mentioned in Table I.

It is understood from XRD observations, that the average bond length between the transition metal ion and the oxygen ions in the MeO_6 octahedra having a local O_h symmetry has been decreased as a function of y in $LiNi_{0.7}Al_xB_yO_2$. This is further supported by the shift in the FTIR spectral bands for the substituted solid solutions when compared to the normal vibrational modes of the unsubstituted nickel oxide that are present around 400-700 cm^{-1} region. Peaks around 860 and 1430 cm^{-1} are observed invariably for all the compounds, an indication of the presence of Ni—O bond. The IR spectrum of undoped $LiNiO_2$ shows two peaks around 511 and 860 cm^{-1}, which are shifted to lower and higher wave numbers respectively, when doped suitably with B or Al or B and Al. Note that when $LiNiO_2$ is substituted either by B or Al, a shift in the peak at 511 cm^{-1} to lower wavelengths has been observed. On the contrary, when $LiNiO_2$ is simultaneously substituted with both B and Al, a shift to higher wavelengths is noted. The dopants may induce changes in NiO_2 vibrations thus substantiating the fact that the dopants occupy mainly the NiO_2 slabs. However, the reverse trend observed for the bisubstitution may be due to the combined effects of B and a probable interstitial tetrahedral occupancy of lesser fraction of Al. Typical bands around 1436 cm^{-1} and 668 cm^{-1} may be attributed to the effect of B and Al in terms of B—O bond stretching vibrations and Al—O bond vibrations, respectively. Thus the existence of a series of solid solutions *viz.*, $LiNi_{0.7}Al_xB_yO_2$ has been understood from IR spectral studies also.

Other physical properties.—BET surface area was estimated to be around 25 and 15 m^2/g for $LiNi_{0.7}B_{0.3}O_2$ and $LiNi_{0.7}Al_{0.3}O_2$, respectively. Due to the fine and foamy nature of the products, the estimated powder density of the compounds were found to be about 70-80% of the theoretical density values, which is commonly observed for the combustion derived products.[28] SEM images captured under the same magnification (400 times) for $LiNi_{0.7}B_{0.3}O_2$ and $LiNi_{0.7}Al_{0.3}O_2$ samples are shown in Fig. 3 (a and b), respectively. It is evident from the micrographs that the particles of the former sample with boron as the substituent were of submicrometer size whereas for the latter compound with Al as the substituent, the particles were slightly higher in dimension. For the samples $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$ and $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$, the size of the particles was found to be almost similar to that of $LiNi_{0.7}Al_{0.3}O_2$. From this

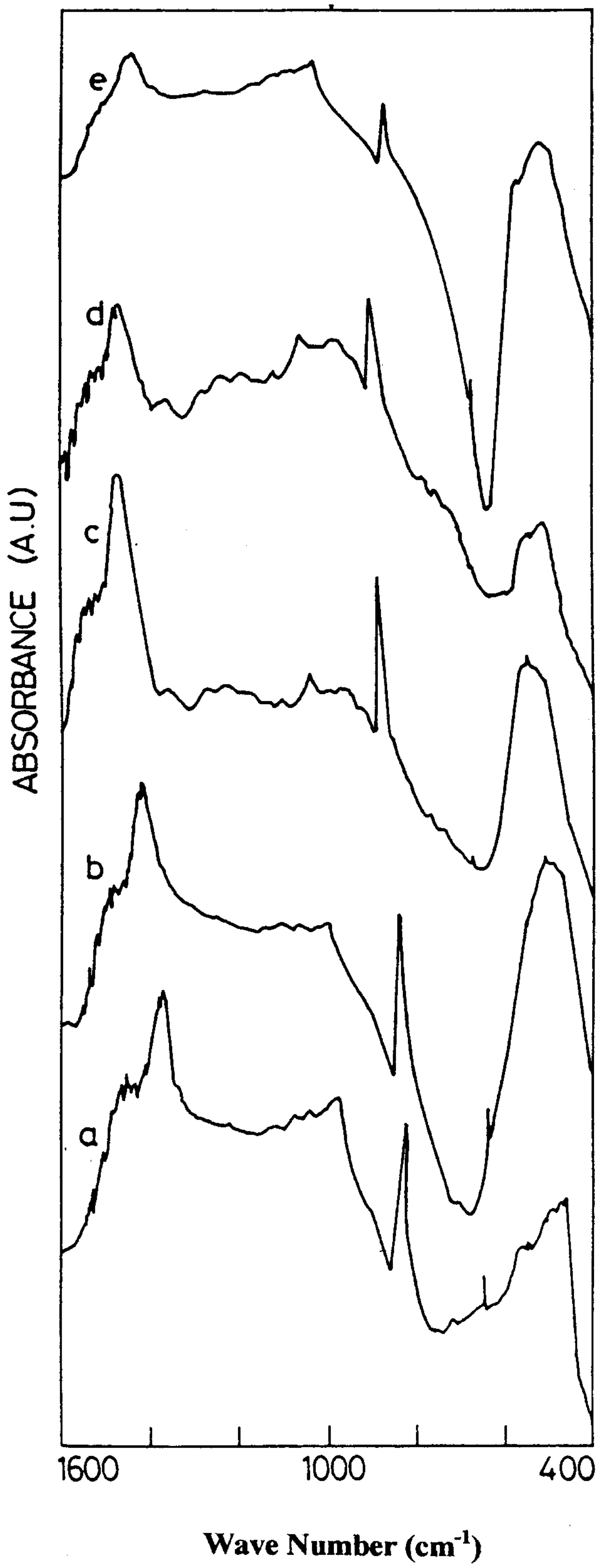

Figure 2. FTIR spectra of (a) $LiNi_{0.7}B_{0.3}O_2$, (b) $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$, (c) $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$, (d) $LiNi_{0.7}Al_{0.3}O_2$, and (e) $LiNiO_2$.

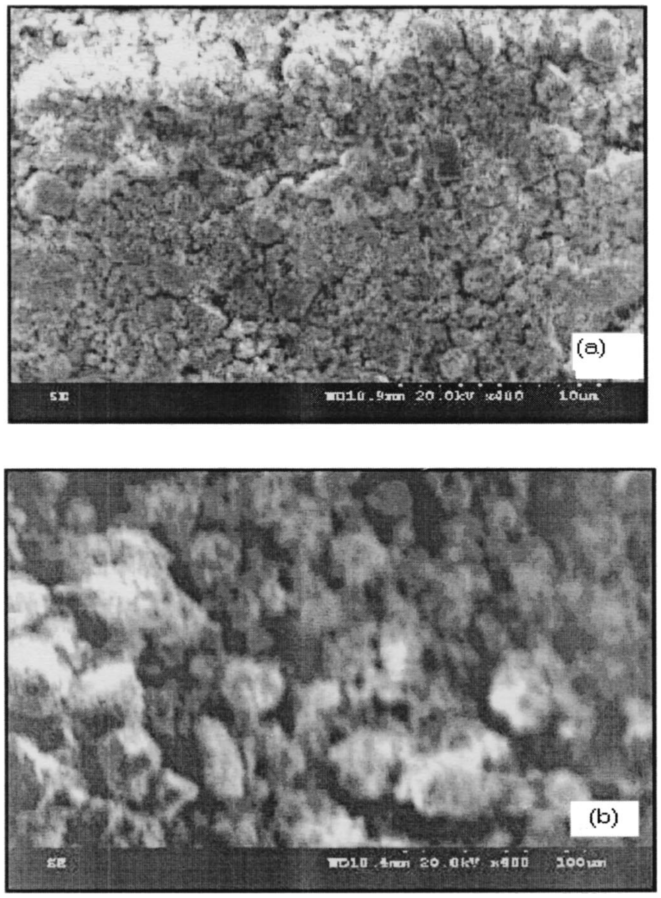

Figure 3. SEM of $LiNi_{0.7}Al_{0.3}O_2$ and $LiNi_{0.7}B_{0.3}O_2$.

observation, we may conclude that the presence of aluminum as dopant may very well be correlated with the size of the particles, *i.e.*, the presence of Al as one of the dopants or as the only dopant has led to the formation of sintered nature of the final product. As a result, the size of the particles was found to be slightly higher than that of the corresponding boron-substituted derivative. This has further been confirmed from the lower BET surface area values $(15\ m^2/g)$, determined invariably for all the aluminum-substituted compounds.

Electrochemical Analysis

Cyclic voltammetry.—Figure 4 shows the cyclic voltammogram of $Li//LiNi_{0.7}Al_xB_yO_2$ $(x + y = 0.3)$ cells fabricated as 2016 coin type, using a mixture of 1 M $LiAsF_6$ in 1:1 v/v of EC and DMC as the electrolyte. The cyclic voltammogram recorded between 3.6 and 4.4 V at a scan rate of 0.1 mV/s indicates that with the increasing boron content, the anodic current decreased and a broad maximum at 4.1-4.3 V was observed. On the contrary, cathodic peak current at lower voltage region started diminishing and the peak at higher voltage region increased as a function of boron content. But for all the samples except $LiNi_{0.7}Al_{0.3}O_2$, a significant shift in the reduction peak toward higher voltages has been observed. As a result, the voltage difference between anodic and cathodic peaks has been narrowed down which is an indication of the high Li^+ reversibility. On the contrary, the large difference between the anodic and cathodic peaks observed for the $LiNi_{0.7}Al_{0.3}O_2$ may be attributed to the partial occupancy of Al in the interstitial $6c$ sites of nickel oxide crystal structure. Therefore, as already mentioned in the XRD analysis, the hindered Li^+ diffusion due to the interstitial occupancy of Al can thus be understood from the CV studies also.

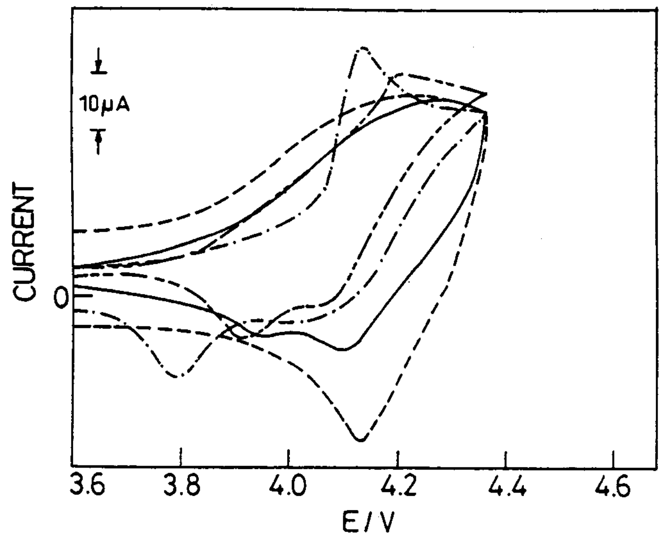

Figure 4. Cyclic voltammograms of the oxide cathodes cycled between 3.6 and 4.4 Vat a scan rate of 0.1 mV/s. (–·–) $y = 0.3$, (–··–) $y = 0.2$, (——) $y = 0.1$, and (----) $y = 0.0$.

Charge/discharge cycling studies.—Charge/discharge cycling has been performed at a current density of 0.1 mA/cm^2 between the cutoff voltages of 3 and 4.5 V. Figure 5 shows the cyclability of these samples up to 25 cycles. The cyclability of the cathodes was found to be satisfactory only for the 10 and 20% boron containing lithium nickel oxides, *viz.*, $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$ and $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$. This has further been supported by the calculated $I_{(003)}/I_{(104)}$ ratio value derived from XRD, which was found to be *ca.* 1.3 for these two samples only.

The better cyclability of the doped nickelate derivatives may also be explained from the thermodynamic point of view. Veluchamy *et al.*[20] in their studies with B-doped $LiMn_2O_4$ ascribed the stability of the compound to the high Gibbs energy of formation (ΔG_f^o) of Mn_2O_3 and B_2O_3. Like wise, the higher ΔG_f^o values[29] of Al_2O_3 (−1582 KJ/mol) and B_2O_3 (−1192 KJ/mol) are in favor of the stability of the nickel oxide derivatives substituted simultaneously with Al^{3+} and B^{3+}. The structural stability of the $LiNi_{0.7}Al_xB_yO_2$ compounds may also be viewed as a function of bond strength[29] of the respective metal-oxygen bonds. Since the bond strength values of

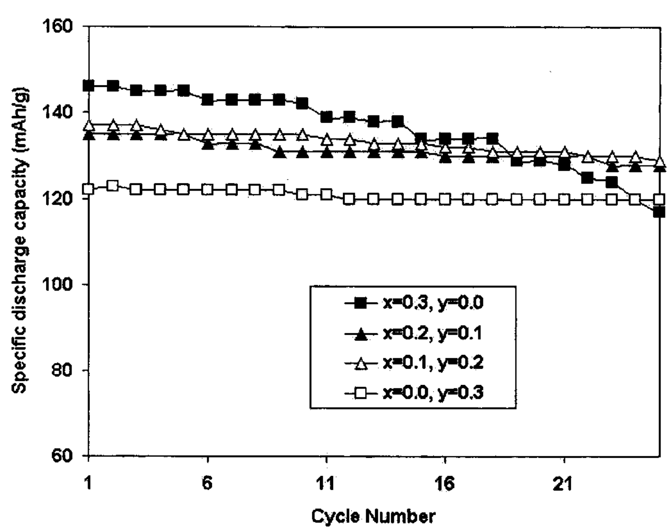

Figure 5. Cylability of $Li//LiNi_{0.7}Al_xB_yO_2$ cells (scan rate = 0.1 mV/s).

Al—O (511 KJ/mol) and B—O (809 KJ/mol) are higher than those of Ni—O (380 KJ/mol) and Li—O (78 KJ/mol), the stability of the structure of $LiNi_{0.7}Al_xB_yO_2$ compounds is understood. Therefore, based on the above reasons, it may be concluded that boron and aluminum could confer stability to the oxide compound by forming strong coordinate bonds with oxygen, thus favoring facile Li^+ removal and leads to an increased crystal structure stability and cell cyclability ultimately.

A maximum capacity of about 145 mAh/g was realized for $LiNi_{0.7}Al_{0.3}O_2$, which showed a capacity fade (20%) after 25 cycles. On the other hand, for the bisubstituted oxides, *i.e.*, $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$ and $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$, about 130 mAh/g was obtained without any significant capacity fade. For the $LiNi_{0.7}B_{0.3}O_2$ sample, a constant capacity of about 120 mAh/g was obtained throughout, demonstrating excellent battery activity and cyclability. Though the initial discharge capacity of this compound was found to be lesser than the rest of the compounds in the series, the cycling performance was found to improve at the cost of capacity. Therefore, a compromise between capacity and cyclability may be arrived at when Al and B are substituted for Ni in the layered $LiNiO_2$ structure. Generally, good capacity retention is attributed to a smaller volume change of the cathode material crystal lattice upon Li^+ intercalation and deintercalation process.[30] Evidently in the present study also, the diamagnetic nature of Al^{3+} and B^{3+} dopants are expected to exclude the possible volume shrinkage/expansion of the interslab space of the cathode oxide lattice during the process of Li^+ intercalation/deintercalation. This is found to be in good agreement with that of the reported results of Pouillerie *et al.*[31] Hence, better cyclability and capacity retention has been realized for $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$, $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$ and $LiNi_{0.7}B_{0.3}O_2$, from the charge/discharge studies.

Conclusion

By adopting a novel urea-nitrate solution combustion method, a set of phase pure compounds of Al and/or B substituted lithium nickel oxide cathode materials with the composition of $LiNi_{0.7}Al_xB_yO_2$ ($x = 0.3, 0.2, 0.1, 0.0$, and $y = 0.3 - x$) was synthesized. The heat-treatment conditions such as dwelling time and formation temperature were found to decrease with increasing boron content. On the other hand, the effect of aluminum substitution seems to reflect on the sintered nature of the final product, as evidenced from the SEM image, which indicated a slightly higher crystalline size of the particles compared to the analogous boron-substituted nickelate derivatives. Charge/discharge studies carried out at 0.1 mA/cm^2 for all the compounds revealed better capacity retention and cyclability. Interestingly, $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$ and $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$ compounds were found to perform satisfactorily (135 mAh/g) without much capacity fade ($<5\%$) at the end of the 25th cycle. However, a slightly lower but a constant capacity of about 120 mAh/g has been exhibited by $LiNi_{0.7}B_{0.3}O_2$ derivative. In spite of having delivered a higher capacity of 140 mAh/g, the compound $LiNi_{0.7}Al_{0.3}O_2$ suffers from degradation of capacity immediately after 10 cycles. Therefore, among the compounds investigated, $LiNi_{0.7}Al_{0.2}B_{0.1}O_2$ and $LiNi_{0.7}Al_{0.1}B_{0.2}O_2$ were evaluated as better candidates for use in rechargeable lithium batteries.

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