

Divalent cation incorporated $\text{Li}_{(1+x)}\text{MMg}_x\text{O}_{2(1+x)}$ ($\text{M} = \text{Ni}_{0.75}\text{Co}_{0.25}$): viable cathode materials for rechargeable lithium-ion batteries

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Abstract

A new class of divalent cation incorporated materials, $\text{Li}_{1+x}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_x\text{O}_{2(1+x)}$, corresponding to $\text{Li}(\text{Ni}_{0.75}\text{Co}_{0.25})_{1-y}\text{Mg}_y\text{O}_2$ ($y = x/(1+x)$), have been successfully synthesized and electrochemically characterized. Good cyclability, high voltage durability (up to 4.4 V during charging) and high capacity (> 150 mA h/g) are the main characteristics of this class of materials. The successful introduction of the divalent cations alone on the transition metal sites helps to attain these characteristics while also maintaining a large nominal capacity of the material without the interference of the aliovalent cations on the Li sites. Good cycling behavior at high voltages is probably due to the prevention of overcharging of the material caused by the overoxidation of the transition metal as well as the presence of divalent cations on the transition metal site. The presence of the overoxidized transition metal as well as divalent cations on the transition metal site not only increases the cycling voltage but also enhances the phase stability of the materials during cycling. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lithium-ion battery; Cathode material; Mg-doped lithium nickel cobalt oxide; High voltage durability

1. Introduction

Lithiated transition metal oxides LiMO_2 ($\text{M} = \text{Mn}, \text{Ni}, \text{Co}, \text{Ni}_x\text{Co}_{1-x}$) are technically important cathode materials for lithium-ion battery applications because they possess high energy density and capacity [1–11]. These materials are 2-D intercalation compounds, which have a layered structure with Li^+ cations inserted in between the MO_2^- ($\text{M} =$ transition metal cations) slabs, as shown in Fig. 1. Among these materials, Ni-based layered oxides $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ ($x = 0-0.25$) are especially attractive because they are either cost-efficient, less toxic or relatively easy to synthesize in comparison to LiCoO_2 and LiMnO_2 . In the case of pure LiNiO_2 , many attempts have been made to synthesize the stoichiometric form of the oxide [12–16]. The importance of achieving stoichiometric LiNiO_2 is to enhance its capacity by removal of Ni^{2+} from the Li sites that retard the diffusion of Li. Unfortunately, with the increase in capacity brought about by the synthesis of the stoichiometric form, the cyclability of the material decreases probably owing to the phase transfor-

mations during cycling. This leads to significant volume changes in the material causing either microcracking or debonding of the active material from the binder [17]. Similarly, although the substitution of Co for Ni helps to alleviate the misposition of Ni^{2+} cations on Li sites [15,16], the material fades in capacity during cycling especially when charged up to higher voltages (e.g., 4.4 V).

In the present study, a new class of materials have been synthesized, which are represented by the formula $\text{Li}_{1+x}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_x\text{O}_{2(1+x)}$ (corresponding to $\text{Li}(\text{Ni}_{0.75}\text{Co}_{0.25})_{1-y}\text{Mg}_y\text{O}_2$, $y = x/(1+x)$). The use of this formula helps to indicate the complete saturation of the Li sites and the corresponding creation of oxygen sites with the addition of excess lithium. The formula also suggests the complete occupation of the transition metal sites by the divalent cations. Furthermore, this representation is also convenient for expressing the variation in the oxygen content with lithium. For example, in the case of $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{Mg}_x\text{O}_{2(1+x/2)}$, oxygen sites may be reduced from $2(1+x)$ to $2(1+x/2)$ if one half of Mg cations occupy the Li sites that causes significant differences in the electrochemical property (as will be described in detail in Section 3). With the introduction of divalent cations on the transition metal sites alone, the cyclability of these

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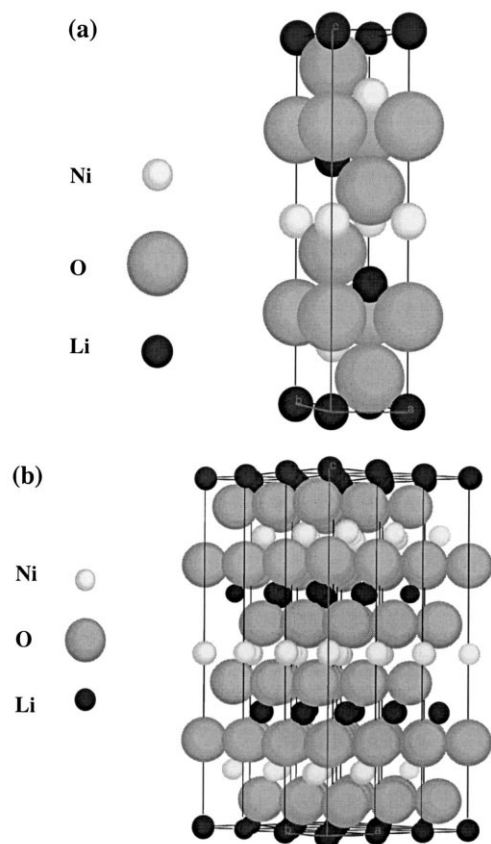


Fig. 1. (a) The unit cell of LiMO₂ (M = transition metal)-type materials possessing $R\bar{3}m$ symmetry. The Li⁺ cations occupy the 3(b) site with Ni³⁺ and O²⁻ occupying the 3(a) site and 6(c) site, respectively. (b) The representation of the layered structure with Li⁺ cations inserted in between the MO₂⁻ (M = transition metal cations) slabs.

materials is enhanced even when cycled up to 4.4 V. Furthermore, in the absence of divalent cations on the Li sites, the materials exhibit capacities in excess of 150 mA h/g when discharged at a rate of C/2. The present manuscript focuses on the validity of the chemical formula representing the occupation of divalent cations on the transition metal site as well as their influence on the electrochemical properties. It should be noted that the chemical formula Li_{1+x}Ni_{0.75}Co_{0.25}Mg_xO_{2(1+x)} is used throughout the manuscript for the purpose of clarifying the relationships between the metal ratios in the starting precursor (Li:Ni:Co:Mg) and the atomic ratio (Li:Ni:Co:Mg:O) in the final product.

2. Experimental

The particulate sol-gel (PSG) technique, which was reported earlier for synthesizing LiNiO₂ and LiNi_{0.75}Co_{0.25}O₂ [15,16], is employed in the present study for synthesizing Li_(1+x)Ni_{0.75}Co_{0.25}Mg_xO_{2(1+x)}. This particular technique is chosen because it affords improved

mixing of cations at a molecular level in contrast to the conventional solid state processes. The resultant oxides were prepared using lithium hydroxide monohydrate (Aldrich, 99%) and proper stoichiometric amounts of nickel acetate tetrahydrate (Aldrich, 98%), cobalt acetate tetrahydrate (Aldrich, 98%) and magnesium hydroxide (Aldrich 98%) as starting materials. The specific procedure for synthesizing Li_{1.1}Ni_{0.75}Co_{0.25}Mg_{0.1}O_{2.2} (LiNi_{0.682}Co_{0.227}Mg_{0.091}O₂) is as follows: 0.11 mol of lithium hydroxide monohydrate and 0.075 mol of nickel acetate tetrahydrate with 0.025 mol of cobalt acetate tetrahydrate precursors were each first dissolved in de-ionized (DI) water separately to obtain clear solutions. Magnesium hydroxide (0.01 mol) was then dissolved in another 30 ml DI water by adding 3–5 ml of nitric acid. Mixing of the individual solutions resulted in dark purple colored suspensions (~210 ml in volume). Ethyl alcohol (90 ml) was then added to the solutions in order to facilitate the removal of the liquid products during the subsequent drying process described later. The dark purple turbid solutions were stirred for 15–20 min immediately prior to drying.

A rotary evaporator (Buchi) was used for the subsequent drying process employing an initial pressure of 500 mbar at 120°C for 3 h followed by a reduced pressure of 100 mbar at 140°C for 1 h to dry the solutions completely. The resultant precipitates were collected and then ground before being subjected to further heat treatments. The heat treatments were conducted in air at 800°C for 5 h in the case of Li_{1.03}Ni_{0.75}Co_{0.25}Mg_{0.03}O_{2.06} (LiNi_{0.728}Co_{0.243}Mg_{0.029}O₂) and Li_{1.05}Ni_{0.75}Co_{0.25} × Mg_{0.05}O_{2.1} (LiNi_{0.714}Co_{0.238}Mg_{0.048}O₂), and 10 h for Li_{1.1}Ni_{0.75}Co_{0.25}Mg_{0.1}O_{2.2} (LiNi_{0.682}Co_{0.227}Mg_{0.091}O₂). All these compounds represent the case wherein the Li sites are largely saturated. High-density alumina boats were used as the sample containers for conducting all heat treatments. For comparison, materials corresponding to the formula LiNi_{0.75}Co_{0.25}Mg_xO_{2(1+x/2)}, (x = 0.05, 0.10, and 0.20) were also synthesized using the same procedure described above except that different amounts of Li were used. This formula represents the case where the divalent cation is distributed equally on both the lithium and transition metal sites. All these precursors were heat treated at 800°C for 5 h in air.

The synthesized materials were characterized for their phase purity using X-ray diffraction (XRD) (Rigaku θ/θ diffractometer). The XRD patterns were also refined for their structure using the Rietveld refinement technique. Rietveld refinement on the synthesized powders was conducted using the refinement program RIETAN 94. Simultaneous thermogravimetric and differential thermal analysis (TGA/DTA, SDT2960; TA Instruments, New Castle, DE) was also used to validate the chemical composition of the final oxide. The TGA/DTA analysis was done on ~10 mg of powders in the presence of reconstituted air. Chemical analysis was conducted by Galbraith Laboratories, Inc., Knoxville, Tennessee using inductively-coupled

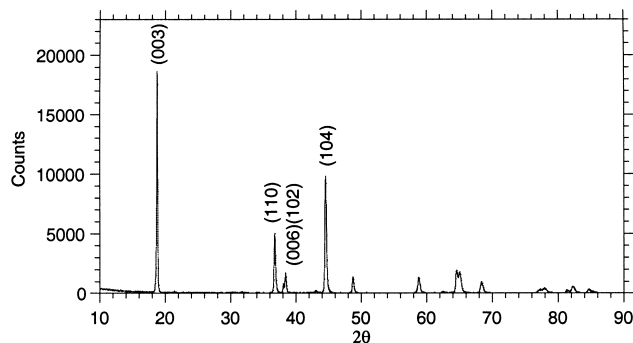


Fig. 2. X-ray analysis of the sample with 10 mol.% Mg addition. The “phase pure” nature of the synthesized materials actually suggests that Mg cations should occupy the transition metal sites.

plasma (ICP). Each sample was dried under vacuum at 150°C for 3 h before conducting the analysis.

Cathodes for electrochemical characterization were fabricated by coating aluminum foils with the synthesized powders. This was done by making a slurry containing 87.1 wt.% synthesized material, 7.6 wt.% acetylene black and 5.3 wt.% copolymer binder (ethylene/propylene copolymer containing 60% ethylene content) using Trichloroethylene (TCE) as a solvent. The punched out cathodes were 1 cm² in area, 0.0076 cm in thickness and 0.01 g in weight. A three-electrode (“Hockey Puck”) type cell design was used [18,19] employing lithium foil as an anode and 1 M LiPF₆ in EC/DMC (with an EC to DMC wt.% ratio of 2:1) as the electrolyte. All the test batteries (except those tested at high voltage and high current, which are specified in Section 3) in this study were cycled in the voltage range of 3.1–4.4 V employing a current density of 0.25 mA/cm² which corresponds to a C-rate of

~ C/2. All the electrochemical analysis for the prototype test batteries was conducted using a potentiostat (Arbin Electrochemical Instrument, College Station, TX).

3. Results and discussion

The goal of this work was to synthesize the oxide containing all the Mg ions on the transition metal sites. However, although this is implied by the nominal chemical formula discussed earlier and by the experimental procedure, it is necessary to confirm this in the synthesized materials. This is of particular importance since some of the Mg ions could also occupy the Li sites similar to the Ni ions contributing to the anti-site disorder well known for LiNiO₂. The feasibility of introducing divalent cations alone on the transition metal sites is particularly tested on LiNi_{1-x}Co_xO₂ ($x = 0.25$). This composition is chosen because of its lowest potential for exhibiting disorder caused by the misposition of Ni or Co cations on the Li sites. This is largely due to the more oxidizable nature of Ni²⁺ in the presence of Co³⁺ rendering the composition easy to be synthesized in comparison to LiNiO₂ [15,16]. In order to introduce Mg cations alone on the transition metal sites, a series of compositions were synthesized by maintaining the ratio of Li:(Ni + Co):Mg = (1 + x):1:x in the general chemical formula, Li_{1+x}Ni_{0.75}Co_{0.25}Mg_xO_{2(1+x)}, ($x = 0.03, 0.05, \text{ and } 0.10$), which implies the introduction of Mg cations on the transition metal sites alone to maintain a site ratio of Li:M:O = 1:1:2 (M = transition metal site).

This representation of the compound is indicative of the stoichiometric form of Li(Ni_{0.75}Co_{0.25})_{1-y}Mg_yO₂ with all

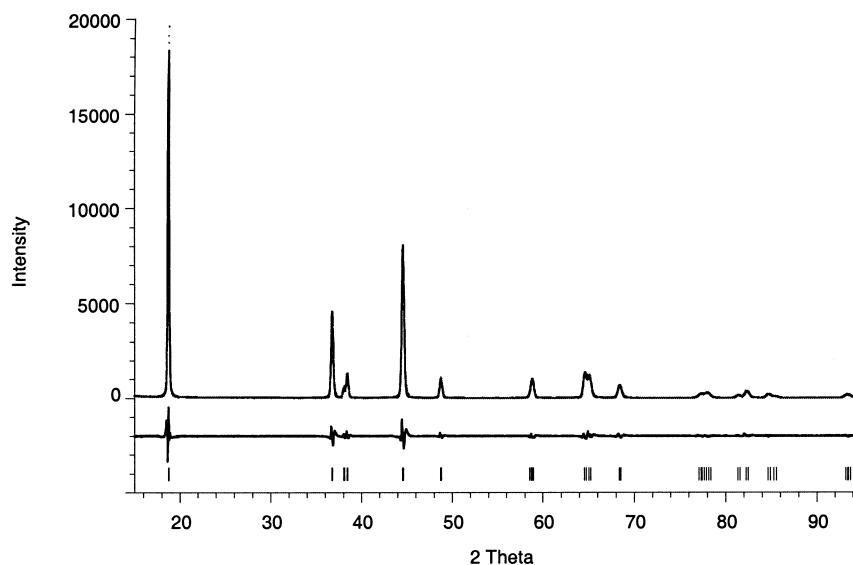


Fig. 3. Results of the Rietveld refinement performed on the experimentally obtained X-ray diffraction pattern of the material Li_{1.10}Ni_{0.75}Co_{0.25}Mg_{0.10}O_{2.2} (LiNi_{0.682}Co_{0.227}Mg_{0.091}O₂) using $R\bar{3}m$ symmetry.

the lithium sites completely saturated. Before initiating a further study of the relationship between structure and property, a set of experiments were conducted to verify the occupation of divalent cations alone on the transition metal sites. The X-ray analysis shows that all the three materials synthesized are phase pure. Fig. 2 shows the X-ray diffraction pattern of a representative oxide containing a maximum amount of Mg (0.10). The phase pure nature of these synthesized materials actually suggests that Mg cations indeed sit on the transition metal sites since the number of Li sites is equal to the sum of Ni, Co and Mg sites, and Li atoms do not preferably occupy the transition metal sites because of the large defect formation energy required for monovalent cations to sit on trivalent metal sites. This aspect is also supported by the results of Rietveld refinement obtained on $\text{Li}_{1.1}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.10}\text{O}_{2.2}$ ($\text{LiNi}_{0.682}\text{Co}_{0.227}\text{Mg}_{0.091}\text{O}_2$) as shown in Fig. 3. The detailed summary of the Rietveld refinement analysis is shown in Table 1. The result was obtained by assuming the following constraints: (i) The ratio of Co, Ni and Mg is constant. (ii) Occupancy of the transition metal site and Li site is set to unity thereby allowing for the deviation of Mg cations on both sites. The results of the Rietveld refinement clearly show that the majority of Mg occupy the transition metal sites.

Chemical analysis was also conducted to analyze the stoichiometry of the synthesized materials. The purpose of conducting chemical analysis on these materials is to resolve the site ratio of Li, (Ni + Co + Mg) and O. The results of chemical analysis conducted by Galbraith Laboratories, Inc., Knoxville, Tennessee is shown in Table 2. Based on the calculations and the suggested formula, it can be seen that the number of oxygen is actually very close to twice the sum of Ni, Co and Mg (moles of oxygen is twice the sum of moles of Ni, Co, and Mg), which again suggests that the Mg cations are occupying the transition metal sites. It should be noted that there is always some lithium loss as can be seen from the analysis during heat

Table 1
Results of the Rietveld refinement analysis of $\text{Li}_{1+x}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_x\text{O}_{2(1+x)}$, $x = 0.10$ ($\text{LiNi}_{0.68}\text{Co}_{0.23}\text{Mg}_{0.09}\text{O}_2$)

Space group: $R\bar{3}m$	
$a = 2.8655 \text{ \AA}$	
$c = 14.1859 \text{ \AA}$	
Cell volume = $100.8754 (\text{\AA}^3)$	
Atoms	Occupancy*
Ni on transition metal sites	0.689
Co on transition metal site	0.230
Mg on transition metal sites	0.081
Mg on Li sites	0.009
Li on Li sites	0.991
O on O sites	1.000

* $R_{\text{wp}} = 0.158$.

Table 2

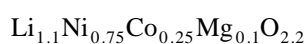
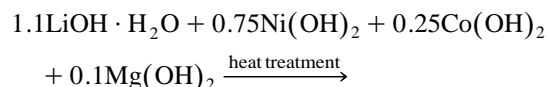
Results of chemical analysis showing that the number of oxygen is actually very close to twice the sum of Ni, Co and Mg (moles of oxygen equal to twice the sum of moles of Ni, Co, and Mg)

Nominal composition	Analyzed (wt.%)	Composition (%)	Suggested formula
$\text{Li}_{1.05}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.05}$	Lithium	6.89	(NiCo):Mg:O = 1.00:0.045:2.096
	Nickel	43.90	
	Cobalt	14.68	
	Magnesium	1.09	
$\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.10}$	Lithium	6.91	(NiCo):Mg:O = 1.00:0.093:2.196
	Nickel	42.70	
	Cobalt	14.18	
	Magnesium	2.19	

Each sample was dried under vacuum at 150°C for 3 h before analysis. The subscripts of the suggested formula were obtained by assuming Ni + Co = 1.00.

treatment. The occupation of some (half of total) Mg on the lithium site can, therefore, not be discounted, although the amount is low as indicated by the refinement results in Table 1. However, the results of the analysis are still a good indicator of the site occupancy of Mg on the transition metal site.

Thermogravimetric analysis was also used to verify the occupation of the divalent cations on the transition metal sites. This was done by analyzing the conventional solid state reaction of a mixture of hydroxides corresponding to the desired formula. The TGA result also supports the hypothesis of occupation of the transition metal sites by Mg cations. In the present case, if Mg cations were to occupy the Ni (or Co) sites, the stoichiometry of O would be twice the sum of the stoichiometry of Ni, Co and Mg as explained earlier. Assuming Li:Ni:Co:Mg = 1.1:0.75:0.25:0.1 as an example for illustration, the chemical formula representing the occupation of all Mg on Ni (or Co) sites should be $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$ (or $\text{LiNi}_{0.682}\text{Co}_{0.227}\text{Mg}_{0.091}\text{O}_2$ following the LiMO_2 convention). The proposed reaction as well as the accompanying theoretical weight loss corresponding to the solid state reaction of the hydroxide precursors to yield the oxide with this chemical formula would be as follows:



(calculated weight loss = 28.16%)

The weight loss resulting from the thermogravimetric analysis (TGA) is shown in Fig. 4. The experimental values of the weight change between the starting precursors ($\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$) and the final products are listed in Table 3. The results of Table 3

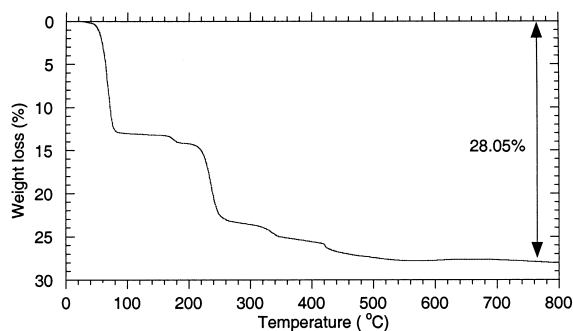


Fig. 4. The weight loss of starting precursors ($\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$) during heat treatment revealed by TGA, which validates the proposed chemical formula $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$.

clearly show that the weight loss data satisfies the proposed chemical formula $\text{Li}_{1.1}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$ (0.4% difference with respect to the calculated value) implying that the Mg ions occupy the transition metal site by saturating the Li sites.

In order to further supplement the chemical analysis results of the oxide, chemical analysis was also conducted to analyze the Mg content in the electrolyte after the cells were subjected to 30 charge/discharge cycles. This was done to further validate the agreement of the final product composition with the proposed chemical formula. It is reported that the occupation of Mg on Li sites lead to the transport of Mg ions into the electrolyte during cycling [20]. If this were true in the present case, the concentration of Mg cations in the electrolyte should increase with the Mg content in the electrode material. The results of the chemical analysis are shown in Table 4. It can be seen that the Mg concentration in the electrolyte decreases with the increase in Mg content in the electrode material suggesting that the Mg cations should reside on the transition metal sites. It should be noticed that a very slight excess of Mg concentration is observed in the cycled electrolyte in comparison to the fresh electrolyte. However, this slight increase in Mg concentration only corresponds to about 1% of the total Mg content in the cathode tested. This small amount of Mg detected in all cycled electrolytes may originate from contamination of the reusable parts of the test batteries that were cleaned with a detergent.

Finally, the electrochemical response of the synthesized materials also reflects the differences caused by the variations in the site occupancy of Mg. By comparing the materials synthesized using the formula $\text{Li:Ni:Co:Mg} = 1:0.75:0.25:x$ (assuming that one half of Mg cations occupies the Li site and the other half sits on the transition

Table 4

The results of the chemical analysis conducted on the electrolyte before and after 30 cycles of the charge/discharge process

Composition of cathode	Magnesium content in electrolyte after 30 cycles (ppm)
$\text{Li}_{1.03}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.03}\text{O}_{2.06}$	7.9
$\text{Li}_{1.05}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.05}\text{O}_{2.10}$	7.3
$\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.10}\text{O}_{2.20}$	7.1

* The initial Mg content in the electrolyte prior to cycling was 5.7 ppm.

metal sites) and $\text{Li:Ni:Co:Mg} = (1+x):0.75:0.25:x$ (refer to Fig. 5), it is seen that the capacity of the material drops drastically with the increase in Mg addition for the former set of materials. The drastic decrease in capacity caused by the addition of Mg can be attributed to the fact that some Mg cations occupy the Li sites limiting the diffusion of lithium. Therefore, the capacity of the materials can be expected to decrease with increase in the addition of Mg similar to the case of disordered LiNiO_2 where Ni atoms occupy Li sites. In contrast, the capacity of the materials do not decrease significantly with an increase in Mg addition even up to at least 10 mol% for the materials corresponding to $\text{Li:Ni:Co:Mg} = (1+x):0.75:0.25:x$. This result implies that Mg cations occupy the transition metal sites in the case of the materials represented by the stoichiometry of $\text{Li:Ni:Co:Mg} = (1+x):0.75:0.25:x$, thereby exhibiting no barrier to the diffusion of lithium during cycling.

Based on the results presented above, it is clear that maintenance of the ratio of $\text{Li:}(\text{Ni} + \text{Co} + \text{Mg}) = 1:1$ promotes the occupancy of Mg cations on the transition metal sites. One interesting phenomena which is obtained by introducing the Mg cations only on the transition metal sites is that good cyclability of the material can be observed even when the material is cycled up to 4.4 V in comparison to phase pure $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$. The difference in stability between the phase pure $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Li}_{1.1}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$ can be seen from the plot of capacity vs. cycle number shown in Fig. 6. A capacity fade of 0.01%/cycle is observed for $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ in comparison to virtually no fade per cycle for $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.10}\text{O}_{2.2}$. Fig. 7(a) also shows the cycling behavior of $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.10}\text{O}_{2.2}$ using coke as an anode which is cycled between 3.1 and 4.4 V with a charge/discharge rate of C/2. Since all the Mg cations are sitting on the transition metal sites, the stable cycling behavior cannot be attributed to the “pillaring” effect that is reported to be caused by the divalent cations on the Li sites in

Table 3

The weight change between the starting precursors ($\text{LiOH} \cdot \text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$) and the final product $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$

Proposed chemical formula	Weight of starting precursors (mg)	Weight of final product (mg)	Weight change observed (%)	Weight change calculated (%)
$\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$	19.6641	14.1479	28.05	28.16

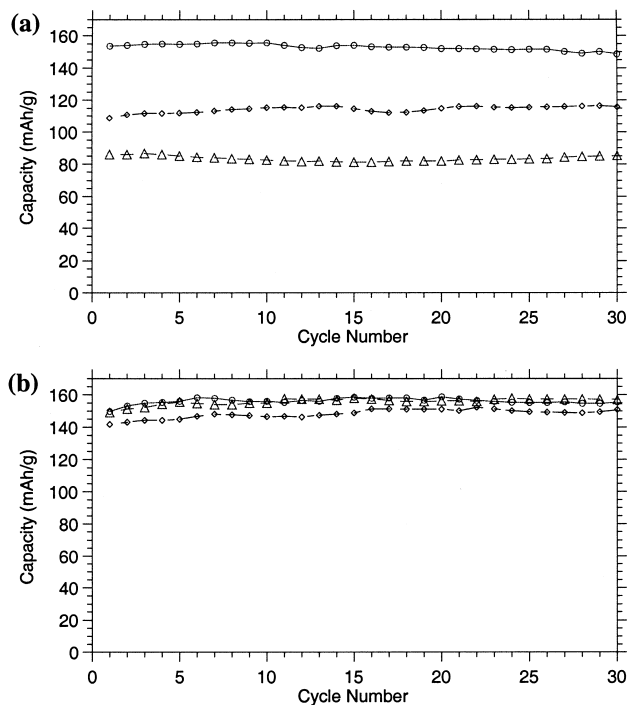


Fig. 5. Plots of capacity vs. cycle number for two sets of materials. (a) The materials synthesized using the formula $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{Mg}_x\text{O}_{2(1+x/2)}$. ($-\circ-$) Represents $x = 0.05$, ($-\diamond-$) represents $x = 0.10$ and ($-\triangle-$) represents $x = 0.20$, respectively. (b) The materials synthesized using the formula $\text{Li}_{1+x}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_x\text{O}_{2(1+x)}$. ($-\circ-$) Represents $x = 0.03$, ($-\diamond-$) represents $x = 0.05$ and ($-\triangle-$) represents $x = 0.10$.

disordered LiNiO_2 [12]. Additional test results are shown in Fig. 7(b) for $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$ cycled between 3.1 and 4.6 V employing a current density of 0.5 mA/cm^2 , combined with the battery that was cycled under a high a current density of 2 mA/cm^2 ($\sim 4 \text{ C}$ in C-rate) for 150 cycles using Li as an anode as shown in Fig. 7(c). These results again demonstrate the unique cycling behavior of this material. A capacity of $\sim 130 \text{ mA h/g}$ with a capacity fade rate of $0.006\%/ \text{cycle}$ is observed for this Mg-doped oxide when cycled under high current. These

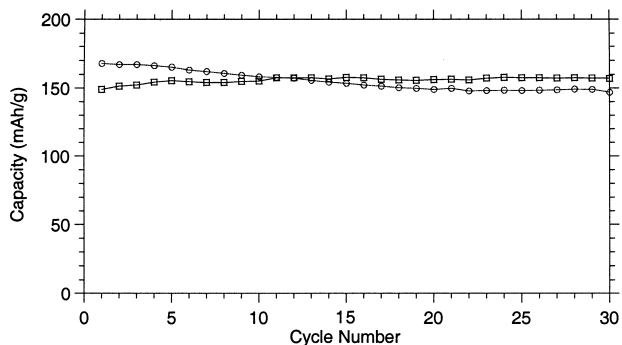


Fig. 6. Plot of the capacity vs. cycle number plot showing the difference in stability between phase pure $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ (\circ) and $\text{Li}_{1.1}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$ (\square).

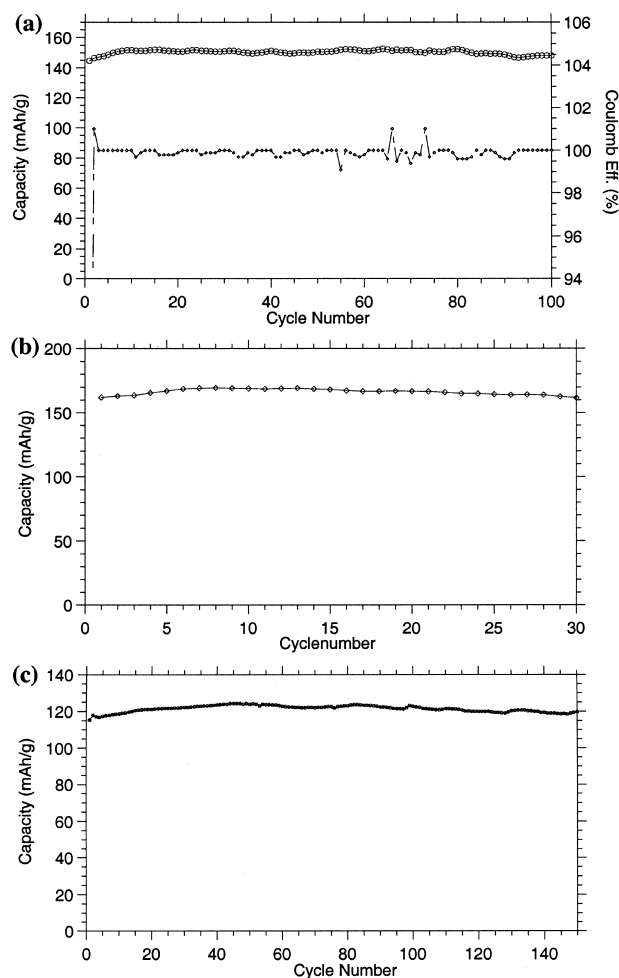


Fig. 7. The cycling behavior of $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.20}$ cycled between 3.1 and 4.4 V for 100 cycles using coke as an anode. ($-\circ-$) Represents the specific capacity and ($-\diamond-$) represents the Coulomb efficiency of the material during cycling. (b) The high voltage durability test of the same oxide cycled between 3.1 and 4.6 V using lithium as an anode with a current density of 0.5 mA/cm^2 . (c) Same cathode material cycled under a current density of 2.0 mA/cm^2 (corresponds to 4C in C-rate). The test battery was cycled between 3.1 and 4.4 V for 150 cycles using lithium as the anode.

electrochemical results not only demonstrate the remarkable stability at high voltages but also excellent capacity retention (Coulomb efficiency > 0.995) of these oxides achieved by the introduction of lower valent (divalent) metal cations on the trivalent transition metal sites. Thus, both enhanced voltage durability at high voltage and excellent cyclability is exhibited by the introduction of the divalent cations on the transition metal sites.

The stabilization mechanism caused by the introduction of Mg cations on the transition metal sites is not yet very clear. One of the possible reasons for this stabilization is that with the introduction of divalent cations on the trivalent cations sites, an equivalent amount of trivalent cations are forced to be pre-oxidized to $4+$ oxidation state based on charge balance. This is evident from the decrease in

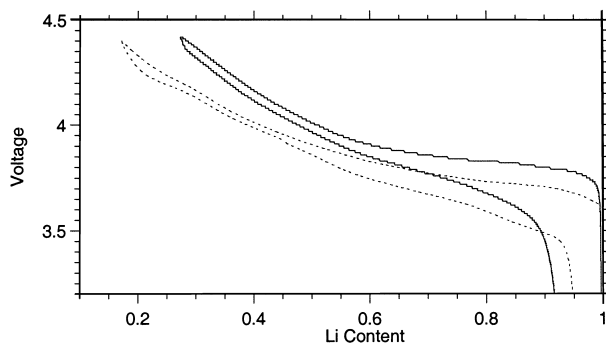


Fig. 8. Plot of voltage vs. Li content showing the first charge and discharge cycle for both $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ (—) and $\text{Li}_{1.1}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$ (---). The cell was cycled using a small current density ($10 \mu\text{A}/\text{cm}^2$). The decrease in capacity of the material is probably caused by the presence of inactive Mg^{2+} and Ni^{4+} on Ni sites.

capacity of the material caused by the presence of inactive Mg^{2+} and Ni^{4+} on the Ni site as seen in the plot of voltage vs. Li content for the first cycle shown in Fig. 8. Fig. 8 shows the charge and discharge behavior of $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Li}_{1.1}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.1}\text{O}_{2.2}$ when tested under a small current ($10 \mu\text{A}/\text{cm}^2$). The presence of inert species (Mg^{2+} and Ni^{4+}) on the transition metal site however helps to prevent overcharging during the charging process enhancing the cyclability of the material. In addition, the stable cycling behavior at high voltages can be attributed to the upward shift of the voltage during cycling (see the higher voltage for the Mg incorporated oxide at a fixed lithium content in comparison to the pure oxide shown in Fig. 8) that can be caused by this overoxidation phenomenon. The average cycling voltage for $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.10}\text{O}_{2.20}$ is further calculated using the formula:

$$\bar{V} = \left(\int_{Q_1}^{Q_2} V dQ \right) / Q_{\text{sum}}$$

where \bar{V} is the average voltage and Q is the number of Coulombs. The calculations indicate an average voltage during charge (\bar{V}_{charge}) and discharge ($\bar{V}_{\text{discharge}}$) of 3.95 and 3.87 V, respectively for pure $\text{LiNi}_{0.75}\text{Co}_{0.25}\text{O}_2$ and $\bar{V}_{\text{charge}} = 4.01$ V, $\bar{V}_{\text{discharge}} = 3.92$ V for $\text{Li}_{1.10}\text{Ni}_{0.75}\text{Co}_{0.25}\text{Mg}_{0.10}\text{O}_{2.20}$. This tendency of the higher average voltage exhibited by the Mg incorporated oxide could also probably be the reason contributing to the enhanced durability of this oxide when charged to 4.4 V. The results of further studies elucidating the exact role of Mg and its contribution to the electrochemical stability of this oxide has been conducted and will be reported elsewhere [21].

4. Conclusions

The PSG process has been used to synthesize a new family of Mg-incorporated materials, $\text{Li}_{1+x}\text{Ni}_{0.75}\text{Co}_{0.25}$ -

$\text{Mg}_x\text{O}_{2(1+x)}$. The introduction of divalent cations such as Mg on the transition metal sites stabilizes the oxide thus enhancing the cyclability as well as voltage durability of the materials up to at least 4.4 V. The long cycle test utilizing coke anode as well as high current test ($2 \text{ mA}/\text{cm}^2$ at a C rate of 4 C) demonstrates the remarkable cyclability and stability of these materials. The validity of this formula was confirmed by X-ray analysis, chemical analysis of the synthesized compounds, TGA analysis, chemical analysis of the electrolyte before and after cycling as well as electrochemical characterization. The results unequivocally validate the occupation of divalent cations alone on the transition metal sites. The occupation of divalent cations on the Li site is however not the key to the stabilization of these doped oxides. Instead it decreases the diffusivity of Li in the material which causes the increase in polarization during the charge/discharge process therefore decreasing the nominal capacity during cycling. The capacity drop caused by the occurrence of divalent cations on the Li sites can however be minimized by saturating the Li sites with excess Li thus promoting the divalent cations onto the transition metal site. The stabilization mechanism is not yet well understood. A possible explanation is provided by the creation of inactive Ni^{4+} due to the substitution of Mg, which not only helps prevent overcharging but also increase the average voltage of the material. These inactive pairs (Ni^{4+} , Mg^{2+}) contribute to the enhanced voltage durability and cyclability of the material when cycled up to 4.4 V.

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