High-voltage LiMg$_{\delta}$Ni$_{0.5-\delta}$Mn$_{1.5}$O$_4$ spinels for Li-ion batteries

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Abstract

New high-voltage cathode materials for lithium and Li-ion batteries, with the general formula LiMg$_{\delta}$Ni$_{0.5-\delta}$Mn$_{1.5}$O$_4$ ($\delta=0.00$, 0.05 and 0.10), have been synthesized and characterized. The crystal structure of these cubic spinel materials has been refined with space group $P4_332$ with the following site occupation: Li$^+$ on 8c, Mg$^{2+}$ on 4b, Ni$^{2+}$ on 4b/12d, Mn$^{4+}$ on 12d/4b and O$_2$/C0 on 24e and 8c. Refinement with space group $Fd3m$ was not possible. As a function of the Mg content, it was found that: (I) the cubic lattice constant increases from 8.1685 Å ($\delta=0.00$) and 8.1703 Å ($\delta=0.05$) to 8.1733 Å ($\delta=0.10$); (II) the flat potential profile at 4.7 V vs. Li/Li$^+$ ($\delta=0.00$) changes to a slightly sloping profile with an increased average potential of 4.75 V ($\delta=0.10$); (III) the cyclability and the conductivity of the materials improve. It is concluded that LiMg$_{\delta}$Ni$_{0.5-\delta}$Mn$_{1.5}$O$_4$ ($\delta<0.10$) are promising cathode materials that, when combined with a low-voltage anode material like LiCrTiO$_4$, can result in $\sim$3.25 V rechargeable Li-ion battery with spinel electrodes.

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1. Introduction

The ‘classical’ Li-ion batteries that are available today utilize a $\sim$4-V lithium transition metal oxide as positive electrode and carbon as negative electrode. The transition metal oxides currently used are LiCoO$_2$ and LiMn$_2$O$_4$. Research has been directed towards new anode materials like Li$_4$Ti$_5$O$_12$ [1,2] and LiCrTiO$_4$ [3,4] with potentials of $\sim$1.5 V vs. Li/Li$^+$. They should be safer and show higher rate capabilities than carbon anodes. However, combining these anode materials with the 4-V LiMeO$_2$ materials results in $\sim$2.5 V Li-ion batteries, which is quite low. An example is the system Li$_4$Ti$_5$O$_12$ vs. LiCoO$_2$, which has been shown by Jansen et al. [5].

A way to compensate for this loss in battery potential and energy is to use a high-voltage oxide with a potential in the range of 4–5 V vs. Li/Li$^+$. This approach has been shown by Panero et al. [6] with the system Li$_4$Ti$_5$O$_12$ vs. Li$_2$Co$_{0.4}$Fe$_{0.4}$Mn$_{3.2}$O$_8$ and, recently, by our laboratory with the spinel-based system LiCrTiO$_4$ vs. LiMg$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ [4].

The research for high-voltage materials has been hampered by the stability of the organic electrolytes. Although the LiPF$_6$-based electrolytes have shown to be very good for the 4-V systems, it will be necessary to develop new, more stable electrolytes to exploit the high-voltage materials commercially. The high-voltage...
materials that have been reported fall in two categories: the inverse spinels and the normal spinels. Here, we focus on the literature reporting on normal spinels.

Sigala et al. [7] demonstrated in 1995 the chromium-doped spinel materials LiCr,Mn2−yO4 in which a 4.5–5.0 V plateau vs. Li/Li+ appears as a function of y. In 1996 and 1997, Amine et al. [8] reported on the spinel LiNi0.5Mn1.5O4. At first instance, they reported the 3-V behavior when intercalating lithium in LiNi0.5Mn1.5O4. Later, they demonstrated the high-voltage profiles of LiMe2Mn2−yO4 with Me=Fe, Ni for y=0.5 and 1 [9]. Gao et al. [10] investigated the origin of the voltage profile for LiNi,Mn2−yO4. For the same system, Zhong et al. [11] showed the effects of the synthesis route (sol–gel vs. solid state) on some structural and electrochemical properties. Ein-Eli et al. [12] showed in 1998 that the system LiCu2Mn2−yO4 also develops a high-voltage regime as a function of y, even going to 4.9 V for y=0.5.

Kawai et al. [13] reported in 1998 the LiCo0.5Mn1.5O4 and LiFe0.5Mn1.5O4 spinels operating around 5 V vs. Li/Li+ [14]. In 1999, they presented an overview of high-voltage spinels, covering most of the materials just mentioned [15]. It is clear from Table 2 in Ref. [15] that only the LiCrMnO4 and LiNi0.5Mn1.5O4 spinels have essentially a single high-voltage plateau, while the other components show a distinct low-voltage (∼4.1 V) and high-voltage (4.5–5.1 V) part. This was confirmed by the data reported by Ohzuku et al. [16], indicating that only LiNi0.5Mn1.5O4 has really an almost flat voltage profile. The earliest reports on LiNi0.5Mn1.5O4, however, are not related to lithium intercalation but deal with the magnetic properties. Blasse [17] showed in 1966 that LiNi0.5Mn1.5O4 is a ferrimagnetic spinel material with Ni3+ and Mn4+ on octahedral sites and Li on tetrahedral sites.

Since our interest was to make a flat-potential Li-ion battery with a Li4Ti5O12 or LiCrTiO4-based anode, we tried to improve the LiNi0.5Mn1.5O4-based spinels. Initial measurements on the parent spinel LiNi0.5Mn1.5O4 showed fading and quite high polarization, especially at the start and end of the charge and discharge. This effect can also be observed for the spinel material LiMn2O4 and is linked to the conductivity of the material as a function of lithium content (Li,Mn2−yO4, 0<y<1).

Several authors have tried to stabilize and modify the spinel LiMn2O4 [18–20], and Mg doping in Li4Ti5O12 resulted in an increased electronic conductivity [21]. In this paper, we show that with Mg doping, it is possible to improve the overall conductivity in LiMg0.5Ni0.5−yMn1.5O4 as well as the rate capability and the cycling stability of the material.

2. Experimental

The cathode materials were made with a combination of a sol–gel synthesis and solid-state processing. The precursors, LiOH·H2O (Merek), Mg(Ac)2·4H2O (Fluka), Ni(Ac)2·4H2O (Aldrich) and Mn(Ac)2·4H2O (Fluka) (Ac=CH3COO), were ball-milled in distilled water for 15 min. In this step, the hydroxide reacted with the acetates, forming a gel-like substance. The use of hexane instead of water was tried but a tough, gumlike substance separated out in the hexane, which was impossible to ball-mill. The homogeneous water-based mixture was dried at low temperatures to a homogeneous precursor powder and subsequently calcined (three times) at 800 °C in air for a total of 30 h. The heating and cooling rate for the first two calcination steps was always 10 °C/min. The obtained powders in each step were ball-milled in hexane for 30 min using a planetary ball mill with agate jars/balls (Fritsch Pulverisette 7). The final dwell-time was 6 h and a very slow cooling rate of 0.1 °C/min was used to avoid oxygen uptake. The materials are listed in Table 1.

The structure and phase purity of the active materials was checked by X-ray diffraction (XRD, Bruker AXS D8 advance, Cu-Kα, no filter) and neutron diffraction, using the HB3 diffractometer of the high flux reactor in Petten (The Netherlands) with an incident neutron wavelength of 0.14265 nm. The particle size and morphology of the powders was examined by SEM (JEOL JSM-5800LV).

FT-IR measurements were done using a Perkin Elmer Spectum 1000. About 1.5 mg of sample material was thoroughly mixed with 200 mg KBr

![Table 1](image)

<table>
<thead>
<tr>
<th>δ</th>
<th>Nominal composition</th>
<th>ICP composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>LiNi0.50Mn1.50O4</td>
<td>Li0.98Ni0.50Mn1.45O4</td>
</tr>
<tr>
<td>0.05</td>
<td>LiMg0.05Ni0.45Mn1.50O4</td>
<td>Li0.99Mg0.05Ni0.45Mn1.50O4</td>
</tr>
<tr>
<td>0.10</td>
<td>LiMg0.10Ni0.40Mn1.50O4</td>
<td>Li0.99Mg0.10Ni0.40Mn1.50O4</td>
</tr>
</tbody>
</table>
and pressed into 13-mm pellets. The scans were made directly after pressing the pellets to avoid water absorption. The frequency range was 1000–3400 cm⁻¹ with a resolution of 2 cm⁻¹.

For electrochemical tests, the active materials were coated with a doctor-blade on 10-μm-thick aluminium current collectors using a mixture of carbon-black (MMM SuperP), graphite (Timrex SFG10) and PVDF (Solvay) dissolved in NMP (Merck) in the mass ratio 80:3:10:7. The coatings were quickly dried under vacuum at 140 °C for ~10 min followed by drying under vacuum at 80 °C overnight. The resulting coatings were rolled using a hand roller to densify the coatings and improve the electronic contacts. The final products had a porosity of 40–50% and a smooth, shiny surface and were dried at least for 24 h at 60 °C under vacuum.

Samples of Ø14–16 mm were cut from the coatings for the electrochemical tests. All electrochemical tests were done in CR2320 type coin-cells (Hohsen). To prevent corrosion of the coin-cell cans (SUS304) at high potentials, the bottom of the cans was covered with aluminium foil. The cells were assembled in the filling glove box (H₂O<5 ppm). Since the current collectors were not welded to the can, the coin-cells had a porosity of 40–50% and a smooth, shiny surface and were rolled using a hand roller to densify the coatings.

The electrolyte used was 1 m LiPF₆ EC/EMC/DMC with a 1:2:2 volume ratio (Mitsubishi Chemical). The PE Solupor® separators were obtained from DSM Solutech and were tested previously for their performance [22]. The coin-cells were sealed in a He-filled glove box (H₂O<5 ppm). Since the current collectors were not welded to the can, the coin-cells were kept under pressure during the tests with a Hoffman clamp to ensure good electrical contact.

The electrochemical tests were done with an Autolab (Ecochemie, The Netherlands) and a Maccor S4000 tester using separate leads for current and voltage to prevent IR drops. The cells were thermostated at 25.0±0.1 °C in a climate chamber (Vötsch VT4004).

3. Results and discussion

3.1. Chemical and structure analysis

The synthesis of the LiMgₓNi₀.₅₋ₓMn₁.₅O₄ samples yielded black, fine powders. The SEM image in Fig. 1 reveals the highly crystalline particles, which were often shaped like micron-sized octahedra.

The ‘overall’ composition of the samples derived from ICP-OES measurements (see Table 1) is close to the nominal composition for the Mg-doped materials but shows a shortage in Mn for the LiNi₀.₅Mn₁.₅O₄ material. This can be explained very well with the formation of a second phase according to:

\[ Li_{0.98}Ni_{0.50}Mn_{1.45}O_4 \leftrightarrow zLiNi_{0.50}Mn_{1.50}O_4 + \beta Li_1Ni_{1-x}O + \gamma O_2 \]  (1)

The assumption that has been made here is that the oxygen host structure of the materials was not defective. This leads to the fractions \( x = 0.967 \), \( \beta = 0.030 \) and \( \gamma = 0.052 \) with composition Li₁₄₄Ni₉₆₆O in the \( \delta = 0.00 \) sample, which is qualitatively supported by the XRD characterization below.

The XRD pattern for LiNi₀.₅Mn₁.₅O₄ in Fig. 2 is typical for all three synthesized LiMgₓNi₀.₅₋ₓMn₁.₅O₄ materials. The intensity of the patterns is normalized to the highest reflection. The XRD pattern suggests that the materials adopt the spinel structure, as was reported by several authors [10] and has been identified as LiₑNi₁₋ₓO with 0<x<0.33 [11]. The LiNi₀.₅Mn₁.₅O₄ and LiMg₀.₀₅Ni₀.₄₅Mn₁.₅O₄ materials were not phase pure and contained traces of a NiO phase, as seen in the inset in Fig. 2. The amount of this impurity phase diminishes with increasing Mg content and no NiO-like phase was visible in the LiMgₓNi₀.₅₋ₓMn₁.₅O₄, as shown in Fig. 4. The appearance of a NiO impurity in LiNi₀.₅Mn₁.₅O₄ has been reported by several authors [10] and has been identified as Li¹Ni₁₋ₓO with 0<x<0.33 [11]. The LiMgₓNi₀.₅₋ₓMn₁.₅O₄ samples yielded black, fine powders. The SEM image in Fig. 1 reveals the highly crystalline particles, which were often shaped like micron-sized octahedra.

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by: (1) Li\(^{+}\) ions, which are not observed in the XRD patterns, and (2) ordering on the sublattices in the materials, induced by the very slow cooling of the samples.

In 1998, Kawai et al. [24] published the refinements of XRD patterns of Li\(_2\)MeM\(_3\)O\(_8\) spinel phases with Me\(^{2+}\)=Co, Mg, Ni, Zn and M\(^{4+}\)=Ge, Ti. All of

![Fig. 1. An SEM image of LiNi\(_{0.50}\)Mn\(_{1.5}\)O\(_4\). The bar shows that the particle size is \(\sim 1\ \mu\text{m}\). Small single crystals can be seen in the shape of an octahedra.](image1)

![Fig. 2. The ND and XRD patterns for LiNi\(_{0.50}\)Mn\(_{1.5}\)O\(_4\) (crosses) and the fit according to space group Fd3m (solid line). The ND data could not be fitted with Fd3m. The inset zooms in on the Li\(_{x}\)Ni\(_{1-x}\)O impurity.](image2)
them were refined with the space group $P4_{3}32$, which describes an octahedrally ordered spinel structure. We assumed similar atom positions as were published for $\text{LiNi}_{0.5}\text{Ge}_{1.5}\text{O}_{4}$ (a normal spinel, $\text{Ni}^{2+}$ and $\text{Ge}^{4+}$ on octahedra) and refined the $\text{LiMg}_{\delta}\text{Ni}_{0.5-\delta}\text{Mn}_{1.5}\text{O}_{4}$ materials according to $P4_{3}32$ with: $\text{Li}^{+}$ on 8c; $\text{Mg}^{2+}$ and $\text{Ni}^{2+}$ on 4b; $\text{Mn}^{4+}$ on 12d; $\text{O}^{2-}$ on 24e and 8c. The $\text{NiO}$ phase was not included in the refinement process. The details were published earlier [25], but a summary is given in Table 2.

It is clear from Figs. 3 and 4 that the XRD and the ND patterns for $\text{LiMg}_{\delta}\text{Ni}_{0.5-\delta}\text{Mn}_{1.5}\text{O}_{4}$ could be refined quite well. The refinement [25] showed that $\text{Ni}$ (4b) and $\text{Mn}$ (12d) are slightly distributed over the 4b and 12d sites. The $a$ parameter increases with $\delta$ in $\text{LiMg}_{\delta}\text{Ni}_{0.5-\delta}\text{Mn}_{1.5}\text{O}_{4}$, as seen in the inset in Fig. 3. This was expected based on the lattice parameters for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4}$ (8.176 Å) [8,11] and $\text{LiMg}_{0.5}\text{Mn}_{1.5}\text{O}_{4}$ (8.18 Å) [17], respectively. The expansion is small but so is the difference in ionic radius of $\text{Ni}^{2+}$ (0.70 Å) and $\text{Mg}^{2+}$ (0.72 Å).

3.2. FT-IR analysis

The FT-IR absorbance curves of the samples are shown in Fig. 5, together with a curve for $\text{LiMn}_{2}\text{O}_{4}$. The minimum in the absorbance, around 780 cm$^{-1}$, has been set to zero for all samples and the curves have been shifted for clarity. For a good comparison, an $\text{LiMn}_{2}\text{O}_{4}$ sample was selected with a similar particle size ($\sim$ 2 μm) as that of the samples. The curve for $\text{LiMn}_{2}\text{O}_{4}$ is characterized by two strong absorbance peaks at 612 and 495 cm$^{-1}$, consistent with literature [26–28].

The curves for the $\text{LiMg}_{\delta}\text{Ni}_{0.5-\delta}\text{Mn}_{1.5}\text{O}_{4}$ materials, however, show many more peaks in the range 650–400 cm$^{-1}$ than $\text{LiMn}_{2}\text{O}_{4}$. In Fig. 5, three peaks at 725, 495 and 370 cm$^{-1}$ have been indicated for their appearance in all samples. An explanation why more peaks appear in the spectra of the $\text{LiMg}_{\delta}\text{Ni}_{0.5-\delta}\text{Mn}_{1.5}\text{O}_{4}$ materials can again be found in the ordering of the $\text{Ni}$ and $\text{Mn}$ ions in the octahedral sites. It has been pointed out by several authors that ordering of the ions in the tetrahedral [29] or octahedral

---

**Table 2**

<table>
<thead>
<tr>
<th>$\delta$</th>
<th>$a$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$R_p$</th>
<th>$R_{wp}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>8.1685</td>
<td>545.04</td>
<td>4.45</td>
<td>6.1</td>
<td>8.1</td>
<td>2.11</td>
</tr>
<tr>
<td>0.05</td>
<td>8.1703</td>
<td>545.40</td>
<td>4.41</td>
<td>5.9</td>
<td>7.9</td>
<td>2.02</td>
</tr>
<tr>
<td>0.10</td>
<td>8.1733</td>
<td>546.00</td>
<td>4.36</td>
<td>7.4</td>
<td>9.5</td>
<td>1.88</td>
</tr>
</tbody>
</table>

$R_p$ and $R_{wp}$ are in percent (%).

---

**Fig. 3.** The ND and XRD patterns for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4}$ (crosses) and the very good fit according to space group $P4_{3}32$ (solid line). The inset shows the lattice constant as a function of $\delta$, illustrating Vegard’s law.
[30–32] sites lowers the symmetry of the crystal, resulting in the appearance of more vibrational bands. The differences among the LiMg$_{0.10}$Ni$_{0.40}$Mn$_{1.5}$O$_4$ materials is hard to see, but there is a tendency that the peaks are less pronounced with increasing $\delta$. This is most clear for the peaks at 725, 649 and 370 cm$^{-1}$. The reason could be the Mg ions interfering with the coupling of the MnO$_6$ and NiO$_6$ octahedra. A similar smoothing effect, even stronger, was observed for samples that were cooled faster (1 °C/min, not

![Fig. 4. The ND and XRD patterns for LiMg$_{0.10}$Ni$_{0.40}$Mn$_{1.5}$O$_4$ (crosses) and the fit with space group $P4_332$ (solid line). The inset shows the spinel host (NiO$_6$ dark and MnO$_6$ light) with Li ions in tunnels (spheres).](image)

![Fig. 5. The absorbance of LiMn$_2$O$_4$ and LiMg$_{0.50}$Ni$_{0.50}$Mn$_{1.5}$O$_4$ measured in KBr. The absorbance at ~780 cm$^{-1}$ has been set to zero. The curves have been shifted for clarity.](image)
shown). Similar changes in spectra for ordered/disordered Mn$_3$O$_4$ [33], CuMn$_2$O$_4$ [34] and NiMn$_2$O$_4$ [35] were observed, as well as for delithiated LiMn$_2$O$_4$ [27].

Several attempts have been published to assign specific bands or peaks to certain ionic vibrations, e.g. LiO$_4$ tetrahedra and MeO$_6$ octahedra. In the older literature [36–38], where it was shown that a normal AB$_2$O$_4$ spinel theoretically should have four IR modes, some assignments were proposed based on extensive studies of spinels and isotopic exchanges (7Li–6Li) [38], e.g. the LiO$_4$ bending and stretching modes were assigned to the range 400–500 cm$^{-1}$. More recently, it was shown that the tetrahedral and octahedral units are too strongly coupled to assign the bands to specific ionic vibrations [27].

It is without question, however, that in the spectra of mixed spinels or spinels with different cations on B sites like LiMg$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$, more bands should appear.

3.3. Electrochemical analysis

Because the LiMg$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ compounds were intended as cathode materials for rechargeable Li-ion batteries, discharge curves vs. Li/Li$^+$ at a C/10 rate are shown in Fig. 6. The redox mechanism accompanying the (de)intercalation process has been reported as [39,40]:

$$\text{Li}_1^+[[\text{Ni}_{0.5}^{2+}\text{Mn}_{1.5}^{4+}]_4 \rightarrow \text{Li}_{1-2x}^+[[\text{Ni}_{0.5-x}^{2+}\text{Ni}_x^{4+}\text{Mn}_{1.5}^{4+}]_4$$

$$+ 2x\text{Li}^+ + 2xe^-$$

(2)

It is apparent that not only does the discharge capacity decrease with $\delta$ (as expected, because the amount of Ni$^{2+}$ decreases), but the potential vs. Li/Li$^+$ also increases. The profiles of the curves transform from flat for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ to sloping for LiMg$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$. For all materials, however, a small potential step at $x \approx 0.50$ in Li$_{1-x}$Mg$_{0.5}$Ni$_{0.5}$Mn$_{1.5}$O$_4$ remains visible, as seen also in Fig. 7. This is illustrated as well in the cyclic voltammograms (CVs) in Fig. 7 by the small separation of the two high-voltage peaks, and is analogous to the ordering phenomena that has been described for LiMn$_2$O$_4$ [40]. The CVs also reveal faster insertion kinetics for the Mg-doped material.

The inset in Fig. 6 shows the transition of the charge to discharge for the three materials. There is not much difference between the $\delta=0.05$ and $\delta=0.10$ materials, but the parent material LiNi$_{0.5}$...
Mn$_{1.5}$O$_4$ clearly shows a higher polarization than the Mg-substituted materials. It was found that the polarization over the total (de)intercalation range is lower for the Mg-doped materials (not shown).

The discharge capacities of the samples are plotted in Fig. 8, together with the theoretical values. The gravimetric and volumetric energies are indicated next to the data points. This makes it clear that, even for a
\( \delta = 0.10 \) where the capacity is similar to the practical capacity of \( \text{LiMn}_2\text{O}_4 \), the energy density is still higher due to the higher voltage and density of the material.

A rate test was done for the \( \text{LiMg}_\delta\text{Ni}_{0.5-\delta}\text{Mn}_{1.5}\text{O}_4 \) materials in lithium cells. Normally, this results in lower rate capabilities than when a suitable, fast counter electrode is used like \( \text{Li}_4\text{Ti}_5\text{O}_{12} \). The results are presented as a bar chart in Fig. 9. It is clear from the C/5 reference level in the intermediate cycles (100\% in Fig. 9, between the high-rate discharges)

\[ \text{Fig. 9. The discharge capacity as a function of the discharge rate as percentage of the C/5 capacity in cycle 3 (=100\% for each sample).} \]

\[ \text{Fig. 10. The cyclability of LiMg}_\delta\text{Ni}_{0.5-\delta}\text{Mn}_{1.5}\text{O}_4 \text{ vs. Li/Li}^+ \text{ at a C/2 rate (after the rate test in Fig. 9). The inset, however, shows two fresh cells, for } \delta = 0.00 \text{ and } 0.10, \text{ that have been cycled only at a C/2 rate.} \]
that all materials lose some capacity, however, in the Mg-doped samples less than in the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ material. The rate capability is much improved in the LiMg$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$ material, showing more than 50% of the C/5 capacity at a 2C rate.

The cyclability curves in Fig. 10 reveal that Mg doping not only changes the voltage profile of the materials but also stabilizes the host structure against repeated (de)intercalation of the Li$^+$ ions, demonstrating the reversibility of the system. The cycling was performed at a 0.5C rate. Prior to this cycling test, the same cells had been tested in the rate test. During the rate test, the cells with the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiMg$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ materials had lost a considerable amount of their initial capacity. The cell with the LiMg$_{0.05}$Ni$_{0.45}$Mn$_{1.5}$O$_4$ cathode showed a good capacity retention. However, in a new experiment with fresh cells, LiMg$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ also proved to be much more stable than LiNi$_{0.5}$Mn$_{1.5}$O$_4$, as seen in the inset in Fig. 10.

It was shown elsewhere [4] that these new high-voltage cathode materials can be combined with a 1.5-V LiCrTiO$_4$ anode to a rechargeable Li-ion battery with a voltage plateau around 3.25 V, as shown in the inset in Fig. 11. This battery, with two spinel-based electrodes, was tested for its power capability according to PNGV tests [41].

The cyclability curve of this battery is shown in Fig. 11 where the rate was 1C. The battery showed a good stability over prolonged cycling, apart from some initial loss due to improperly balanced electrodes and the history of the PNGV pulse testing, prior to the cycle test.

4. Conclusions

Doping with Mg in LiNi$_{0.5}$Mn$_{1.5}$O$_4$ resulted in LiMg$_{0.1}$Ni$_{0.4}$Mn$_{1.5}$O$_4$ with an ordered spinel-type crystal structure that could be refined with space group $P4_3m2$. The reversible intercalation of lithium proceeds at voltages of 4.70–4.75 V vs. Li/Li$^+$. The experimentally obtained discharge capacities are close to the theoretical values, i.e. over 120 mA h/g. Due to the high voltage and gravimetric densities, increased energy densities could be realized compared to LiMn$_2$O$_4$. If the materials are combined towards low-voltage anodes like Li$_4$Ti$_5$O$_12$, the extra 0.5 V compared to, e.g. LiMn$_2$O$_4$, partly compensates the loss in voltage due to the anode. Based on the improve-

![Figure 11](image-url)
ments in cyclability, rate capability and voltage, the \( \text{LiMg}_{x}\text{Ni}_{0.5-x}\text{Mn}_{1.5}\text{O}_{4} \) materials are most interesting as high-voltage cathodes for Li-ion batteries.

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