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# Novel $\text{LiNi}_{1-x}\text{Ti}_{x/2}\text{Mg}_{x/2}\text{O}_2$ Compounds as Cathode Materials for Safer Lithium-Ion Batteries

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A new class of  $\text{LiNi}_{1,x}\text{Ti}_{x/2}\text{Mg}_{x/2}\text{O}_2$  materials has been synthesized. The compound  $\text{LiNi}_{0.75}\text{Ti}_{0.125}\text{Mg}_{0.125}\text{O}_2$  showed a reversible capacity of 190 mAh/g and stable cycling was demonstrated. Differential scanning calorimetry studies showed much improved thermal stability of these materials in their totally charged states in contact with electrolyte. The exothermic peak at 220°C in a charged electrode containing  $\text{LiNi}_{0.70}\text{Ti}_{0.15}\text{Mg}_{0.15}\text{O}_2$  was drastically reduced as *x* increases in  $\text{LiNi}_{1,x}\text{Ti}_{x/2}\text{Mg}_{x/2}\text{O}_2$ . No exotherm was observed below 400°C for  $\text{LiNi}_{0.70}\text{Ti}_{0.15}\text{Mg}_{0.15}\text{O}_2$  in its totally charged state. We believe that the use of these materials will improve the overall safety of Lion batteries.

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Lithium-ion rechargeable batteries not only have important applications in portable electronics but also are potential long-term candidates for powering emission-free vehicles.<sup>1</sup> LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, and  $LiMn_2O_4$  are the most attractive cathode (positive electrode) materials used in lithium-ion batteries. At present, most commercial lithium-ion batteries use LiCoO<sub>2</sub> as the cathode material, whereas LiMn<sub>2</sub>O<sub>4</sub> has just begun to be used. However, cobalt is a relatively rare and expensive transition metal, which makes the positive electrode expensive. LiNiO<sub>2</sub>, like LiCoO<sub>2</sub>, has a theoretical capacity of 275 mAh/g. However, the full capacity cannot be achieved from these materials in practice. For pure LiNiO2 and LiCoO2, only about 140-150 mAh/g can be utilized. Further removal of lithium not only degrades the cycleability but also causes exothermic decomposition of the oxide releasing oxygen at elevated temperatures, which poses safety hazards.<sup>2,3</sup> LiNiO<sub>2</sub>, in particular, raises safety concerns because it exhibits a sharper exothermic reaction at a lower temperature than LiCoO<sub>2</sub>.<sup>2,3</sup> On the other hand, LiMn<sub>2</sub>O<sub>4</sub> is believed to be safer on overcharge. For instance, it has no removable lithium to plate on the anode beyond the practical end of charge. However its capacity is low, its theoretical capacity is only 148 mAh/g, and typically no more than about 115-120 mAh/g can be obtained with good cycleability.

Substituting a portion of Ni in LiNiO<sub>2</sub> with other cations has been pursued to improve its safety characteristics. For example, Ohzuku et al. showed that LiNi<sub>0.75</sub>Al<sub>0.25</sub>O<sub>2</sub> was more thermally stable in the fully charged state than LiNiO<sub>2</sub>.<sup>4</sup> Moreover, LiNi<sub>0.75</sub>Al<sub>0.25</sub>O<sub>2</sub> would be expected to be safer on overcharge because the end member  $Li_{0.25}Ni_{0.75}Al_{0.25}O_2$  is an insulator, which prevents any additional lithium from being removed within practical voltages when further charging is attempted.<sup>4</sup> However, the capacity fade of this material is relatively large at present.<sup>5</sup>

We have synthesized novel LiNi<sub>1-x</sub>Ti<sub>x/2</sub>Mg<sub>x/2</sub>O<sub>2</sub> compounds with a hexagonal layered structure. The use of these materials as cathodes has the potential to improve the safety characteristics of lithium-ion batteries. A larger capacity compared to current cathode materials in commercial lithium-ion batteries can also be achieved with good cycleability.

## Synthesis and Structural Analysis

Samples were prepared by mixing appropriate amounts of LiOH•H<sub>2</sub>O, NiO, TiO<sub>2</sub> anatase, and Mg(OH)<sub>2</sub> with 5% excess Li, and firing at 800°C for 20 h in an O<sub>2</sub> atmosphere. The cooling was controlled at 1°C/min to 500°C followed by natural cooling to room temperature. The use of a Ti-Mg combination is expected to maintain the charge balance in LiNi<sub>1-x</sub>Ti<sub>x/2</sub>Mg<sub>x/2</sub>O<sub>2</sub> and to achieve the same end-of-charge electrochemical properties as with Al, because Ti<sup>4+</sup> and Mg<sup>2+</sup>, just like Al<sup>3+</sup>, have no remaining valence electrons.



**Figure 1.** X-ray diffraction patterns of four samples with compositions as indicated.

A Rigaku-2500 X-ray diffractometer equipped with a rotating Cu anode and a diffracted beam monochromator (graphite 002) was used for X-ray diffraction (XRD) studies of the samples. The measurement range was 15-120° and the step size was 0.02°. We were able to record a large number of counts owing to the powerful rotating anode used. Rietveld refinement was performed with these high-precision and high-intensity XRD spectra to obtain the lattice parameters. Hill and Howard's version of the refinement program<sup>6</sup> was used. Figure 1 shows the XRD patterns of a series of samples with different *x* in LiNi<sub>1-x</sub>Ti<sub>x/2</sub>Mg<sub>x/2</sub>O<sub>2</sub>. Only the range of 15-80° is shown so that the interesting features in this region can be seen more clearly. As shown, pure single-phase materials can be made with a wide range of *x*, and they all still maintain the same rhombohedral structure as the parent compound LiNiO<sub>2</sub> (space group  $R\bar{3}m$ ).

In such structures, the oxygen sublattice can be considered as a close-packed face centered cubic (FCC) lattice with a distortion in the *c* direction (or in the 111 direction if a cubic index system is used). Because of the slight distortion in the *c* direction, the values of the lattice-constant ratios c/a of LiNiO<sub>2</sub> and LiCoO<sub>2</sub> are 4.935 and 4.99, respectively, and there are distinct splits of the 006-012 and 018-110 pairs in the XRD pattern with those of LiCoO<sub>2</sub> more pro-

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nounced. When this distortion in the *c* direction is absent (or the structure is totally cubic), the ratio of the lattice constants c/a is  $\sqrt{24}$  or 4.899, and the 006-012 and 018-110 pairs in the diffraction pattern merge into single peaks.

The lattice constants *a* and *c*, as well as the *c/a* ratio are shown in Fig. 2 as a function of *x* in LiNi<sub>1-x</sub>Ti<sub>x/2</sub>Mg<sub>x/2</sub>O<sub>2</sub>. As shown, both *a* and *c* increase steadily as *x* increases. This means that the lattice expands with the introduction of Ti and Mg codopants. Interestingly, the *c/a* ratio increases with *x* below x = 0.20, reaches a plateau in the region of  $0.20 \le x \le 0.25$ , and decreases abruptly when x = 0.30. This suggests increased layered characteristics, or that the lattice expands preferentially in the *c*-direction, in the region of  $0.00 \le x \le 0.25$ . As the *x* value further increases, the structure reverts toward a more cubic one. This is accompanied by an increased degree of cation mixing as evidenced by the decreased height of the 003 peak of LiNi<sub>0.70</sub>Ti<sub>0.15</sub>Mg<sub>0.15</sub>O<sub>2</sub>.

#### **Electrochemical Studies**

Electrochemical tests were conducted in 2325 coin cells with Li foil as the anode. The electrolyte used was 1 M LiPF<sub>6</sub> in a 50/50 vol % mixture of ethylene carbonate and dimethyl carbonate (EC/DMC). Figure 3 shows the voltage curve of a sample with x = 0.25 cycled at 0.075 mA. The active mass of the cell was 9.1 mg, so the current was close to an equivalent of C/17 for LiNiO<sub>2</sub> (assuming the C rate for LiNiO<sub>2</sub> is 140 mA/g). After the first conditioning cycle, the subsequent cycles exhibit very good reversibility. We do not know the nature of the difference in the voltage profile between the first charge and the subsequent cycles at this point. We suspect, however, there is a contribution from the electrolyte decomposition at high voltages to



Figure 4. The derivative -dy/dV of the second cycle, where y denotes the amount of intercalated lithium in  $\text{Li}_y\text{Ni}_{1-x}\text{Ti}_{x/2}\text{Mg}_{x/2}\text{O}_2$ . The phase transitions in LiNiO<sub>2</sub> are labeled after those in Ref. 7.

the first charge. As shown in Fig. 3, in subsequent cycles, the voltage rises very rapidly at the end of charge, and little additional capacity is realized above approximately 4.4 V. The reversible capacity between 3.0 and 4.4 V is about 190 mAh/g.

Figure 4 shows the derivative -dy/dV of the second cycle for a series of samples with different x, where y denotes the amount of intercalated lithium as in  $Li_v Ni_{1-x}Ti_{x/2}Mg_{x/2}O_2$ . As shown, pure LiNiO<sub>2</sub> characteristically exhibits many sharp peaks, which have been thoroughly studied with in situ XRD on active electrochemical cells by Li et al.<sup>7</sup> It has been found that many phase transitions occur during the course of the lithium intercalation/deintercalation in LiNiO<sub>2</sub>. The sharp peaks are where first-order phase transitions (twophase coexistence) occur, and the broad ones are one-phase continuous phase transitions. As shown in Fig. 4, the shape of the derivative curve changes dramatically even when as little as 10% of Ni is replaced by Ti and Mg (x = 0.10). The sharp peaks diminish completely. This is very suggestive that the first-order phase transitions are no longer present in the system, or at least that the first-order phase transitions are very much suppressed. By the time x reaches 0.30, the derivative curve no longer has any resemblance to that of LiNiO<sub>2</sub>, which implies a likely continuous phase transition for the



Figure 5. Constantcurrent cycling of  $LiN_{0.75}Ti_{0.125}Mg_{0.125}$ O<sub>2</sub> at C/3 rate. The cell was first cycled between 3.0 and 5.0 V, and then switched to 3.0-4.5 V cycling.

entire region. These interesting features warrant future in situ XRD studies. Nevertheless the change in the derivative curves in Fig. 4 demonstrates that Ti and Mg are indeed incorporated into the structure, and the incorporation causes significant changes in the electrochemical potential of Li in the material.

Figure 5 shows cycle-life results for a sample with x = 0.25 at the C/3 rate. The cell was first cycled between 3.0 and 5.0 V. After 11 cycles it was switched to cycle between 3.0 and 4.5 V. As shown in Fig. 5, the material demonstrates excellent cycle stability at large capacities.

#### **Differential Scanning Calorimetry Studies**

Differential scanning calorimetry (DSC) tests were performed in order to study the thermal stability of the  $LiNi_{1-x}Ti_{x/2}Mg_{x/2}O_2$  materials, especially in the charged (delithiated) state. As shown in Fig. 3, no more Li can be removed electrochemically from these materials within practical voltages above 4.5 V. Therefore we considered the materials fully charged at 4.5 V. Test coin cells were first charged to 5.0 V and discharged to 3.0 V at 0.6 mA, then charged to 4.5 V at 0.2 mA and potentiostated at 4.5 V for 40 h to ensure equilibrium conditions. The cells typically contained about 10-20 mg of active material. At the end of the 40 h potentiostatic charge, the current typically dropped to below 5 µA. The charged coin cells were then opened in an argon-filled glove box and the cathodes recovered. The excess electrolyte on the recovered cathode was removed with a piece of Kimwipes cloth. About 0.1-1.0 mg of cathode materials was then taken and hermetically sealed into DSC cans made of aluminum. All of the samples contained consistently 10-15% electrolyte by weight. A ramp rate of 10°C/min was used for all of the DSC experiments. Figure 6a shows the comparison of the DSC results of charged LiNiO<sub>2</sub> and LiNi<sub>1-x</sub>Ti<sub>x/2</sub>Mg<sub>x/2</sub>O<sub>2</sub> with different x values. The heat flow is calculated as per the total sample weight containing the electrolyte. The electrode contains 85% active material, 5% polyvinylidene fluoride (PVDF) binder, and 10% carbon black (Super S, Chemetals).

The DSC curve of LiNiO<sub>2</sub> charged to 4.5 V has a sharp exothermic peak at about 220°C. This is consistent with the earlier report by Zhang et al.<sup>3</sup> This sharp exothermic peak is obviously of great safety concern for Li-ion batteries using LiNiO<sub>2</sub> as the cathode.<sup>2,3</sup> As shown in Fig. 6a, the exothermic peak of the charged electrode decreases rapidly as *x* in LiNi<sub>1-x</sub>Ti<sub>x/2</sub>Mg<sub>x/2</sub>O<sub>2</sub> increases. By *x* = 0.30, the exotherm has completely disappeared. This shows the much improved thermal stability of LiNi<sub>1-x</sub>Ti<sub>x/2</sub>Mg<sub>x/2</sub> materials in the totally charged state and in contact with the electrolyte.

As a comparison, the DSC curve of  $\text{LiNi}_{0.75}\text{Ti}_{0.125}\text{Mg}_{0.125}\text{O}_2$  is shown in Fig. 6b together with the DSC curves of  $\text{LiNiO}_2$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ , and  $\text{LiCoO}_2$ . All of the materials shown in Fig. 6b had been charged to 4.5 V for 40 h. This illustrates much more benign thermal behavior of  $\text{LiNi}_{0.75}\text{Ti}_{0.125}\text{Mg}_{0.125}\text{O}_2$  compared to the other materials in the overcharged state.

#### Conclusions

The new LiNi<sub>1-x</sub>Ti<sub>x/2</sub>Mg<sub>x/2</sub>O<sub>2</sub> materials could improve the safety of Li-ion batteries in two ways: first, they themselves are thermally stable in the totally charged state in contact with the electrolyte; sec-



**Figure 6.** DSC scans of charged electrodes containing samples with compositions as indicated. Positive is the exothermic direction. The axes of the inset have the same units as the main axes. The electrodes were potentiostatly charged to 4.5 V before the DSC experiments.

ond, these materials exhibit a rapid rise in voltage at end of charge and cannot be further delithiated even at voltages as high as 5 V. Thus, should a cell be inadvertently overcharged, the cell voltage will rise sharply and no additional lithium can be removed from the cathode material, thereby preventing lithium from plating on the anode in a properly balanced lithium-ion cell. This property is very much like that of LiMn<sub>2</sub>O<sub>4</sub> spinel.

The safety of Li-ion batteries involves many components and factors in the battery, such as anode-electrolyte interaction in the lithiated state. Nevertheless we feel that the thermal stability of the new  $\text{LiNi}_{1-x}\text{Ti}_{x/2}\text{Mg}_{x/2}O_2$  cathode materials, especially in the totally charged state, will improve the overall safety. As shown in Fig. 5, the new  $\text{LiNi}_{0.75}\text{Ti}_{0.125}\text{Mg}_{0.125}O_2$  material can be cycled at large capacities with good stability, which suggests that it is a good candidate for Li-ion battery applications.

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### References

- 1. See, for example, *Lithium Batteries, New Materials, Developments and Perspectives,* G. Pistoia, Editor, Elsevier, New York (1994).
- J. R. Dahn, E. W. Fuller, M. Obrovac, and U. von Sacken, *Solid State Ionics*, 69, 265 (1994).
- 3. Z. Zhang, D. Fouchard, and J. R. Rea, J. Power Sources, 70, 16 (1998).
- 4. T. Ohzuku, A. Ueda, and M. Kouguchi, J. Electrochem. Soc., 142, 4033 (1995).
- T. Ohzuku, T. Yanagawa, M. Kouguchi, and A. Ueda, J. Power Sources, 68, 131 (1997).
- 6. R. J. Hill and C. J. Howard, J. Appl. Crystallogr., 18, 173 (1985).
- 7. W. Li, J. N. Reimers, and J. R. Dahn, Solid State Ionics, 67, 123 (1993).