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Synthesis of ternary Li–Mn–O phase at a temperature of 260 °C and electrochemical lithium insertion into the oxide

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Abstract

A lithium–manganese oxide, Li_xMnO_2 ($x = 0.3$–0.6), has been synthesized by heating a mixture (Li/Mn ratio = 0.3–0.8) of electrolytic manganese dioxide (EMD) and $LiNO_3$ in air at moderate temperature, 260 °C. The formation of the Li–Mn–O phase was confirmed by X-ray diffraction, atomic absorption and electrochemical measurements. Electrochemical properties of the Li–Mn–O were examined in $LiClO_4$-propylene carbonate electrolyte solution. About 0.3 Li in Li_xMnO_2 ($x = 0.3$–0.6) was removed on initial charging, resulting in characteristic two discharge plateaus around 3.5 V and 2.8 V vs Li/Li^+. The Li_xMnO_2 synthesized by heating at Li/Mn ratio = 0.5 demonstrated higher discharge capacity, about 250 mAh (g of oxide)$^{-1}$ initially, and better cyclability as a positive electrode for lithium secondary battery use as compared to EMD.

1. Introduction

Lithium-ion cells that operate between 3 and 4 V are gaining increasing popularity for powering electronic equipment such as cellular phones, camcorders and laptop computers. As candidates for cathode materials of lithium-ion batteries, lithium manganese oxides are attractive because of the well-known advantages compared to lithium cobalt oxide. Especially, from the standpoint of constructing large lithium-ion batteries for electric vehicle and load-leveling of electric power supply, low-cost cathode materials, such as manganese oxides, are of great importance.

It is well known that lithiated manganese oxide products formed by the reaction of LiOH or $LiNO_3$ with CMD or EMD at moderate temperature around 300–400 °C offer superior properties in rechargeable lithium cells compared to conventionally heat-treated CMD and EMD electrodes [1–15]. The lithium-stabilized materials were generally known as CDMO (composite dimensional manganese oxide) materials, that is, the formation of CDMO consisting of γ-MnO_2 and Li_2MnO_3 from heating MnO_2 and LiOH mixtures has been reported by Nohma et al. [1, 2]. An optimum performance is obtained when EMD is reacted with LiOH in a 7:3 molar ratio at 370 °C. Thackeray and co-workers reported that ramsdellite–MnO_2 structure is stabilized by reaction with LiOH or $LiNO_3$ at 300–400 °C [3, 4]. Yoshio et al. [5–7] examined the product from heating MnO_2 and $LiNO_3$ mixtures in the range 320–400 °C using the lithium nitrate method. Moreover, Li and Pistoia reported [8, 9] that lithiated manganese oxides formed from HNO_3-treated MnO_2 (CMD) and $LiNO_3$ (7:3 molar ratio) at 370 °C shows an especially satisfactory cycling behaviour. The crystal system and electrochemical characteristics of γ-MnO_2 formed by heat-treating EMD at low temperature (200–300 °C) and the sample prepared from heating EMD and LiOH (Li/Mn = 0.25) at 380 °C were analyzed by Ohzuku et al. [10–12]. In particular, the structural and electrochemical behaviour of 3 V Li_xMnO_2 cathodes for rechargeable Li batteries were recently reported by Bar-Ilan University and Tadiran Battery Limited group [13–15]. They showed that the optimum Li/Mn ratio for a heat-treated mixture of $LiNO_3$ and γ-MnO_2 at 370 °C for 20 h with a minimum of impurities, such as γ-β-MnO_2 or spinel, was shown to be equal to 0.33. The four intercalation process stages and the mechanism of the capacity fading were also discussed [15]. For the low temperature synthesis of Li–Mn–O phases, consequently, the kinds of starting lithium and manganese salts and the Li/Mn ratio are the key factors. Further, there are no reports of lower temperature synthesis of Li–Mn–O than 300 °C, which is expected to be a new synthesis route for a pure Li–Mn–O phase without impurity phases.

Previously, we reported the preparation of new quaternary Li–Mn–V–O spinels and the lithium insertion characteristics into the crystal lattice [16–18]. In this paper, we report the preparation of a ternary Li–Mn–O phase by heating a mixture of EMD and $LiNO_3$ at a lower temperature of 260 °C (a melting point of $LiNO_3$) and the electrochemical performance of the ternary phase.

2. Experimental details

2.1. *Synthesis of manganese oxide*

The ternary Li–Mn–O was prepared by heating mixtures of EMD (international common sample 17; IC-17) and $LiNO_3$ (Kanto Chemical Co.) in given Li/Mn atomic ratios in air for several days. The heating rate was about 50 °C h^{-1}. After cooling in air, the products obtained were ground in an agate mortar. In most cases, the products were washed with about 20 ml of distilled water per 1 g of the product five times, and then dried at 80 °C.

2.2. *Analysis and characterization*

The manganese compounds were characterized by powder X-ray diffractometry (XRD), thermogravimetry (TG), differential thermal analysis (DTA) and atomic absorption (AA) spectroscopy. The powder XRD measurement was performed on Rigaku RINT system using CuK_α radiation. For AA analysis, the compounds were dissolved in aqueous hydrochloric acid solution and diluted in order to determine the Li and Mn contents. TG measurement was carried out in air from 50 to 900 °C at 10 °C min^{-1}.

Average oxidation degree of Mn within the compound was determined by chemical titration. Such a titration consists in (i) dissolving the compound in hot sulfuric acid, (ii) reducing the Mn ions by adding a known amount of oxalic acid, and (iii) backtitrating the excess oxalate anion by using a potassium permanganate solution of well-defined molarity.

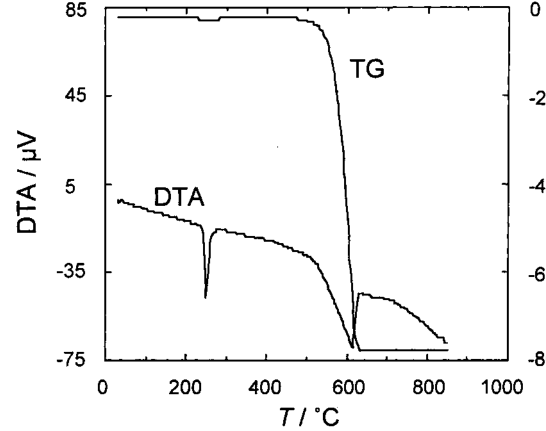
2.3. *Electrochemical measurement*

The preparation of the electrodes and electrolyte, the design of the cell, and electrochemical measurement method have been described previously [16–18]. The mixtures (~40 mg) of the synthesized manganese compounds and graphite as a conducting agent, in a weight ratio of 1:1, were compression molded on an Ni net under about 49 MPa. The pellets thus obtained (diameter 13 mm, thickness: ~0.4 mm) were used as working electrodes after drying under vacuum at 80 °C for one day. Lithium pellets were used for both the reference and counter electrodes. The electrolyte used was 1 mol dm^{-3} $LiClO_4$-propylene carbonate (PC), containing only trace amounts of water (less than 20 ppm). A glass beaker-type cell filled with 15 cm^3 of the electrolyte solution at 25 ± 2 °C was used. Positive electrode charge–discharge tests were carried out between 1.5 and 4.5 V vs Li/Li^+ at a constant current density of 0.2 mA cm^{-2}.

3. Results and discussion

The choice of heat treatment temperature of the starting mixtures is important for preparing a ternary Li–Mn–O compound. Therefore, the thermal properties of $LiNO_3$ and EMD were first investigated by TG and DTA measurements as shown in Figure 1. Pure lithium nitrate was melted at 260 °C as shown by an endothermic peak at 260 °C. Furthermore, its decomposition occurred from 500 °C to 600 °C as seen by the large weight loss in TG and an endothermic peak around 600 °C in DTA. The weight loss corresponds to decomposition to Li_2O, since the TG result agrees well with a weight loss of −78.3% calculated from the weight ratio of Li_2O/2 $LiNO_3$ (Figure 1(a)). Figure 1(b) shows TG and DTA curves of the mixture of EMD and $LiNO_3$ at a Li/Mn atomic ratio of 0.5. In this case, $LiNO_3$ was melted around 260 °C, and EMD powder was impregnated with melted $LiNO_3$ [5–7]. In contrast to pure $LiNO_3$, a gradual decrease in weight was observed from 50 °C, and an apparent weight loss occurred with increase in temperature from 300 to 400 °C. The decomposition of $LiNO_3$ at considerably lower temperature was probably catalysed by EMD. Although more

(a) $LiNO_3$



(b) EMD and $LiNO_3$

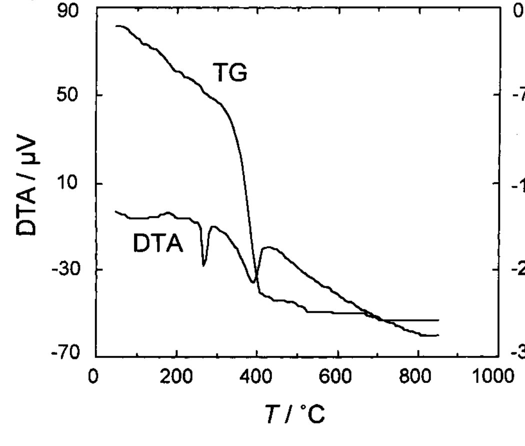


Fig. 1. TG and TDA curves of (a) pure $LiNO_3$ and (b) mixture of EMD and $LiNO_3$ (Li/Mn = 0.5).

investigations are required for further understanding this weight loss, we investigated the electrochemical property of the product at this moderate temperature of 260 °C, compared to spinel $LiMn_2O_4$ produced at higher temperature, 700 °C.

Figure 2 shows the initial charge–discharge curves. By heating at 260 °C followed by heating at 700 °C, we obtained the spinel $LiMn_2O_4$ compounds, as confirmed by XRD measurements. Clearly, in the case of two spinel compounds ((b) and (c) in Figure 2), the typical potential plateaux appear around 4 V and 3 V, and there is almost no dependence on the heating period at 700 °C. In contrast, the product synthesized by heating at 260 °C demonstrated different properties from those of the spinel compounds. Because of too low temperature of 260 °C in viewpoint of synthesizing Li–Mn–O compounds, the reaction was expected to occur slowly in consideration of the TG result (Figure 1(b)). Hence, we chose a relatively long duration, 168 h, for the complete reaction at 260 °C. A new potential plateau appeared at about 3.5 V, which is very similar to literature values [2, 15]. In this case, the synthesis temperature, 260 °C, is lower than those reported previously [2, 15]. Its discharge capacity, 250 mAh (g of oxide)$^{-1}$, is a little higher than the spinels as shown in Figure 2(a). In further studies, we investigated the products prepared from heating the $LiNO_3$/EMD mixture at 260 °C.

The $LiNO_3$ and EMD mixtures at various Li/Mn atomic ratios of starting materials were heat treated at 260 °C for 168 h in air, and the products obtained were characterized by XRD. In the cases of Li/Mn ratios of 1.0, 1.5 and 2.0, many sharp peaks attributable to residual $LiNO_3$ appeared. At the ratio of 0.5, a different pattern was obtained and new peaks were observed in comparison to those of EMD and other products obtained at the higher Li/Mn ratios. After washing the heat treated products with water, the sharp peaks due to residual $LiNO_3$ completely disappeared, as seen in Figure 3. All the products were formed from the same materials at the same temperature; nevertheless, new peaks appeared only for Li/Mn = 0.5 (Figure 3(b)), and the XRD patterns of the other products (Figure 3(c)–(e)) are identical to that of EMD. This tendency is different from that of the Li–Mn–O phase prepared at 370 °C [15]. This phase was produced by heating for more than 48 h at 260 °C, although it was thought previously that no reaction between EMD and lithium salt occurred below about 300 °C [11]. As a result, the formation of this phase at 260 °C is found to be strongly dependent on the starting Li/Mn ratio.

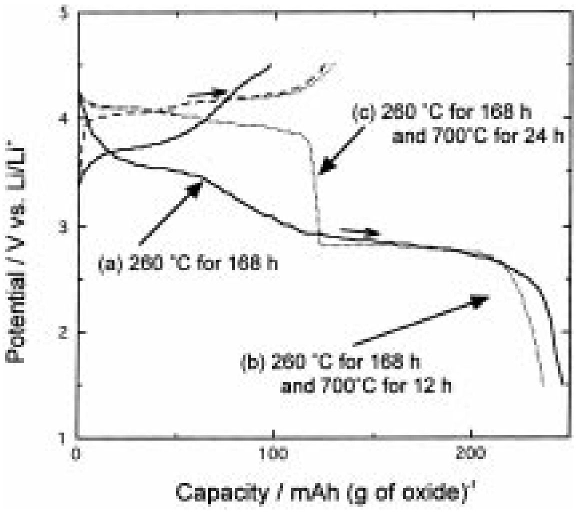


Fig. 2. Initial charge and discharge curves of products formed from heating the mixtures of EMD and $LiNO_3$ (Li/Mn = 0.5): (a) at 260°C for 168 h, (b) at 260°C for 168 h and at 700°C for 12 h and (c) at 260°C for 168 h and at 700°C for 24 h.

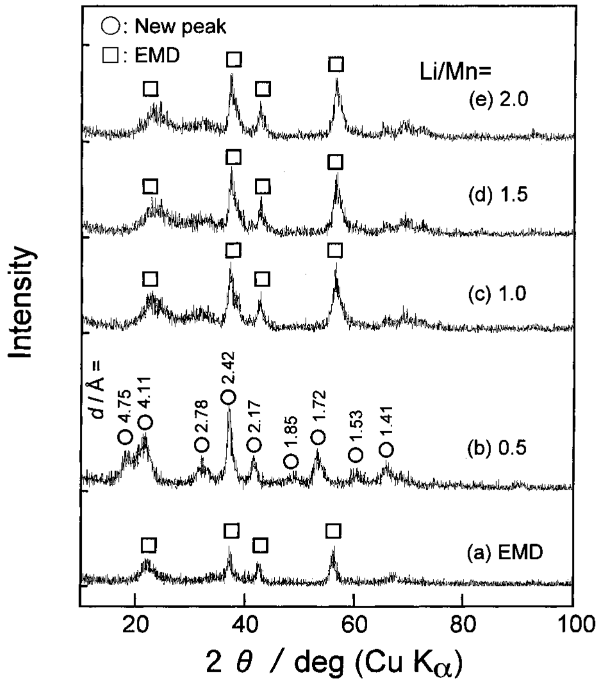


Fig. 3. XRD patterns of (a) EMD (IC-17) and heat treatment products at Li/Mn atomic ratios of (b) 0.5, (c) 1.0, (d) 1.5 and (d) 2.0. All heat treatment products were washed with water. Spacing of lattice planes, *d*, was indicated in the (b).

Moreover, the Li/Mn atomic ratios of the heat treatment products were determined by AA measurements as summarized in Table 1. In the case of the starting ratio of 0.5, a much higher lithium amount was found in the product. From the XRD and chemical analyses, we deduced that different manganese compound, that is, a ternary Li–Mn–O phase (Li_xMnO_2)

Table 1. Li/Mn atomic ratio of products from heating the mixture of EMD and $LiNO_3$ at 260 °C for 168 h

Starting	Heat treatment product
0.5	0.529
0.5	0.436*
1.0	0.052*
1.5	0.039*
2.0	0.034*

* Samples were washed with distilled water after heating

similar to products synthesized from heat-treating manganese oxide and LiOH or $LiNO_3$ (Li/Mn = 0.3–0.4) around 370 °C as reported elsewhere [2, 8, 11, 15, 19], is formed at the specific Li/Mn ratio of 0.5. Particularly, the products at 350–370 °C, contained other phases (e.g., MnO_2, $LiMn_2O_4$ and Li_2MnO_3). The phase ratio was determined by the Li/Mn molar ratio in the initial mixture, and the pure Li_xMnO_2 phase was formed at the limited Li/Mn range of 0.36–0.5 [15] or 0.25–0.33 [19]. We thought that a similar tendency appeared in the case of 260 °C as seen in Table 1 and Figure 3, although there appeared no side products ($LiMn_2O_4$ and Li_2MnO_3) because of the much lower temperature of 260 °C. An appropriate amount of molten $LiNO_3$ impregnating porous surface of EMD particles may be catalytically decomposed. We guessed that an excess molten $LiNO_3$ at a higher ratio of $Li/Mn > 1.0$ prevents the catalytic decomposition on the EMD surface.

Furthermore, the discharge characteristics of these products were examined as shown in Figure 4. As expected from the XRD results in Figure 3, the discharge curves of the products at the higher ratios were similar to that of EMD. By using Li/Mn = 0.5, the products before and after washing with water exhibited higher capacity and the new potential plateau at 3.5 V as mentioned in Figure 2. The electrochemical properties also differ from the other products, such as EMD.

To consider the differences in detail, the mixtures at various Li/Mn ratios from 0.1 to 1.0 were annealed at 260 °C for 168 h. The XRD patterns of the heat treated products after washing with water are illustrated in Figure 5. In the Li/Mn ratio range between 0.8 and 0.3, new peaks appear in the diffraction patterns, however, identical patterns to that of EMD were obtained for the higher or lower Li/Mn ratio. By comparison with XRD patterns of the products formed from EMD and LiOH (Li/Mn = 0–2) at 380 °C [11], the patterns of Figure 5(d)–(i) are very similar to that at Li/Mn = 1/4 [6, 7, 11]. However, the ternary Li–Mn–O phase formed at a higher heat-treatment temperature of 320–380 °C were more or less contaminated with species, such as Li_2MnO_3, γ-β-MnO_2 and the spinel $Li_xMn_2O_4$ [2, 8, 11, 15, 20]. The products for 260 °C demonstrate pure single phase of Li_xMnO_2 because of the lower reaction temperature and the separation process by washing the products with water. The XRD peaks of the product for Li/Mn = 0.5 (Figure 3(b)) was indexed with the orthorhombic system [10], and its lattice parameters were estimated as $a = 0.989\,\text{nm}$, $b = 0.475\,\text{nm}$ and $c = 0.281\,\text{nm}$.

The Li/Mn ratios of the products after washing obtained by chemical analysis are given in Figure 6, as

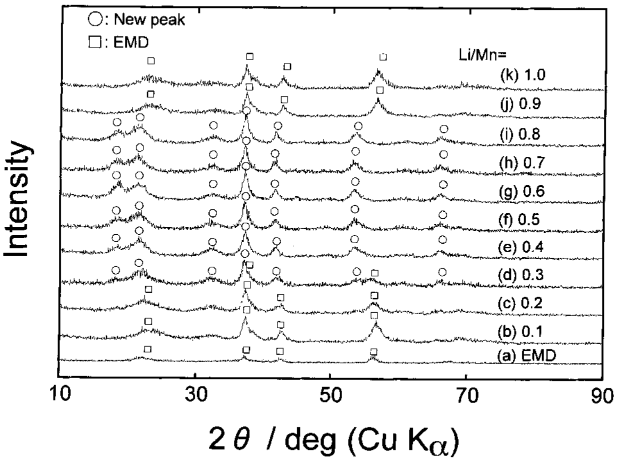


Fig. 5. XRD patterns of (a) EMD (IC-17) and heat treatment products at Li/Mn = 0.1 (b), 0.2 (c), 0.3 (d), 0.4 (e), 0.5 (f), 0.6 (g), 0.7 (h), 0.8 (i), 0.9 (j) and 1.0 (k). All heat treatment products were washed with water.

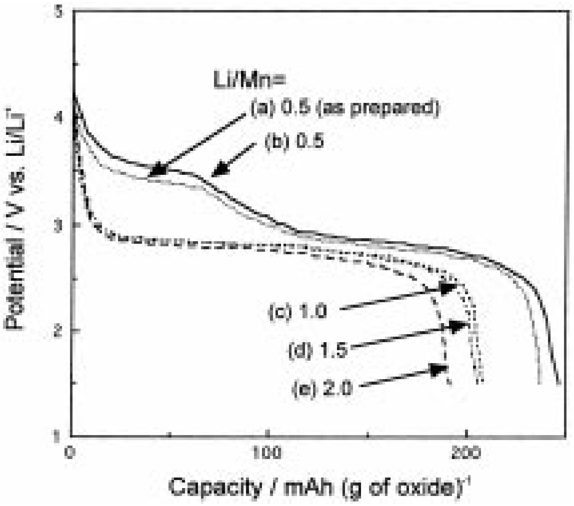


Fig. 4. Discharge curves after the first charging (electrochemical oxidation up to 4.5 V vs Li/Li^+) of (a) heat treatment products at Li/Mn atomic ratio of 0.5 as prepared, and heat treatment products washed with water at the Li/Mn = 0.5 (b), 1.0 (c), 1.5 (d) and 2.0 (e).

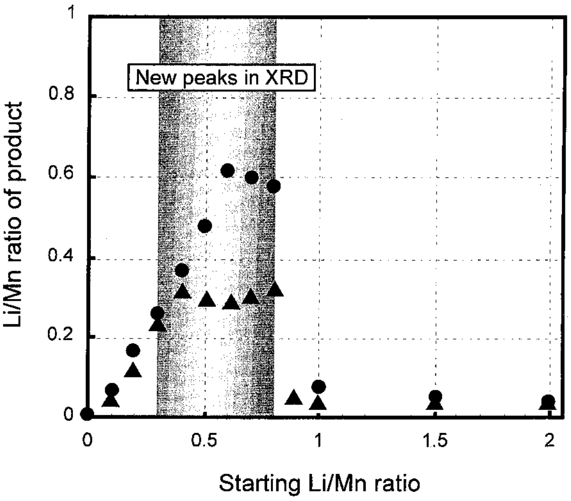


Fig. 6. Starting Li/Mn ratio against Li/Mn ratio of products plots; (●) Li/Mn ratio of the products by chemical analysis, and (▲) (intercalated Li)/Mn ratio estimated electrochemically from the initial discharge (Li intercalation) capacities observed from 4.5 to 3.1 V which corresponded to potential plateau around 3.5 V.

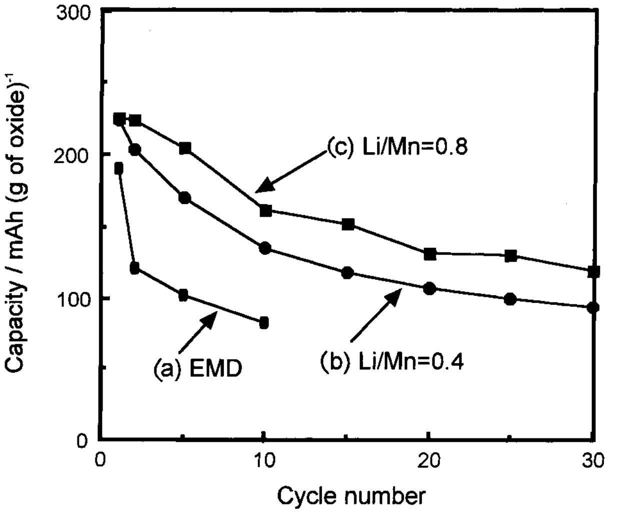


Fig. 7. Relation between cycle number and discharge capacity of (a) EMD (IC-17) and heat treatment products at Li/Mn = 0.4 (b) and 0.8 (c)

a function of starting Li/Mn ratio. When these new peaks appeared in the XRD spectrum, the new potential plateau around 3.5 V was observed in the discharge curve as mentioned above in Figures 3 and 4. Hence, the (intercalated Li)/Mn molar ratios around the plateau at 3.5 V, estimated electrochemically from the discharge capacity from 4.5 to 3.1 V, are also shown as a function of the starting ratio. This figure indicates that a new ternary Li_xMnO_2 ($x = 0.3$–0.6) is formed from the starting Li/Mn ratio of 0.3–0.8, however, about 0.3 Li in Li_xMnO_2 was removed from the oxide lattice on initial charging. From redox titration, an average oxidation state of Mn for Li/Mn = 0.5 was determined as 3.76 which agreed with the fact that 0.3 Li in Li_xMnO_2 was inserted into the oxide. These results show that two kinds of lithium, occupying different crystallographic sites in the crystal lattice, may exist in this compound.

Figure 7 shows the cyclability of the compounds synthesized at Li/Mn ratios of 0.4 and 0.8 as a fundamental cycling test in a wider range between 4.5 V and 1.5 V. In the case of EMD, the cyclability was lower under this condition, that is, lower discharge capacity and decreasing discharge capacity immediately. The Li–Mn–O compounds demonstrated higher discharge capacity, more than 200 mAh (g of oxide)$^{-1}$, in the initial cycles. The capacity, however, gradually decreased, for example, 100–120 mAh (g of oxide)$^{-1}$ at the 30th cycle. This slow decay of the electrode capacity of Li_xMnO_2 ($x = 0.3$–0.6) would be correlated to the gradual phase transition (from Li_xMnO_2 to $LiMn_2O_4$ spinel) as described by Levi et al. [15]. Further analyses on crystal change and improvement of cycle performance are in progress.

4. Conclusion

By heating mixtures of $LiNO_3$ and EMD in air at 260 °C, the ternary compound Li_xMnO_2 ($x = 0.3$–0.6) was produced at Li/Mn ratios around 0.5. This manganese compound was examined in $LiClO_4$–propylene carbonate electrolyte solution. It demonstrated initial higher discharge capacity, about 250 mAh (g of oxide)$^{-1}$, and better cyclability as a positive electrode for lithium secondary batteries as compared to EMD.

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