

Stable phases of the isothermal (800°C) cross-section of the pseudo-ternary Li–Mn–Co–O system

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The equilibrium phase composition has been studied in two (pseudo)binary cross-sections of the Li–Mn–Co–O system at 800°C in ambient air atmosphere: I – $\text{LiMn}_{2-x}\text{Co}_x\text{O}_n$ ($0 \leq x \leq 2$) and II – $\text{LiMn}_x\text{Co}_{1-x}\text{O}_n$ ($0 \leq x \leq 1$). Section I contains a homogeneous spinel-structured phase in the composition range $0 \leq x \leq 1$, with the lattice parameter decreasing with increasing Co content. The compositions become 2-phase for $1 < x \leq 2$, consisting of a Li-deficient spinel structure Me_3O_4 ($\text{Me} = \text{Co}, \text{Mn}$) and layered LiMeO_2 with the structure of $\alpha\text{-NaFeO}_2$. The compositions in section II are single-phase only if the Mn/Co atomic ratio does not exceed $\frac{1}{4}$ ($0 \leq x \leq 0.25$). Further increase of the Mn content results in the decomposition of this phase into three compounds with fixed compositions according to the overall reaction $\text{LiMn}_x\text{Co}_{1-x}\text{O}_n \rightarrow a \text{LiMn}_{0.25}\text{Co}_{0.75}\text{O}_2 + b \text{LiMn}_{1.1}\text{Co}_{0.9}\text{O}_4 + c \text{Li}_2\text{MnO}_3$. The phase $\text{LiMn}_{0.25}\text{Co}_{0.75}\text{O}_2$ disappears for $0.6 \leq x \leq 1$. Electrochemical testing of single-phase samples from both cross-sections showed that the replacement of up to 20% of the Mn atoms in lithium-manganese spinel increases the reversible capacity of this compound when used as material for the positive electrode of a Li-ion cell. The electrochemical performance of LiCoO_2 deteriorates with the partial replacement of Co atoms by Mn.

Lithium / Manganese / Cobalt / Oxides / Stable phases / Electrochemical properties / Li-ion cell

Introduction

Reversible electrochemical lithium intercalation into the layered structure of LiCoO_2 ($\alpha\text{-NaFeO}_2$ type), which was discovered almost 30 years ago [1], is still successfully employed in a variety of commercial Li-ion batteries [2]. In spite of the commercial success, this material has a few evident disadvantages – toxicity, high cost and sensitivity to occasional overcharge are the most important ones. For this reason worldwide research is going on in order to replace lithium-cobalt oxide by a non-toxic and inexpensive material. The spinel-structured lithium-manganese oxide LiMn_2O_4 has been recognized as the most promising candidate – it is abundant and relatively harmless. However, its structure, being sensitive to over-discharge because of Jahn-Teller distortions, is unstable in the course of long-term cycling, especially at elevated temperatures [3]. Hence, numerous researches are currently under way in two main directions: 1) replacement (at least partial) of Co in the layered structure of LiCoO_2 by other metal cations, 2) partial replacement of Mn in LiMn_2O_4 by other metals in order to improve the cycling stability of this structure. As discussed earlier [4], metastable phases, though exhibiting good

electrochemical performance at the initial time, are unlikely to be used in long-term power applications. Thermodynamic stability of the electrode materials is important, in addition to good electrochemical properties.

We have started a series of physico-chemical studies of Li-Mn-Me-O oxide systems in order to find out the fields of existence for the homogeneous thermodynamically stable phases with the structures of spinel and $\alpha\text{-NaFeO}_2$. This work presents the main results on the Li–Mn–Co–O system. When maintained under a constant pressure of oxygen, normally in ambient air, this system can be considered as pseudo-ternary.

Experimental

Three cross-sections of the Li-Mn-Co-O system were investigated at 800°C (Fig. 1). 11-13 samples for each cross-section were prepared and investigated by XRD.

The samples were synthesized as follows. Chemical purity grade chemicals were used: lithium carbonate Li_2CO_3 , manganese nitrate $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and concentrated nitric acid HNO_3 . Weighed quantities of

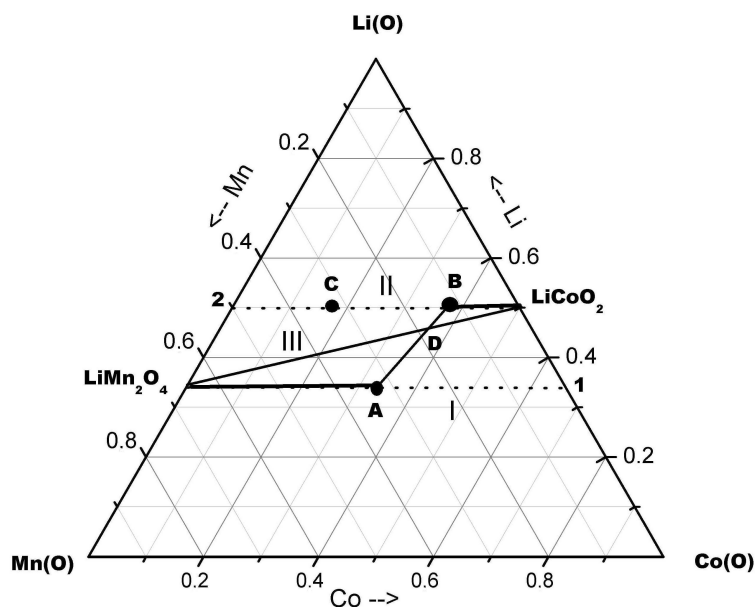


Fig. 1 Position of the cross-sections under examination on the composition triangle of the pseudo-ternary Li-Mn-Co-O system: I – “spinel” section $\text{LiMn}_{2-x}\text{Co}_x\text{O}_n$ ($0 \leq x \leq 2$); II – “cobaltite” section $\text{LiMn}_x\text{Co}_{1-x}\text{O}_n$ ($0 \leq x \leq 1$); III – “diagonal” $\text{Li}_{1+x}\text{Mn}_{2-2x}\text{Co}_{2x}\text{O}_4$ ($0 \leq x \leq 1$).

salts were placed in a beaker and nitric acid was added up to the full dissolution of the lithium carbonate. The solutions were then removed to alumina crucibles and cautiously heated at 100°C to 300°C till the end of NO_2 evolution from the mixtures. After that, the samples were calcinated at 800°C for one hour. The phase composition of the samples had stabilized after 30-40 min and did not change during subsequent heating for several hours, indicating the formation of thermodynamically stable phases under the conditions of the experiment.

The samples were investigated by XRD with a DRON-3M diffractometer and $\text{CuK}\alpha$ radiation. Due to the relatively high background, identification of weak diffraction peaks became sometimes unreliable. For such samples, measurements were repeated with $\text{CoK}\alpha$ radiation, where the background fluctuations were lower.

Electrochemical tests were performed in a Li/EC:DMC + 1M LiPF_6 /Sample mockup button cell of 2016 dimension. The cells were assembled in an argon-filled dry glove box. The positive electrode was prepared by slurring the testing material (85 wt.%) with KS6 graphite (10 wt.%) and PVDF as a binder in N-methyl-pyrrolidone, and pasting the slurry onto a thin aluminium foil. Testing of the cells was performed by a PC-governed multichannel equipment in galvanostatic conditions.

Results and discussion

“Spinel” section $\text{LiMn}_{2-x}\text{Co}_x\text{O}_n$ ($0 \leq x \leq 2$) (I)

Fig. 2 shows the XRD patterns of the end members of this cross-section, lithium manganese spinel LiMn_2O_4 and composition 1 (**Fig. 1**), LiCo_2O_n . One can see that

the latter cannot be crystallized as an individual phase, but represents a mixture of LiCoO_2 and Co_3O_4 .

According to the literature, several homogeneous phases should exist in this cross-section. “Modified spinel structures” $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ were reported in [5] for $x=1/9$ and $1/6$ and homogeneous spinel $\text{Li}[\text{Co}_{0.5}\text{Mn}_{1.5}]\text{O}_4$ ($x=0.5$) was obtained in [6]. Our data agree with these results. It was found that the homogeneous region in the “spinel” section I extends up to $x=0.9-1$, that is, approximately one half of the Mn atoms in the basic structure of LiMn_2O_4 can be replaced by Co^{1+} .

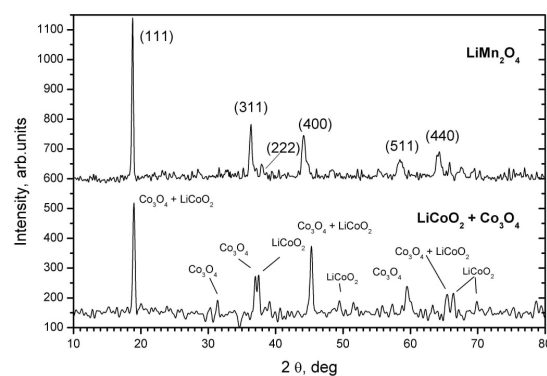


Fig. 2 XRD patterns of samples corresponding to the initial ($x=0$) and final ($x=2$) members of the series I (see **Fig. 1**), $\text{LiMn}_{2-x}\text{Co}_x\text{O}_n$.

¹ In fact, it is slightly less than one half. The composition $\text{LiMn}_{1.1}\text{Co}_{0.9}\text{O}_4$ seems to be more exact for the Co-saturated spinel phase.

A series of XRD patterns for spinel phases with different Co content is shown in Fig. 3. A slight shift of the diffraction peaks toward large angles is observed as the amount of Co in these spinel phases increases. This indicates a decrease of the lattice parameter when Mn is replaced by Co in the 16d positions. As follows from the calculations, the lattice parameter decreases linearly with increasing Co content, Fig. 4.

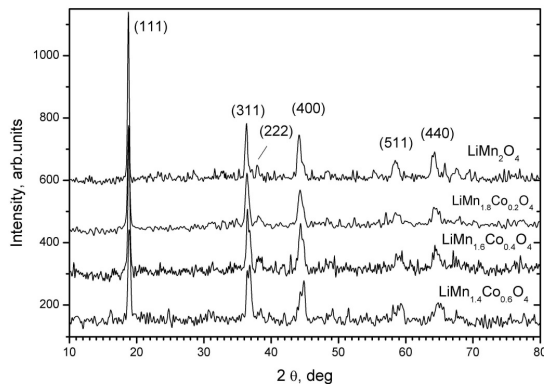


Fig. 3 XRD patterns of spinel phases with different Co content.

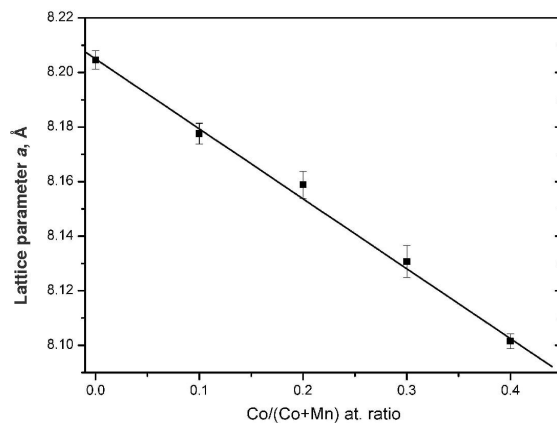
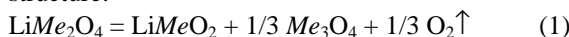


Fig. 4 Dependence of the lattice parameter of the spinel phase in cross-section I on the Co content.

The spinel phase $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ becomes unstable in the composition region $1 \leq x \leq 2$, decomposing with the formation of layered LiMeO_2 ($\alpha\text{-NaFeO}_2$ structure) and Me_3O_4 ($\text{Me}=\text{Co}, \text{Mn}$) with spinel structure:

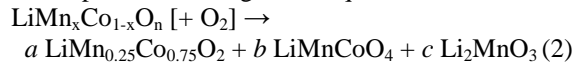


Thus, part A-1 of cross-section I, Fig. 1, represents a two-phase region of compositions.

“Lithium cobaltite” section $\text{LiMn}_x\text{Co}_{1-x}\text{O}_n$ ($0 \leq x \leq 1$) (II) The formation of a “modified spinel phase”, $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$, was reported for this cross-section [7]. However, according to our data, this phase cannot be stable at 800°C. The results of the XRD investigations

show that the compositions II form a single phase $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ with LiCoO_2 -type structure in a rather narrow range, $0 \leq x \leq 0.25$ (Fig. 5).

As the content of Mn increases ($x > 0.25$), the layered phase, in the presence of ambient oxygen, decomposes according to the equation below:



The coefficients a , b , c on the right side of (2) depend on x and can be calculated for each particular composition from material balance equations.

When moving along the line $\text{LiCoO}_2\text{-2}$ in Fig. 1, we enter a 3-phase region passing by the point B. The part B-C corresponds to the coexistence of layered $\text{LiMn}_{0.25}\text{Co}_{0.75}\text{O}_2$ phase saturated with Mn, spinel phase saturated with Co and having a composition close to LiMnCoO_4 , and monoclinic lithium manganate Li_2MnO_3 (Fig. 6). The qualitative phase composition remains unchanged until the point C ($x=0.7$) is reached (Fig. 1). After that, the layered phase $\text{LiMn}_{0.25}\text{Co}_{0.75}\text{O}_2$ disappears and the compositions C-2 of section II at $0.7 \leq x \leq 1$ consist of equimolar quantities of partly Co-substituted spinel and Li_2MnO_3 :

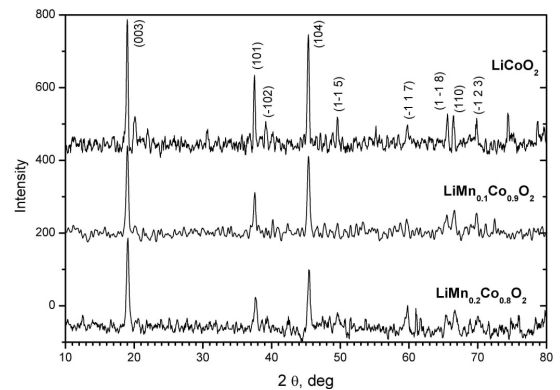
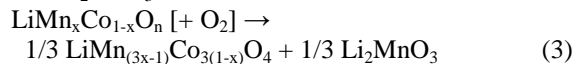


Fig. 5 XRD patterns of $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ samples in the homogeneity range $0 \leq x \leq 0.25$.

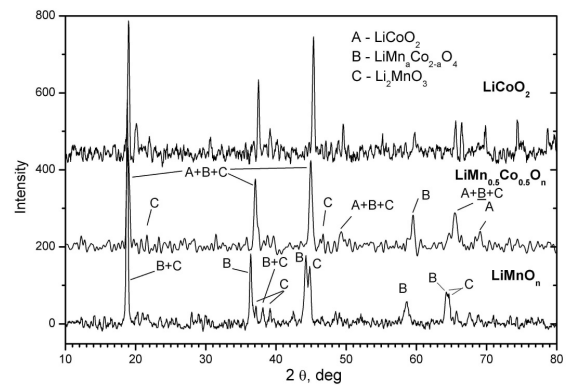


Fig. 6 XRD patterns of $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ samples in the heterogeneous region B-C-2 of Fig. 1.

“Diagonal” section $\text{Li}_{1-x}\text{Mn}_{2-2x}\text{Co}_{2x}\text{O}_4$ ($0 \leq x \leq 1$) (III)

One can conclude *a priori* that the “diagonal” compositions III, Fig. 1, should consist of two phases only, with the structures of spinel and $\alpha\text{-NaFeO}_2$ (lithium cobaltite). Point D should correspond to a mixture of cobaltite saturated with Mn (composition B) and manganese spinel saturated with Co (point A). Then the part $\text{LiMn}_2\text{O}_4\text{-D}$ must be a mixture of spinel phase with a composition varying from LiMn_2O_4 to LiMnCoO_4 , and cobaltite phase with the limiting constant composition $\text{LiCo}_{0.75}\text{Mn}_{0.25}\text{O}_2$. *Vice versa*, the mixture of the limiting spinel composition LiMnCoO_4 and cobaltite varying from $\text{LiCo}_{0.75}\text{Mn}_{0.25}\text{O}_2$ to LiCoO_2 must correspond to part D– LiCoO_2 of the cross-section.

This conclusion agrees with the experimental data. The two-phase composition of cross-section III was confirmed by XRD analysis. As expected, the lattice parameter of the spinel phase diminishes with increasing Co content until composition D is attained, and remains constant in the cobalt-rich compositions D– LiCoO_2 , Fig. 7.

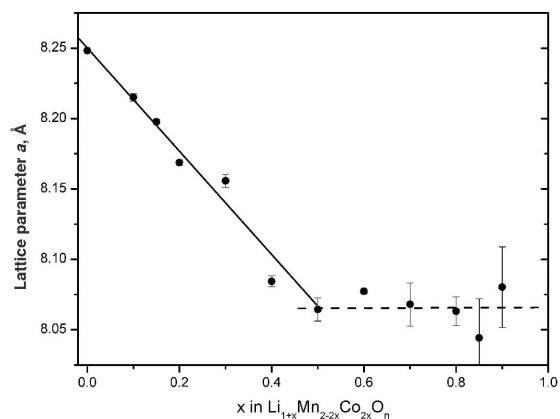


Fig. 7 Composition dependence of the lattice parameter of the spinel phase $\text{Li}_{1-x}\text{Mn}_{2-2x}\text{Co}_{2x}\text{O}_4$.

Thus, the formation of two types of homogeneous phases was proven in the pseudo-ternary system Li–Mn–Co–O at 800°C in ambient air atmosphere: partly substituted lithium-manganese spinel $\text{LiMn}_{2-x}\text{Co}_x\text{O}_4$ ($0 \leq x \leq 1$) and partly substituted layered LiCoO_2 , $\text{LiMn}_x\text{Co}_{1-x}\text{O}_2$ ($0 \leq x \leq 0.25$). Their ranges of existence are shown by solid lines in Fig. 1, $\text{LiMn}_2\text{O}_4\text{-A}$ and $\text{LiCoO}_2\text{-B}$. As can be deduced from the composition of cross-section III, these two phases of variable compositions should coexist in equilibrium inside the quadrangle $\text{LiMn}_2\text{O}_4\text{-B-LiCoO}_2\text{-A}$. The phases other than these two should appear outside this quadrangle: Me_3O_4 to the right and Li_2MnO_3 to the left of this area. Hence, the compositions inside the field $\text{LiMn}_2\text{O}_4\text{-B-LiCoO}_2\text{-A}$ are of potential interest for electrochemical investigations with regard to Li insertion. In this work we have studied the electrochemical properties of single-phase samples corresponding to the compositions $\text{LiMn}_2\text{O}_4\text{-A}$

(Co-substituted lithium manganese spinel) and $\text{LiCoO}_2\text{-B}$ (Mn-substituted lithium cobaltite).

Electrochemical activity of single-phase samples

Fig. 8 shows voltage profiles of galvanostatic charge and discharge curves for pure LiMn_2O_4 and spinel phase where 20% of the manganese atoms are replaced by cobalt. Both profiles show two plateaus between 4.0 and 4.2 V, which is common for the lithium manganese spinel structure. Naturally, the absolute values of the specific capacities depend on the working current. However, the ratios of these capacities with respect to pure lithium manganese spinel under the same experimental conditions are practically independent of the current load and vary with the Co content in the spinel phase as shown in Fig. 9. An increase of the reversible capacity is observed in the potential range 4.5–3 V vs. Li when up to 20% of the Mn atoms have been replaced by Co. Further increase of the Co content in the structure results in rapid fading of the reversible capacity in this range of working voltage. It was found that the samples with higher Co concentration in the spinel lattice exhibit a partly reversible discharge plateau at ~5 V vs. Li, similar to that observed in the partly substituted spinel $\text{Li}(\text{Mn}_{2-x}\text{Li}_{x/4}\text{Co}_{3x/4})\text{O}_4$ [8] and other spinel structures where part of the Mn atoms attain the oxidation number +4, as a result of the insertion of low-valence cations in the 16d positions [6,9]. Presumably, the capacity of such samples should be redistributed between the 5 V and 4 V regions with the total value remaining at least constant. Unfortunately, we were not able to check this assumption because of the instability of our working electrolyte at 5 V vs. Li or higher. Thus, we can recommend the replacement of no more than 20% of Mn by Co for practical applications.

Replacement of Co by any amount of Mn in the structure of LiCoO_2 results in a deterioration of the electrochemical activity (Fig. 10). Hence, partially substituted $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ phases seem to be of no use for electrochemical applications.

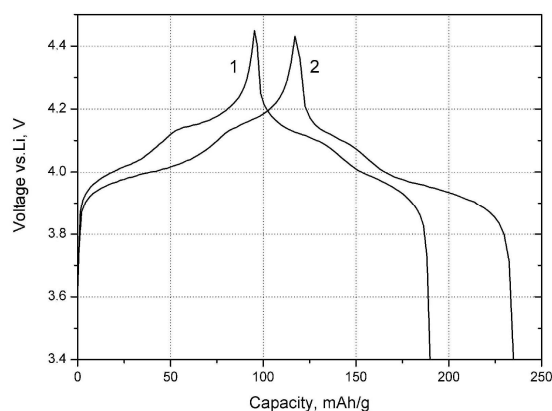


Fig. 8 Voltage profiles of galvanostatic charge and discharge curves (5th cycle) for LiMn_2O_4 (1) and $\text{LiMn}_{1.6}\text{Co}_{0.4}\text{O}_2$ (2) samples. Rate of charge/discharge ~ C/5 (24 mA/g).

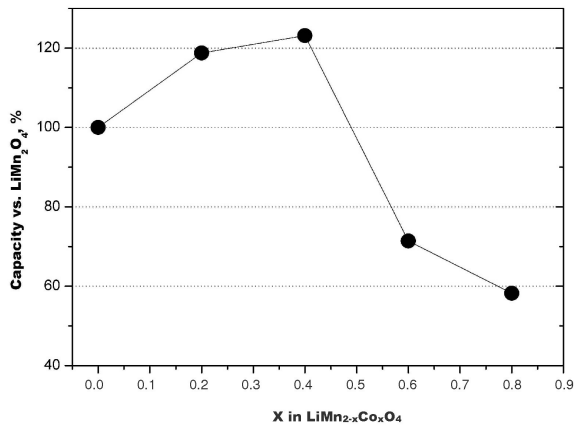


Fig. 9 Relative reversible capacity of lithium-manganese spinel as a function of the Co content.

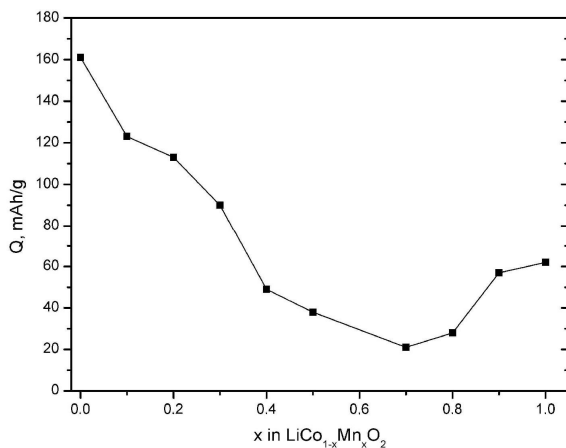


Fig. 10 Reversible capacities (5th cycle) of samples corresponding to the “cobaltite” cross-section II (see Fig. 1). Cut-off potentials 4.5-3 V vs. Li, specific charge and discharge current ~20 mA/g.

Conclusions

Four thermodynamically stable phases are formed inside the composition quadrangle LiMn_2O_4 – LiMnO_n – LiCoO_2 – LiCo_2O_m : 1) LiMeO_2 (rhombohedral, structure of α - NaFeO_2), 2) LiMe_2O_4 (cubic, spinel), 3) Li_2MnO_3 (monoclinic), and 4) Me_3O_4 (spinel). The first two of them are of interest for

possible electrochemical applications. They are located inside the quadrangle LiMn_2O_4 –B– LiCoO_2 –A of Fig. 1.

The structure of lithium-manganese spinel allows the replacement of 50% of the Mn atoms by Co, whereas 25% of the Co atoms can be substituted for in the structure of lithium cobaltite.

Introduction of up to 20% of Co atoms into the spinel structure improves the electrochemical properties of lithium-manganese spinel. However, any replacement of Co by Mn in the structure of lithium cobaltite deteriorates its electrochemical performance.

The electrochemical performance of two-phase compositions consisting of the spinel and cobaltite compounds (LiMn_2O_4 –B– LiCoO_2 –A area in Fig. 1) is still to be explored, especially with regard to its cycle retention in long-term repetitious charge-discharge. There is hope that an efficient active material for the replacement of LiCoO_2 in commercial Li-ion batteries can be found among them.

Acknowledgements

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