

ON THE NEW POSITIVE ELECTRODE MATERIALS FOR HIGH ENERGY DENSITY LITHIUM ION BATTERIES

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The layered $\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$ positive electrode materials were synthesized by the combustion method using sucrose as fuel, and characterized by X-ray diffraction. The powders adopted the $\alpha\text{-NaFeO}_2$ structure (R^{3m} space group). Lithium is located between the transition metal ions slabs made up by edge sharing MO_6 octahedra (M: Ni, Co, Mn). X-ray diffraction data refinement by the Rietveld method shows that both samples present bi-dimensional structure with no Li/Ni cation mixing. Cycling tests revealed a great difference in the electrochemical behaviors. Lithium extraction from $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$ involves only one redox process with a continuous evolution of the potential with composition, while they are two domains in the potential vs capacity curve of the $\text{Li}/\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ electrochemical cell. The first one at 3.6 V corresponds to the $\text{Ni}^{4+}/\text{Ni}^{2+}$ redox couple while the second one at 3.9 V corresponds to the $\text{Co}^{4+}/\text{Co}^{3+}$. More than 190 mA·h/g could be delivered by $\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ electrode which could be considered as a good electrochemical performance by comparison with the most commercialized cathode LiCoO_2 .

Keywords: electric energy storage, structural materials, new structural materials for renewable energy



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Introduction

Development of environmentally friendly and renewable energy sources is of great importance for a sustainable future. Fossil fuels and nuclear power are currently the dominating energy sources and will most likely continue to be so for the next generations. However, these power sources have drawbacks; the amount of fossil available is finite and nuclear waste disposal involves well-known problems. Today, as evidence of global warming accumulates [1], researchers from many fields focus on developing alternative energy sources and storage techniques, eg., photoelectrochemical cells [2], fuel cells [3] and batteries. The major advantages of the batteries (especially lithium-ion batteries) is its high energy density compared to others systems. It is therefore, used successively in portable electronics e.g., cellular phones, laptops and camcorders.

Since cobalt is expensive, the battery manufacturers are looking for other materials, which can help to reduce the price of the final product without decreased performance.

In the present paper, new positive electrode materials based on Co, Ni and Mn elements were prepared by the combustion method. The electrochemical performances of the studied compounds were discussed in relation with their structural properties.

Experiment

Two compositions for the positive electrode materials were selected: $\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$. Stoichiometric amounts of Li, Co, Ni and Mn nitrates (oxidant) were dissolved simultaneously with the sucrose (fuel) in an aqueous solution. The reaction is extremely violent when using a stoichiometric amount of sucrose. To avoid it, the oxidant/fuel ratio was optimized to 0.67. In this way, the reaction is well controlled. The reagents solution was heated at about 120 °C for 1 h, and then dried; it starts to swell up due to the evaporation of the generated gases leading to a foamy mass. After a few minutes, the mass starts to burn spontaneously without flame. The as prepared material is very light and downy. The final thermal treatments are 900 °C/12 h and 900 °C/1 h for $\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$ respectively.

X-ray diffraction patterns of the powdered samples were obtained with a STOE STADI/P diffractometer (Mo- $\text{K}_{\alpha 1}$ radiation, curved Ge (111) monochromator, transmission mode, data step width 0.02° (2θ), linear PSD counter).

Electrochemical properties measurements were performed in lithium cells containing a lithium foil as negative electrode. Positive electrodes were prepared by spreading a mixture of 85 % active material, 10 % carbon black, and 5 % of PVDF [poly(vinylidene fluoride)] in NMP (1-methyl-2-pyrrolidinone) onto an aluminum foil. The electrolyte was 1 M LiPF_6 (lithium hexafluorophosphate) dissolved in a 2:1 volume ratio solution of EC (ethylene carbonate) and DEC (diethyl carbonate). Cells were cycled galvanostatically using a multi-channel potentiostat (VMP2/Z; Ametek) battery testing system.

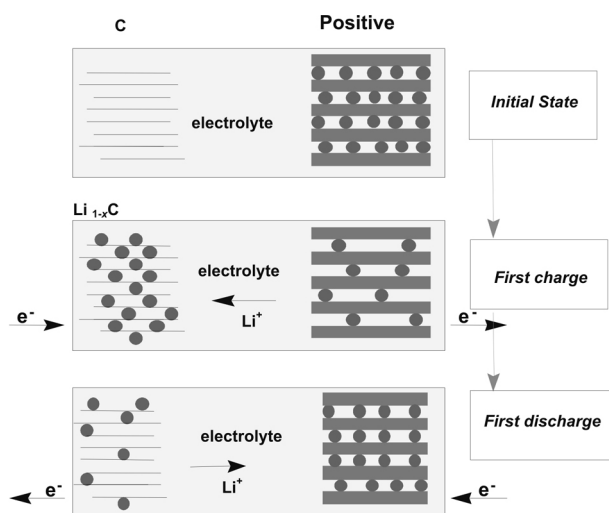


Fig. 1. Schematic representation of the lithium-ion battery

As schematically represented in Fig.1, lithium-ion battery consists of carbon as anode, liquid electrolyte and cathode. During the charge process, lithium ions move from the cathode across the electrolyte to the anode and vice versa as the battery is charged. Choosing the positive electrode material is crucial for the battery's overall performance. The most studied materials are LiCoO_2 [4], LiNiO_2 [5], LiMn_2O_4 [6] and LiFePO_4 [7].

Results and discussion

Fig. 2 shows the X-ray diffraction patterns of $\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$.

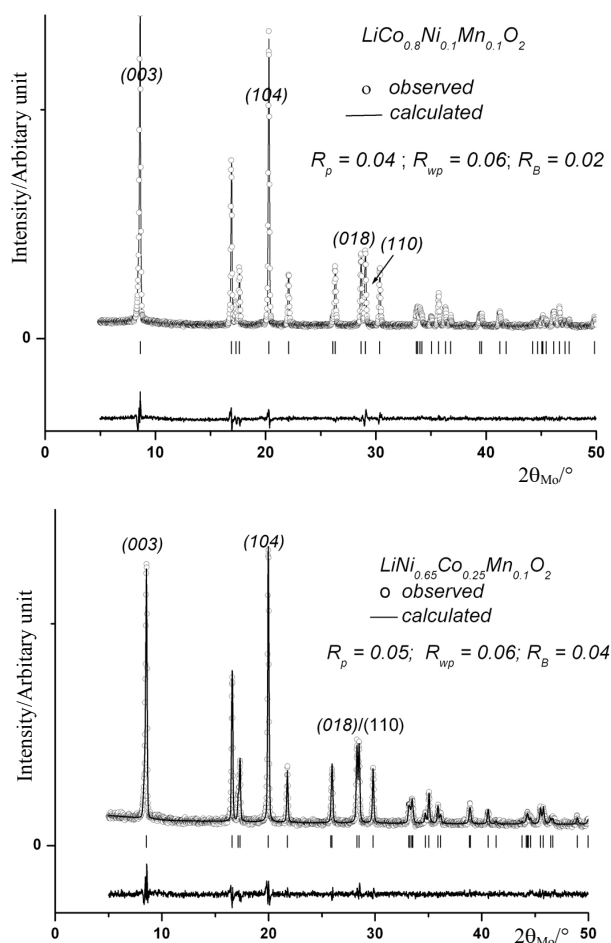


Fig. 2. X-ray diffraction patterns of $\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$

All diffraction peaks can be indexed based on the α - NaFeO_2 -type structure (Space Group R-3m). The relative intensity of (003) to (104) peaks and the splitting of (018)/(110) diffraction lines clearly indicate a good 2D character of the structure. As shown by Fig. 3, Li and transition metal ions (Ni, Co, Mn) occupying alternate layers with an octahedral environment.

The structural refinement of the X-ray data, using the Rietveld method [8], was done assuming that Li, M (M: Ni, Co, Mn) and O occupy (001/2); (000) and (00z) atomic coordinates. It gives a good reliability between the calculated and observed profiles as demonstrated by the low values of the R_p , R_{wp} and R_B reliability factors. The hexagonal unit cell parameters for the two compounds are: $a = 2,8270(1) \text{ \AA}$; $c = 14,1132(1) \text{ \AA}$ for the cobalt rich phase ($\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$) and $a = 2,8459(1) \text{ \AA}$; $c = 14,0980(3) \text{ \AA}$ for the nickel rich phase ($\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$). According to these crystallographic data, we can conclude that within the

(Ni, Mn, Co) sheets, a high covalency exists leading to an easy electronic transfer during the electrochemical process. In the same time, lithium ions establishes only a very weak bonding (Van der Waals type) with the oxygen anions. This also leads to an easy lithium diffusion upon lithium extraction or insertion. We could then expect that this kind of compounds exhibit a convenient features to be used as positive electrode materials in lithium-ion batteries.

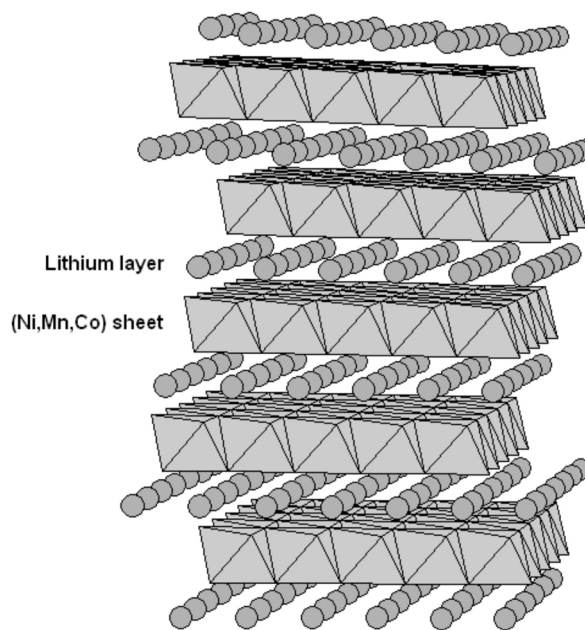


Fig. 3. Structure of the $\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$ oxides showing lithium ions between the $(\text{Ni, Co, Mn})\text{O}_6$ edge sharing octahedra

The two materials have been used separately as cathode materials in lithium batteries in order to study their electrochemical behavior. The voltage vs capacity profiles during the first charge are plotted in Fig. 4. For the cobalt rich phase $\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$, they are two voltage domains separated by a potential plateau at 3.85 V: the first domain is from 3.6 to 3.8 V, the second from 3.85 to 4.5 V. While for the nickel rich phase $\text{LiNi}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.10}\text{O}_2$, a continuous evolution of the potential was evidenced, showing that only one electrochemical process is involved during the lithium extraction from this phase. For the cobalt rich phase, the charge process of the $\text{Li}/\text{LiCo}_{0.8}\text{Ni}_{0.1}\text{Mn}_{0.1}\text{O}_2$ battery starts by the oxidation of Ni^{3+} to Ni^{4+} ions at about 3.6 V. The oxidation of all 0.1 nickel ion present in the starting phase corresponds to the extraction of 0.1 lithium ions (about 55 mA·h/g). After this redox process, Co^{3+} ions start its oxidation process which corresponds to about 3.9 V. The preferential oxidation of Ni^{3+} compared to Co^{3+} ions was already demonstrated by studying the physical properties (Li NMR spectroscopy, magnetism) of the $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ system [9-12].

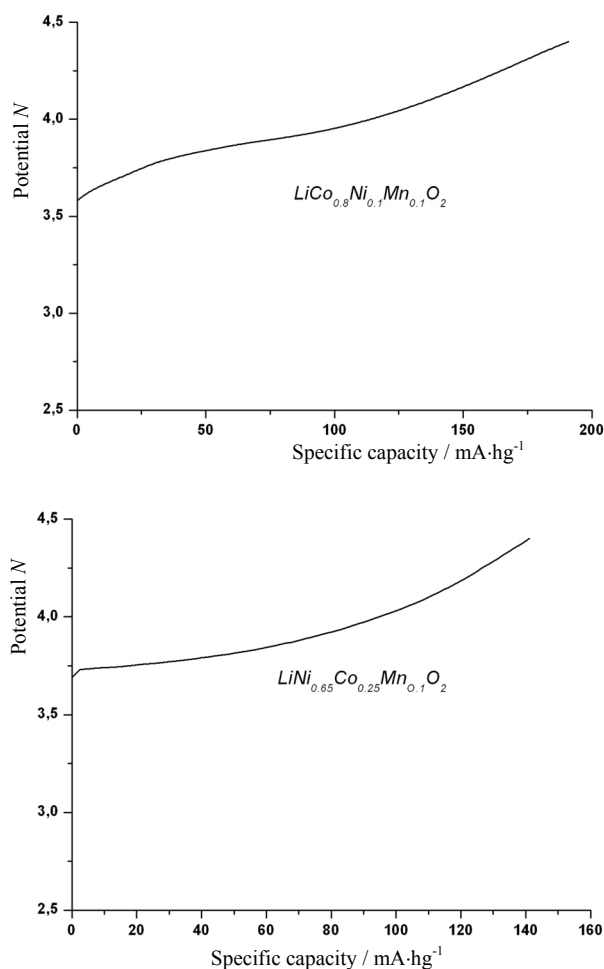


Fig. 4. The voltage vs capacity profile of the Li//LiCo_{0.8}Ni_{0.1}Mn_{0.1}O₂ and Li//LiNi_{0.65}Co_{0.25}Mn_{0.10}O₂ electrochemical cells cycled in the same regime C/20 which corresponds to the extraction of one Li ion in 20 hours

Furthermore, the electrochemical cycling of these two positive electrode materials occurs without structural modifications and with a small variation of the unit cell parameters. This result, which will be published soon, is important from the applications point of view. Indeed, deterioration of the electrochemical performances (long cycle life, cyclability...) is strongly related to the structural stress in the cathode material resulting from the structural changes in the symmetry or/and in the unit cell volume that occur during the cycling [13].

The sample with larger amount of cobalt delivers a charge capacity of 196 mAh/g, which is 35% greater compared to that delivered by the Li//LiNi_{0.65}Co_{0.25}Mn_{0.10}O₂ electrochemical cell. Furthermore, the electrochemical cycling (lithium extraction/insertion) of the Li//LiCo_{0.8}Ni_{0.1}Mn_{0.1}O₂ occurs without significant modifications in the structural features while lithium extraction from Li_xCoO₂ system (the commercialized cathode) involves many structural changes as reported elsewhere [4]. Thus, LiCo_{0.8}Ni_{0.1}Mn_{0.1}O₂ could be considered as much more competitive cathode than LiNi_{0.65}Co_{0.25}Mn_{0.10}O₂ for application in the real batteries.

Conclusions

LiCo_{0.8}Ni_{0.1}Mn_{0.1}O₂ and LiNi_{0.65}Co_{0.25}Mn_{0.10}O₂ were prepared by the simple combustion method using sucrose as fuel. From the results of X-ray diffraction, these two samples were characterized by an α -NaFeO₂ type structure with alternating lithium layers with transition metal slabs. In the two-electrode electrochemical cells, LiNi_{0.65}Co_{0.25}Mn_{0.10}O₂ shows a smooth charge curve with continuous evolution of the potential versus capacity which suggests less structural transformations with intercalation of lithium. For the cobalt rich phase LiNi_{0.65}Co_{0.25}Mn_{0.10}O₂, two electrochemical processes are involved during lithium extraction: the first one corresponds to the oxidation of the Ni ions while the second one corresponds to the Co⁴⁺/Co³⁺ redox couple. For this last phase, about 196 mAh/g can be delivered during the electrochemical cycling which makes this positive electrode material competitive from applications point of view.

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References

1. Houghton J.T. Climate change: the scientific basis. New York, Cambridge University Press. 2001.
2. Grätzel M. Photoelectrochemical cells // Nature. 2001. Vol. 414. P. 338-344.
3. Steel B.C.H., Heintzel A. Materials for fuel cell technologies // Nature. 2001. Vol. 414. P. 345-352.
4. Mizushima K., Jones P.C., Wiseman P.J. et al. Li_xCoO₂ (0 < x < 1.0): A new cathode material for batteries of high energy densities // Material Research Bulletin. 1980. Vol. 15. P. 783-789.
5. Dahn J.R., Von Sacken U., Juszko M.W. et al. Rechargeable LiNiO₂/carbon cells // Journal of the Electrochemical Society. 1991. Vol. 138. P. 2207-2211.
6. Thackeray M.M., David W.I.F., Bruce P.G. et al. Lithium insertion into manganese spinels // Material Research Bulletin. 1983. Vol. 18. P. 461-472.
7. Padhi A.K., Nanjundaswamy K.S., Goodenough J.B. Phospho-olivines as positive electrode materials for rechargeable lithium batteries // Journal of the Electrochemical Society. 1997. Vol. 144. P. 1188-1194.
8. Roisnel T., Rodriguez-Carjaval J. WinPlotr: A windows tool for powder diffraction pattern analysis // Materials Science Forum. 2001. Vol. 378. P. 118-123.
9. Delmas C., Saadoun I., Rougier A. The cycling properties of the Li_xNi_{1-y}Co_yO₂ electrode // Journal of Power Sources. 1993. Vol. 44. P. 595-602.
10. Saadoun I., Delmas C. LiNi_{1-y}Co_yO₂ positive electrode materials: relationships between the structure,

physical properties and electrochemical behavior // Journal of Materials Chemistry. 1996. Vol. 6, No. 2. P. 193-199.

11. Saadoun I., Ménétrier M., Delmas C. Redox processes in $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ cobalt-rich phases // Journal of Materials Chemistry. 1997. Vol. 7, No. 2. P. 2505-2511.

12. Saadoun I., Delmas C. On the $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ system // Journal of the Solid State Chemistry. 1998. Vol. 136. P. 8-15.

13. Song M.Y., Lee R., Kwon I. Synthesis by sol-gel method and electrochemical properties of $\text{LiNi}_{1-y}\text{Al}_y\text{O}_2$ cathode materials for lithium secondary battery // Solid State Ionics. 2003. Vol. 156, No. 4. P. 319-328.

