A Study on the Structural and Electrochemical Properties of $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ Cathode Material Using Synchrotron based *in-situ* X-ray Diffraction

Sol Choi, JeongBae Yoon, Shoaib Muhammad, and Won-Sub Yoon*

Department Of Energy Science, Sungkyunkwan University, 300 Suwon-si, Gyeonggi-do 440-746, Korea

ABSTRACT :

The structural and electrochemical properties of $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ (Fd $\bar{3}$ m, disordered spinel) cathode material were studied and compared with stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (P4 $_3$ 32, ordered spinel). First cycle discharge capacity of $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ was similar to that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at C/3 and 1C rate, but cycling performance of $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ was better than that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ especially at high rate of 1C. This can be explained by performing synchrotron based *in-situ* XRD and results of GITT measurements. It is considered that faster lithium ion diffusion in the $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ cathode results in the improvement of the rate capability. To study structural changes during cycling, synchrotron *in-situ* XRD patterns of both the samples were recorded at C/3 and 1C rate. Compared to stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, disordered $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ spinel sample has pseudo one phase behavior and one step phase transition between two cubic phases. So, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ would experience a much greater strain and stress, originating from the two phase transitions between three cubic phases and suffer from capacity loss during cycling especially at high rate.

Keywords : Lithium ion battery, Cathode material, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$, *In situ* X-ray Diffraction

Received March 22, 2013 : Accepted March 26, 2013

1. Introduction

Today, lithium ion batteries are widely used for portable electronics such as notebooks, digital cameras, smart pads, and mobile phones. Furthermore, lithium ion rechargeable batteries have been considered as promising energy storage device for electric vehicles (EV), plug-in hybrid electric vehicles (PHEV), hybrid electric vehicles (HEV) and energy storage system (ESS) because of their high energy density. This growing worldwide demand for improved batteries has spurred intense research activities both in academic and industrial institutions.

LiCoO_2 is widely used in commercial lithium ion

batteries due to its advantages, such as high theoretical capacity, long cycle life and thermal stability, although LiCoO_2 is expensive and toxic.¹⁻³⁾ LiMn_2O_4 is an attractive cathode material and alternative to LiCoO_2 due to abundance, low cost and non-toxicity. These characteristics are becoming increasingly important in development of next generation high energy power sources.⁴⁻⁶⁾ In addition, spinel structure of LiMn_2O_4 provides a 3D network for fast lithium ion diffusion.⁷⁻¹³⁾ Despite such advantages, capacity fading occurs during cycling especially at high temperature prior to any structural changes.^{14,15)} It is known that the un-doped spinel suffers from the structural degradation due to disproportioning reactions and Jahn-Teller distortion, which is caused by formation of Mn^{3+} in the discharge period.¹⁶⁾ Doping of suitable species can maintain the valence of manganese to Mn^{4+} . Among all doped

*Corresponding author. Tel.: +82-31-299-6276

E-mail address: wsyoon@skku.edu

spinel cathodes, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a promising candidate as cathode material to be used in electric vehicles because of its good cyclability, high operating voltage and high power density.^{17,18)}

In this article, structural and electrochemical properties of stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (P4₃32, ordered spinel) and non-stoichiometric $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ (Fd $\bar{3}$ m, disordered spinel) cathode material has been comparatively studied. Lithium ion diffusion coefficients were obtained by galvanostatic intermittent titration technique (GITT). Synchrotron based *in-situ* X-ray diffraction technique was used to study the structural changes in both the cathode materials during electrochemical cycling.

2. Experimental

The stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (P4₃32, ordered spinel) and non-stoichiometric $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ (Fd $\bar{3}$ m, disordered spinel) cathode materials were synthesized by firing required amounts of the co-precipitated hydroxides of nickel and manganese with lithium hydroxide in air at 1000°C for 24 h followed by additional annealing process at 700°C for 12 h. The working electrodes consisted of 94 wt% active material, 3 wt% Super-P as a conductor material and 3 wt% polyvinylidene fluoride (PVDF) binder with N-methyl pyrrolidone (NMP) solvent respectively. The cathodes were packed in coin type CR2032 cells with a lithium metal foil as a negative electrode and Celgard® separator. The electrolyte used was 1M LiPF_6 and 0.3M LiBF_4 in 3:7 ethyl carbonate (EC)/ diethyl carbonate (DEC).

Charge/discharge cycling test was carried out at room temperature with a battery test station (WBSC3000, Won-A Tech, Korea). Current rate of C/3 and 1C with voltage window of 3.5-4.9 V (vs. Li/Li^+) was selected. C rate was calculated through weight of active material and its theoretical capacity.

GITT measurements were performed on $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ cells at room temperature as a function of voltage and capacity. The cells were discharged at constant current flux of C/3 for 5 minutes followed by an open circuit interval of 30 minutes, so that cell voltage may relax to its steady-state value.

In-situ XRD patterns for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ were collected on beam line 1D with wavelength $\lambda = 1.0000 \text{ \AA}$ and 5A with wave-

length $0.7653 \text{ \AA}$ respectively at Pohang Light Source. The XRD patterns were recorded as a set of circles on a Mar 345-image plate detector in the transmission mode for about 1 minute of exposure time. The total recording time for a pattern was about 2.6 minute because of the scanning time of image plate and transferring time of spectral information. The two theta angles of all the XRD patterns presented in this article has been recalculated to corresponding angles for $\lambda = 1.54 \text{ \AA}$, which is the wavelength of conventional X-ray tube source with Cu-K α radiations, for easy comparison with other published results.

3. Results and Discussion

3.1. Charge-discharge cycling

First charge and discharge profiles of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (ordered spinel, P4₃32) and $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$

Fig. 1. First and fiftieth charge/discharge curves of (a) stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and (b) $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ in Li-half cell measured between 3.5-4.9 V at C/3 and 1C rate.

$\text{Mn}_{1.56}\text{O}_4$ (disordered spinel, $\text{Fd}\bar{3}\text{m}$) cathode materials were obtained between 3.5–4.9 V at room temperature as shown in Fig. 1. These cells were cycled at $C/3$ and $1C$ rate. Cell containing stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited a flat voltage profile at around 4.7 V and no plateau around the 4 V region was observed because all the manganese ions in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are in Mn^{4+} state to maintain the fully ordered stoichiometric structure. On the other hand, the $\text{Li} / \text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ cell showed two distinct plateaus at around 4.7 V during the charge that are attributed to the $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$ redox couples and a small plateau in the 4 V regions was also observed that arises from $\text{Mn}^{3+/4+}$ redox couple.^{19–21} Presence of small quantity of Mn^{3+} in spinel cathode materials alters the local environment. This implies the coexistence of two structures at nano scale in the same crystal that reduces the ordering of transition metals. In perfectly stoichiometric sample manganese ions attain oxidation state of Mn^{4+} and do not take part in electrochemical activity where as in disordered spinel, a small portion of manganese exists as Mn^{3+} .

First cycle discharge capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at $C/3$ and $1C$ rate was measured as 113.54 and 97.87 mAh/g and after 50 cycles discharge capacity dropped 9.2% to 103.09 mAh/g at $C/3$ and 17.7% to 80.55 mAh/g at $1C$ rate. First cycle discharge capacity of $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ at $C/3$ and $1C$ rate is 114 and 99 mAh/g respectively. Both the samples showed similar capacity during first cycle, but the 50th cycle discharge capacity of ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode material dropped significantly as compared to disordered $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ spinel.

Fig. 2 shows galvanostatic discharge capacity of the cathodes at $C/3$ and $1C$ rate as a function of cycle number. The capacity retention of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ after 50 cycles at $C/3$ rate was 89.6% and 98.3%. At $1C$ rate, the capacity retention of the two samples was 82.0% and 95.2% respectively. These results show that the cycling performance of $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ is better than that of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material, particularly at higher C rate. Spinel $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ is a mixed manganese valence compound with $\text{Mn}^{3+}/\text{Mn}^{4+}$ and its electronic conduction takes place mainly by electron hopping between high valence Mn^{4+} and low valence Mn^{3+} cations.^{22–23} Presence of Mn^{3+} in disordered spinel makes $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ a good electronic conductor and capable of performing well at high rates. Low conduc-

Fig. 2. Comparison of the electrochemical cycling performances of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ at (a) $C/3$ and (b) $1C$ rate.

tivity sample offers higher polarization and lower performance at higher cycling rate. But electronic conductivity is not the exclusive factor that makes disordered spinel a better cathode material. In order to further investigate its better rate and cycling performance we performed GITT analysis and studied its structural variations during cycling by *in-situ* XRD.

3.2. GITT analysis: determination of Li^+ Diffusion coefficients

The empirical lithium ion diffusion coefficient (D_{Li}) calculated from GITT analysis of both the samples is plotted in Fig. 3. D_{Li} values of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and the $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ were in the range $2.66 \times 10^{-14} - 9.97 \times 10^{-9}$ and $3.81 \times 10^{-13} - 4.02 \times 10^{-8}$ respectively during the discharge. D_{Li} values were at lowest end in capacity range of 30 mAh/g and 75 mAh/g.

Fig. 3. The calculated D_{Li} from the GITT data for $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_{0.99}Ni_{0.46}Mn_{1.56}O_4$ on discharging.

These regions correspond to phase transition regions (from cubic 1 to cubic 2 and cubic 2 to cubic 3), which were further studied by synchrotron based *in-situ* XRD. Overall lithium diffusion coefficient values in $Li_{0.99}Ni_{0.46}Mn_{1.56}O_4$ are larger than that of $LiNi_{0.5}Mn_{1.5}O_4$, i.e.; lithium ions can easily move in the $Li_{0.99}Ni_{0.46}Mn_{1.56}O_4$ host structure as compared to ordered $LiNi_{0.5}Mn_{1.5}O_4$ spinel structure. The results provided by GITT analysis support the assumption that faster lithium ion diffusion in the $Li_{0.99}Ni_{0.46}Mn_{1.56}O_4$ cathode material results in the improved rate capability.

Even though both the samples belong to spinel family which has three dimensional lithium diffusion paths but lithium diffusivity in these samples is comparable with $LiCoO_2$ (10^{-11} to 10^{-13} cm^2/s) which has layered crystal structure with two dimensional lithium diffusion paths.²⁴ In layered structures lattice parameter along *c* direction has profound effect on lithium diffusivity especially when lithium content goes below $x = 0.4$ in Li_xCoO_2 . But in spinels, lithium diffusion coefficient is almost independent from lithium content in the structure. Lithium diffusivity drops significantly in the both the ordered $LiNi_{0.5}Mn_{1.5}O_4$ and disordered $Li_{0.99}Ni_{0.46}Mn_{1.56}O_4$ cathode materials around capacity range of 30 and 70 mAh/g mainly due to phase transitions in spinel structure associated with Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} .

3.3. *In situ* X-ray diffraction analysis

The structural changes of $LiNi_{0.5}Mn_{1.5}O_4$ and $Li_{0.99}Ni_{0.46}Mn_{1.56}O_4$ cathode materials were studied by *in-situ* XRD. Fig. 4 shows *in-situ* XRD patterns of

Fig. 4. (a) First charge/discharge curves of the stoichiometric $LiNi_{0.5}Mn_{1.5}O_4$ at $C/3$ and (b) corresponding *in-situ* XRD patterns.

$LiNi_{0.5}Mn_{1.5}O_4$ sample during constant current cycling at $C/3$ rate. Bragg reflections were indexed based on a cubic unit cell. The scan numbers marked in Fig. 4(b) correspond to the numbers marked on the charge and discharge curve in Fig. 4(a). The $LiNi_{0.5}Mn_{1.5}O_4$ has two phase transitions from cubic 1 to cubic 2 and cubic 2 to cubic 3 during the charge; these phases are clearly identified in Fig. 4(b). Three cubic phases can be observed from scans 1 to 41, 31 to 69 and 55 to 69. There are two phase coexistence regions from scans 31 to 41 and 55 to 69. Similarly discharge process also has three distinct cubic phase and two phase coexistence regions. Mainly these distinct cubic and two phase co-existent regions lie between 4.5-4.9 V of charge/discharge potential and it has already been shown that Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} transitions correspond to this potential range.^{25,26} So, these three cubic phases can be assigned to spinel structures with Ni^{2+} , Ni^{3+} and Ni^{4+} oxidation states.

Fig. 5. (a) First charge/discharge curves of the stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 1C and (b) corresponding *in-situ* XRD patterns.

Fig. 5 shows the first cycle charge and discharge curve of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 1C rate during *in-situ* XRD experiments, and corresponding *in-situ* XRD patterns. Clearly three distinct cubic phases and two-phase coexistence regions can be observed. Contrary to the case of C/3 rate, phase transition from cubic 2 to cubic 3 during the charge did not occur completely.

The coexistence of two-phases during electrochemical cycling usually causes lattice mismatch, high stress and strain on structure that compromises the stability of the systems, especially at high rate. Thus capacity of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ fades quickly and its rate capability is reduced. This is in good accordance with the experimental results of electrochemical cycling performance. It can be speculated that phase boundary between these cubic phases provides resistance to ionic transport and lithium diffusion coefficient is low in ordered spinel as compared to disordered sample.

Fig. 6 shows first cycle charge/discharge curves of

Fig. 6. (a) First charge/discharge curves of the $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ at C/3 and (b) corresponding *in-situ* XRD patterns.

$\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ at C/3 rate and corresponding *in-situ* XRD patterns. Unlike the stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the positions of Bragg peaks of $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ shifted continuously from scans 1 to 47 throughout the charge process and showed a pseudo one phase behavior during transformation from cubic 1 to cubic 2. Separate cubic 3 phase was observed from scans 35 to 53 during the charge and two phase coexistence region existed only from scans 35 to 47. The discharge process was similar to the charge process. At 1C rate, XRD patterns around rest region were not available due to beam dump but a pseudo one phase behavior of the phase transition from cubic 1 to cubic 2 and two phase coexistence region of cubic 2 and cubic 3 during the charge and discharge can be clearly observed in Fig. 7 namely due to Ni^{3+} to Ni^{4+} transition. Phase transitions during charge and discharge cycles were completely reversible in these 5V spinel cathode materials, unlike the 4V class spinels in which residual peaks of cubic 2 and

Fig. 7. (a) First charge/discharge curves of the $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ at 1C and (b) corresponding *in-situ* XRD patterns.

cubic 3 were left after electrochemical cycling.²⁷⁾

The structural changes in $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ showed a sharp contrast in behavior as compared to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ due to pseudo one phase mechanism. These results interpret that the physical strains and loss of cohesion within particles resulting from these phase transitions are less severe in the $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$, as compared to that of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Therefore, $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ cathode material exhibited better cycling stability and rate capability.

Lattice parameters of ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel showed evolution of a second cubic phase other than solid solution phase after achieving one third of charge capacity and a third cubic phase near the end of charge as shown in Fig. 8. The lattice parameters of the $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ changed slowly between cubic 1 and cubic 2, while those of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has the jumping step region because of two phase reaction mechanism. However, at low rate of C/3, it seems that lithium ion movement was slow enough to complete the phase transitions among three cubic phases, which, in turn, gave rise to relatively good cycling performance. At high rate of 1C cubic 3 phase appeared over a shorter capacity range. Non-stoichiometric $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ contains Mn^{3+} (0.65 Å) which is slightly bigger in size as compared to Mn^{4+} (0.54 Å).²⁸⁾ So, presence of Mn^{3+} in the unit increases the lattice parameters of non-stoichiometric $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$

Fig. 8. Comparison of variation in lattice parameters of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{Li}_{0.99}\text{Ni}_{0.46}\text{Mn}_{1.56}\text{O}_4$ during charge/discharge cycling at C/3 and 1C rate.

as compared to stoichiometric one from 8.175 to 8.180 Å in discharged state.²⁹⁾ In fully charged state unit cell size is same because Mn exists as Mn⁴⁺ in both the samples.

4. Conclusions

In this study structural changes and electrochemical properties of Li_{0.99}Ni_{0.46}Mn_{1.56}O₄ (Fd $\bar{3}$ m) cathode material were studied comparatively with stoichiometric LiNi_{0.5}Mn_{1.5}O₄ (P4₃32) sample by electrochemical tests and synchrotron based *in-situ* XRD and GITT experiments. Non-stoichiometric Li_{0.99}Ni_{0.46}Mn_{1.56}O₄ showed better cycling performance especially at high rate of 1C. GITT measurements showed that average value of D_{Li} in LiNi_{0.5}Mn_{1.5}O₄ and the Li_{0.99}Ni_{0.46}Mn_{1.56}O₄ are between 4.36×10^{-10} to 4.15×10^{-9} . From this result, it can be concluded that faster lithium ion diffusion in the Li_{0.99}Ni_{0.46}Mn_{1.56}O₄ cathode results in improvement of rate capability. Structural changes during cycling were recorded at C/3 and 1C rate. *In-situ* XRD results reveal that non-stoichiometric spinel cathode, Li_{0.99}Ni_{0.46}Mn_{1.56}O₄ has pseudo one phase behavior between cubic 1- cubic 2 phases and one region of two phase coexistence between cubic 2- cubic 3 phases. Whereas LiNi_{0.5}Mn_{1.5}O₄ has three distinguished cubic phases in which two regions of two phase coexist between cubic 1- cubic 2 and cubic 2- cubic 3 phases which induce much greater stain and stress during cycling and degrade the cycling performance.

Acknowledgement

This work was supported by the IT R&D program (KI0018-10039182, 10041856) of the KEIT funded by the Ministry of Knowledge Economy. This work was also supported by the Fundamental R&D Program for Technology of World Premier Materials and Energy Efficiency & Resources (2010T100200295) of Ministry of Knowledge Economy. This work was partly supported by the National Research Foundation funded by the Korean Government (MEST: NRF-2010-0029065 & R31-2008-10029).

References

1. K. Mizushima, P. C. Jones, P. C. Wiseman and J. B. Goodenough, *Mater. Res. Bull.*, **15**, 783 (1980).
2. K. Ozawa, *Solid State Ionics*, **69**, 212 (1994).
3. B. Huang, Y.-I. Jang, Y.-M. Chiang and D. R. Sadoway, *J. Applied Electrochemistry*, **28**, 1365, (1998).
4. R. J. Gummow, A. de Kock and M. M. Thackeray, *Solid State Ionics*, **69**, 59, (1994).
5. D. I. Siapkis, C. L. Mitsas, I. Samaras and K. M. Paraskevopoulos, *J. Power Sources*, **72**, 22, (1998).
6. M. M. Doeff, A. Anapolsky, L. Edman, T. J. Richardson and L. C. De Jonghe, *J. Electrochemical Society*, **148**, A230, (2001).
7. B. J. Hwang, R. Santhanam and S. G. Hu, *J. Power Sources*, **108**, 250 (2002).
8. I. Yamada, T. Abe, Y. Iriyama and Z. Ogumi, *Electrochem. Commun.*, **5**, 502 (2003).
9. T. Ohzuku, M. Kitagawa and T. Hirai, *J. Electrochem. Soc.*, **137**, 769 (1990).
10. M. M. Thackeray, *Prog. Solid State Chem.*, **1**, 25 (1997).
11. S. Kobayashi, I. R. M. Kottagoda, Y. Uchimoto and M. Wakihara, *J. Mater. Chem.*, **14**, 1843 (2004).
12. F. K. Shokoohi, J. M. Tarascon and B. J. Wilkens, *J. Appl. Phys.*, **59**, 1260 (1991).
13. K. H. Hwang, S. H. Lee and S. K. Joo, *J. Electrochem. Soc.*, **141**, 3296 (1994).
14. S. H. Park, K. S. Park, Y. K. Sun and K. S. Nahm, *J. Electrochem. Soc.*, **147**, 2116 (2000).
15. A. D. Pasquier, A. Blyr, P. Courjal, D. Larcher, G. Amatucci, B. Gernand and J. M. Tarascon, *J. Electrochem. Soc.*, **146**, 428 (1999).
16. D. H. Jang, Y. J. Shin and S. M. Oh, *J. Electrochem. Soc.*, **143**, 2204 (1996).
17. Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao and J. R. Dahn, *J. Electrochem. Soc.*, **144**, 205 (1997).
18. T. Ohzuku, S. Takeda and M. Iwanaga, *J. Power Sources*, **81-82**, 90 (1999).
19. K. Amine, H. Tukamoto, H. Yasuda and Y. Fujita, *J. Electrochem. Soc.*, **143**, 1607 (1996).
20. A. N. Mansour, C. A. Melendres, *J. Phys. Chem. A*, **102**, 65 (1998).
21. S.-T. Myung, S. Komaba, N. Kumagai, H. Yashiro, H.-T. Chung and T.-H. Cho, *Electrochim. Acta*, **47**, 2543 (2002).
22. M. Kunduraci, J. F. Al-Sharab and G. G. Amaucci, *Chem. Mater.*, **18**, 3585 (2006).
23. Q.-C. Zhuang, T. Wei, L.-L. Du, Y.-L. Cui, L. Fang and S.-G. Sun, *J. Phys. Chem. C*, **114**, 8614 (2010).
24. C. H. Chen, E. M. Kelder and J. Schoonman, *J. Mat. Sci. Lett.*, **16**, 1967 (1997).
25. T. Yang, N. Zhang, Y. Lang and K. Sun, *Electrochimica Acta*, **56**, 4058 (2011).
26. B. Markovsky, Y. Talyossef, G. Salitra and S. Choi, *Electrochem. Commun.*, **6**, 821 (2004).
27. K. Y. Chung, H. S. Lee, W.-S. Yoon, J. McBreen and X.-Q. Yang, *J. Electrochem. Soc.*, **153**, A774 (2006).
28. S. H. Park, S.-W. Oh, S. H. Kang, I. Belharouk, K. Amine and Y.-K. Sun, *Electrochimica Acta*, **52**, 7226 (2007).
29. R. Santhanam and B. Rambabu, *J. Power Sources*, **195**, 5442 (2010).