

Preparation and cycle performance at high temperature for $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4

S.-B. Kim · K. J. Lee · W. J. Choi · W.-S. Kim ·
I. C. Jang · H. H. Lim · Y. S. Lee

Received: 8 March 2009 / Revised: 21 May 2009 / Accepted: 26 May 2009 / Published online: 23 June 2009
© Springer-Verlag 2009

Abstract $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 was synthesized by a co-precipitation method. It consisted of the parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ as the core and the LiFePO_4 as the coating material, with an average particle diameter of 500 nm. The LiFePO_4 -coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ showed no large initial capacity drop in the first cycle, which generally occurred with cathode materials bearing inactive coating layers such as Al_2O_3 , ZnO , and MgO . Furthermore, it presented a remarkably improved cycle retention rate of over 89% until 400 cycles at 50°C. We suggest that the LiFePO_4 coating technique is a very effective tool to improve the cycle performance of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ at high temperatures.

Keywords $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ · $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 · High temperature performance · Cathode material · Lithium secondary battery

Introduction

The commercial lithium secondary battery with high energy density and good cyclability has been extensively studied as a power source for portable electronics. LiCoO_2 is still

used for these secondary batteries, however, it has many problems such as high cost, environmental aspects, and low practical capacity. The most prospecting next cathode material for these portable devices is $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ and given its high energy density and good cyclability, it can easily satisfy the need for portable devices such as wearable PCs, PMPs, and Net-book computers [1, 2].

Nevertheless, although $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ has a practical capacity larger than LiCoO_2 , exothermic decomposition of the oxide is highly possible, releasing oxygen, and giving a poor cycle retention rate and cell failure at high temperatures. It is well known that the main difficulty in developing a large-scale battery using $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ cathode material with acceptable safety and cycle performance.

Many research groups have adopted coating processes to improve the battery performance of LiCoO_2 or $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ materials, using inactive coating powders such as Al_2O_3 , ZnO , and MgO [3–7]. However, these coating materials hinder diffusion of the lithium ions within the coating layers, resulting in small capacity drops and undesirable side-reactions with the electrolyte during long cycling processes.

Recently, we successfully synthesized a new type of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material using a co-precipitation method in order to reduce the amount of the Co ion resulting in cost reduction. Additionally, we tried forming a coating layer on the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material using LiFePO_4 powder, allowing for facile movement of the lithium ions in the coating layer as well as the core portion with an electrolyte liquid, a process typically limited during high temperature cycling.

We report herein the synthesis and improved cycle performance of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 at high temperature, prepared by a co-precipitation method for the lithium secondary batteries.

S.-B. Kim · K. J. Lee · W. J. Choi · W.-S. Kim
Daejung EM Co. LTD.,
Incheon 405-820, South Korea

I. C. Jang · H. H. Lim · Y. S. Lee (✉)
Faculty of Applied Chemical Engineering,
Chonnam National University,
Gwang-ju 500-757, South Korea
e-mail: leeys@chonnam.ac.kr

Experimental

Firstly, $(\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3})\cdot(\text{OH})_2$ was synthesized from $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ (Jinlin Jien, China), $\text{MnSO}_4\cdot \text{H}_2\text{O}$ (Chuo Denki, Japan), and $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (Jinlin Jien, China) using a conventional co-precipitation method [8, 9]. A stoichiometric amount of each material (Ni:Co:Mn=0.5:0.2:0.3) was dissolved in purified, ion-exchanged water to prepare an aqueous metal solution. The reaction was performed for 48 h to obtain a slurry containing a composite metal hydroxide with uniform size. The slurry was washed and filtered using a centrifugal separation filter such that a pH of a filtered liquid was 9.0 or less, and the obtained composite metal hydroxide powder was dried at 120°C for 24 h or more to generate a composite metal hydroxide. After that, it was heated at 300°C for 12 h and mixed with the lithium salt at a stoichiometric ratio of 1:1.1. The mixture was calcined at 950°C for 24 h and recalined at 500°C for 24 h in order to obtain the resulting $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material.

A cathode material was prepared using the obtained $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ as the coated material and an olivine LiFePO_4 , with an average particle diameter D50 of 500 nm, as the coating material. Pure LiFePO_4 material was synthesized from Li_2CO_3 (Sigma-Aldrich, USA), $\text{FeC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (Aldrich, USA), and $(\text{NH}_4)_2\text{HPO}_4$ (Sigma-Aldrich, USA) using a solid-state method. A stoichiometric amount of each materials was ground and calcined at 400°C for 1.5 h and then at 660°C for 2.5 h in an Ar atmosphere using a tubular furnace. Next, optimum content (1.5 wt.%) of the LiFePO_4 corresponding to a coating material were thoroughly mixed with the composite metal oxides using a dry coating system (NOB-130, Hosokawa micron Ltd., Japan). The mixture was treated with a rotation rate of 2,700 rpm for 3 min and heated at 500°C for 4 h to prepare a core-shell type cathode material. Particle morphology and size distribution of the resulting compound were observed using a scanning electron microscope (SEM, HP-8564E, USA) and particle size analysis system (Mastersizer 2000E, Malvern Instrument, UK), respectively.

Electrochemical characterizations were performed using a CR2032 coin cell for electrochemical analysis and an aluminum pouch type cell for long-term cycling, respectively. For the coin type cell, the cathode was fabricated with 20 mg of accurately weighed active material and 12 mg of conductive binder (8 mg of teflonized acetylene black and 4 mg of graphite). It was pressed on 200 mm² stainless steel mesh used as the current collector under a pressure of 300 kg/cm² and dried at 130°C for 5 h in an oven. For the pouch type cell, the slurry was prepared by mixing a cathode-active material in an *N*-methyl pyrrolidone solution, into which teflonized acetylene black as a

conductive material and polyvinylidene fluoride as a binder were dissolved. The mass ratio between the cathode material, conductive material, and binder material was 92:4:4. The test cell was made of a cathode and a lithium metal (or graphite) anode separated by a porous polypropylene film (Celgard 3401). The electrolyte used was a mixture of 1.2 M LiPF_6 -ethylene carbonate/diethyl carbonate (1:3 by vol., Techno Semichem Co., Ltd, Korea). The charge and discharge current density was 0.2 C with a cut-off voltage of 2.5 to 4.3 V at room (25°C) and high (50°C) temperatures.

Results and discussion

The parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material in this study showed a XRD pattern of a hexagonal structure with a space group R3m as shown in Fig. 1. It was confirmed that $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 also presented a well-developed XRD pattern of a hexagonal structure without any distinct peaks, which may be due to the low amount (1.5 wt.%) of coating material has been taken and the coated material does not induce any impurities. The lattice constants of the parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material were: $a=2.8721\text{Å}$ and $c=14.2576\text{Å}$. These values were similar to those previously reported [10]. $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 showed slightly different values ($a=2.8712\text{Å}$ and $c=14.2596\text{Å}$) to those of the parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$. Although there is a small decrease in the *a*-axis, they show no remarkable difference in the lattice constants between two materials.

Figure 2 shows the scanning electron microscopy image of the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 . This material presented a typical particle morphology synthesized by a co-precipitation method that showed a perfect spherical type with a narrow particle distribution. The average particle size of the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material

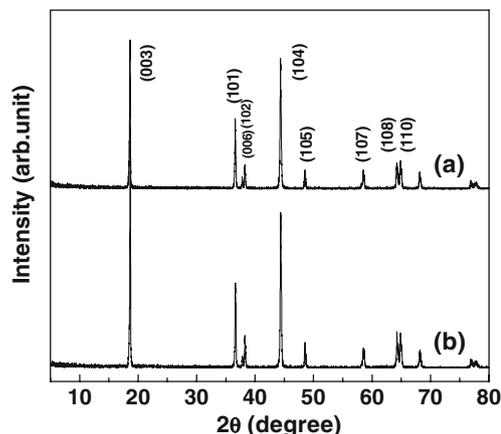
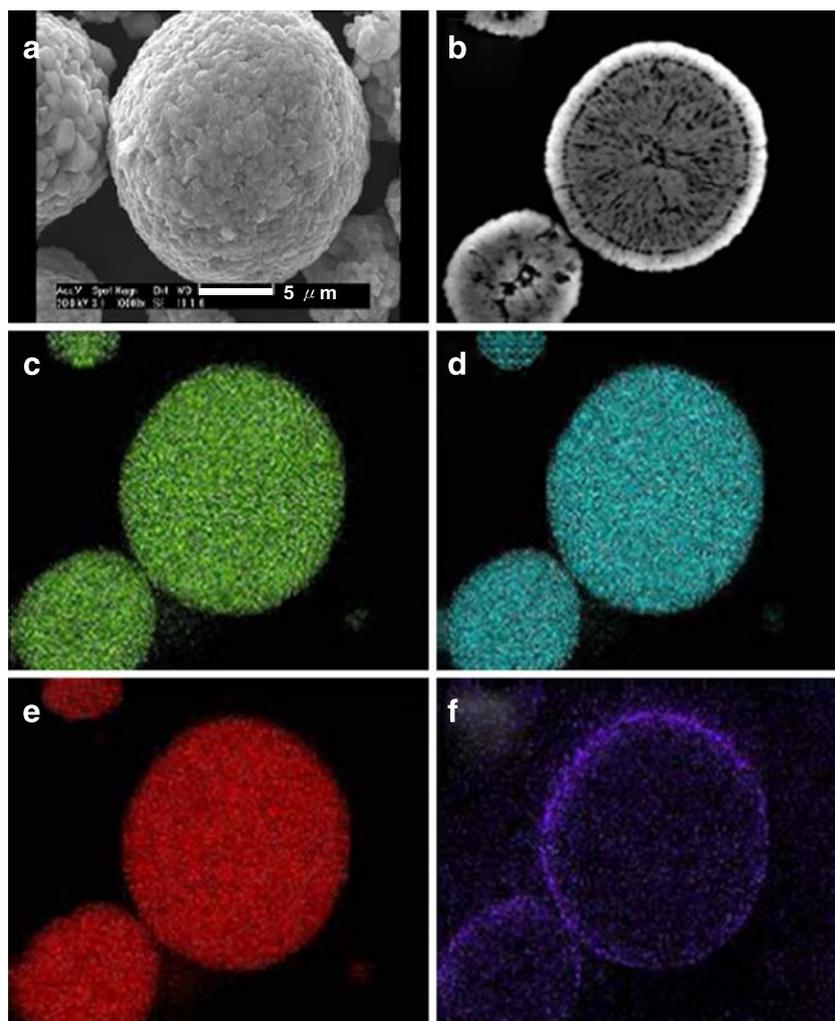


Fig. 1 XRD patterns of (a) parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ and (b) $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with 1.5 wt.% LiFePO_4

Fig. 2 **a** SEM image of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with 1.5 wt.% LiFePO_4 , **b** intersection of core-shell type of coated material, **c** mapping of Co, **d** mapping of Ni, **e** mapping of Mn, and **f** mapping of Fe



was $10\mu\text{m}$ with a primary particle size of 500–800 nm. Figure 2b shows the cross-sectional mapping of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 . The LiFePO_4 material used in the coating process had a small particle size of 500 nm with an even particle morphology, providing it with a high surface area for improvement of coating efficiency. Figure 2c–f present the distribution of the constituent metal ions in the core-shell $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 . All metal ions (Ni, Co, Mn, and Fe) were uniformly distributed in the all range of particles and were well coated by the LiFePO_4 .

Figure 3 shows the results of the electrochemical characterization of the cells of the Li/parent and the Li $[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 . The test conditions were a current density of 0.4 mA/cm^2 (0.2 C) between 2.5 and 4.3 V at room temperature. The Li/parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cell exhibited typical electrochemical behavior with a monotonous voltage plateau in the first charge/discharge process. This cell showed a high initial charge capacity of more than 181 mAh/g; however, it presented a reduced discharge capacity of 163 mAh/g. It is

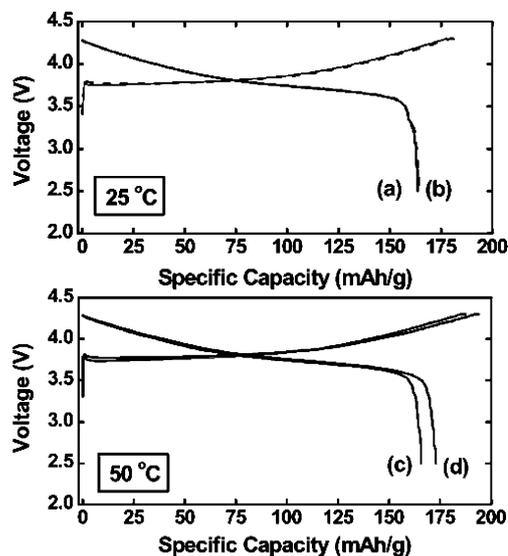


Fig. 3 Initial charge/discharge curves of Li/ (a) parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$, (b) 1.5 wt% LiFePO_4 -coated cells at 25°C , (c) parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$, and (d) 1.5 wt% LiFePO_4 -coated cells at 50°C .

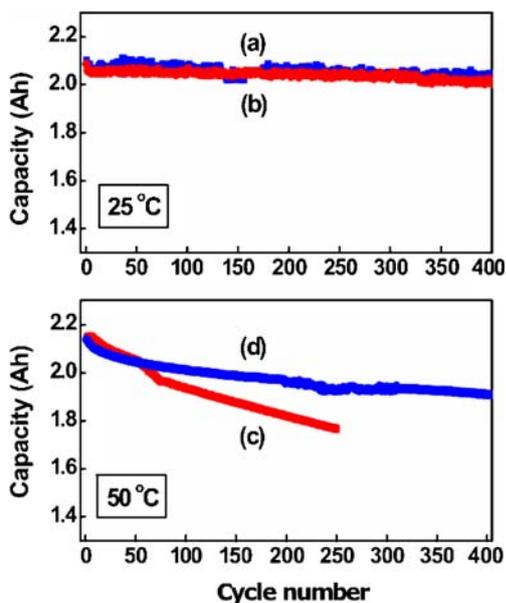


Fig. 4 Cycle performance of (a) parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$, (b) 1.5 wt% LiFePO_4 -coated cells at 25°C , (c) parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$, and (d) 1.5 wt% LiFePO_4 -coated cells at 50°C

well known that the irreversible capacity in the first charge/discharge process results from structural changes of the materials and decomposition of the electrolytes at high potential [11, 12]. Conversely, the $\text{Li}/\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cell coated with LiFePO_4 as shown in Fig. 3(b) presents no capacity drop as shown in previous reports [3–7] and still exhibits a high discharge capacity of 163 mAh/g in the first discharge process. It is the suggestion of the authors that a high initial discharge capacity of the coated material resulted from the uniform LiFePO_4 coating layer that allows for facile immigration of the lithium ions from the anode material as LiFePO_4 is an electrically active material against inactive coating materials such as Al_2O_3 , ZnO , and MnO [3–7].

Figure 4 presents the results of the cycle characterizations of the parent and coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cells at room (25°C) and high temperature (50°C). The charge/discharge current density was 0.4 mAh/g with a cut-off voltage of 2.5 to 4.2 V. As described before, it is well known that the $\text{Li}[\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}]\text{O}_2$ system has serious problems regarding cycle retention rate and thermal stability in high-temperature environments. We suggest that high-temperature battery performance is a very important factor to succeed in the market of various portable devices and electric vehicles that utilize the $\text{Li}[\text{Ni-Co-Mn}]\text{O}_2$ system. As shown in Fig. 4(c), parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cell at high temperature shows a very severe capacity loss until 250 cycles; furthermore, the capacity decline is accelerated after this point and the cycle retention after 250 cycles is only 82% at 50°C . However, the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ coated with LiFePO_4 cell presents excellent cycle behavior until 400 cycles with a

retention rate over 89% under the same test conditions. The authors estimate that the difference in cycle retention after 400 cycles is over 15%, although it is not an exact value because of the cell failure of parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cell after the 250th cycle. Conversely, it suggests that the LiFePO_4 coating for the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ material is one of the very effective tools to improve cell stability in long-term cycling. Moreover, the enhancement of the thermal and cell stability of the $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ cell coated with LiFePO_4 was found to be remarkable and will be reported elsewhere in the near future.

Conclusions

Parent $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ and LiFePO_4 -coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ materials were synthesized by a co-precipitation method. The LiFePO_4 -coated $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ showed a high initial discharge capacity over 163 mAh/g in the first cycle without capacity drop at room temperature. Furthermore, it presented a remarkably improved cycle retention rate over 89% until 400 cycles at high temperature (50°C). We concluded that the LiFePO_4 coating technique is a very effective tool for improving cycling performance of $\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$ at high temperature environment.

Acknowledgements This work was supported by a grant (Code #: 10028974) from the Industry R&D Programs of the Ministry of Knowledge Economy, Korea

References

- Jang SB, Kang SH, Amine K, Bae YC, Sun YK (2005) *Electrochim Acta* 50:4168–4173. doi:10.1016/j.electacta.2005.01.037
- Kim Y, Kim HS, Martin SW (2006) *Electrochim Acta* 52:1316–1322. doi:10.1016/j.electacta.2006.07.033
- Kweon HJ, Park JJ, Seo JW, Kim GB, Jung BH, Lim HS (2004) *J Power Sources* 126:156–162. doi:10.1016/j.jpowsour.2003.08.037
- Kannan AM, Manthiram A (2002) *Electrochem Solid St* 5:A167–A169. doi:10.1149/1.1482198
- Sun YK, Lee YS, Yoshio M, Amine K (2002) *Electrochem Solid St* 5:A99–A102. doi:10.1149/1.1465375
- Sun YK, Hong KJ, Prakash J (2003) *J Electrochem Soc* 150:A970–A972. doi:10.1149/1.1580819
- Wang ZX, Liu LJ, Chen LQ, Huang XJ (2002) *Solid State Ion* 148:335–342. doi:10.1016/S0167-2738(02)00071-1
- Kim WS, Kim SB, Heo YJ, Koh ST (2008) *IMLB* 2008(277)
- Lee MH, Kang YJ, Myung ST, Sun YK (2004) *Electrochim Acta* 50:939–948. doi:10.1016/j.electacta.2004.07.038
- Liu Z, Yu A, Lee JY (1999) *J Power Sources* 81–82:416–419. doi:10.1016/S0378-7753(99)00221-9
- Zhang ZR, Gong ZL, Yang Y (2004) *J Phys Chem B* 108:17546–17552. doi:10.1021/jp046980h
- Li J, Zhang ZR, Guo XJ, Yang Y (2006) *Solid State Ion* 177:1509–1516. doi:10.1016/j.ssi.2006.03.055