

Short communication

## Effect of carbon on the electronic conductivity and discharge capacity LiCoPO<sub>4</sub>

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### Abstract

The effect of added carbon (3, 5 and 10 wt.%) on the electronic conductivity and discharge capacity of LiCoPO<sub>4</sub> was investigated. It was found after heat-treatment that the samples consisted of a LiCoPO<sub>4</sub> majority phase and Co<sub>2</sub>P second phase. The added carbon was consumed reducing the LiCoPO<sub>4</sub> surface layers to Co<sub>2</sub>P. The electronic conductivity increased as the amount of the Co<sub>2</sub>P phase increased. It was observed that the discharge capacity increased with increased Co<sub>2</sub>P content to ~4–5 wt.%, after which the capacity rapidly decreased with increasing Co<sub>2</sub>P content. The increase in discharge capacity is likely a result of the increase in electronic conductivity. At higher Co<sub>2</sub>P volume fractions the presence of the electrochemically inert Co<sub>2</sub>P phase causes decreased capacity by: (1) reducing the amount of LiCoPO<sub>4</sub> present and (2) preventing Li<sup>+</sup>-ions from entering/leaving LiCoPO<sub>4</sub>, even though the highest values of electronic conductivity were exhibited.

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### 1. Introduction

In order to increase the energy density of Li-ion batteries, cathode materials having higher voltage and capacity than the current LiCoO<sub>2</sub> cathode ( $V \sim 3.7$ ; capacity:  $\sim 140 \text{ mAh g}^{-1}$  [1]) are needed. One such new material that will lead to an increase in both voltage and capacity compared to LiCoO<sub>2</sub> is LiCoPO<sub>4</sub>. LiCoPO<sub>4</sub> ( $V \sim 4.7$ ; capacity;  $\sim 170 \text{ mAh g}^{-1}$ ) is predicted to have  $\sim 1.6$  times the specific energy of LiCoO<sub>2</sub> [2–4]. In order for LiCoPO<sub>4</sub> be used as a cathode it is essential that LiCoPO<sub>4</sub> exhibit good rate capability, which is a function of both of its electronic and ionic conductivity.

Recent studies of LiCoPO<sub>4</sub> [5] have shown that it exhibits low electronic conductivity ( $< 10^{-9} \text{ S cm}^{-1}$ ). Low electronic conductivity has also been observed in another member of the transition metal orthophosphate family, the more widely investigated LiFePO<sub>4</sub> [6–13]. Two common methods have been used to increase the electronic conductivity of LiFePO<sub>4</sub>. The first method involves doping on either the Li<sup>+</sup> or Fe<sup>2+</sup> site with aliovalent elements [8,10–12]. Accordingly, this leads to an increase in the concentration of electronic defects (i.e., electrons/holes) as

a result of charge compensation for the aliovalent elements and hence, an increase in electronic conductivity [9]. The second method is coating the particle surface with an electronic conductor. In this case the most commonly used material is carbon [6,7,14–16]. For LiFePO<sub>4</sub>, it has been shown that the addition of carbon increased the electronic conductivity from  $10^{-9} \text{ S cm}^{-1}$  for pure LiFePO<sub>4</sub> to about  $10^{-5}$  to  $10^{-3} \text{ S cm}^{-1}$  for carbon contents between 3 and 10 wt.% [17,18]. In certain cases, it has been observed that carbon additions heated under a reducing atmosphere resulted in the formation of in situ high conductive Fe<sub>2</sub>P/Fe<sub>3</sub>P layer on the surface [13,17,19,20]. In this, case electronic conductivities as high as  $\sim 10^{-1} \text{ S cm}^{-1}$  were exhibited [13,17,19]. Both carbon and metal phosphide coatings resulted in an increase in the discharge capacity for LiFePO<sub>4</sub> compared to the uncoated material, primarily as a result of the increase in electronic conductivity.

It is the purpose of this paper to investigate if the addition of carbon can be used to increase electronic conductivity and discharge capacity of LiCoPO<sub>4</sub>.

### 2. Experimental

Carbon additions to LiCoPO<sub>4</sub> were accomplished by mixing stoichiometric amounts of Li<sub>2</sub>CO<sub>3</sub>, CoC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O and

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$\text{NH}_4\text{H}_2\text{PO}_4$  along with a high surface carbon (Black pearls 2000, Cabot Corporation with a surface area of  $\sim 1500 \text{ m}^2 \text{ g}^{-1}$ ) and then ball milling this mixture for 4 h. Three different carbon contents were used; 3, 5 and 10 wt.%. These carbon contents were chosen because, it has been shown that between 5 and 10 wt.% carbon a maximum in the specific discharge capacity of  $\text{LiFePO}_4$  was achieved [21,22]. After mixing, the powders were given a two-step heat-treatment. In the first step powders were heated at  $375^\circ\text{C}$  for 10 h. They were then crushed and ground and pressed into a pellet. In the second step the pellet was fired at  $675^\circ\text{C}$  for 24 h. Both heat-treatments were conducted under a high purity argon atmosphere ( $\text{PO}_2 \approx 5 \times 10^{-5} \text{ atm}$ ). The  $\text{PO}_2$  was measured using a zirconia sensor. The three samples were designated as: BM-3 (3 wt.% carbon), BM-5 (5 wt.% carbon) and BM-10 (10 wt.% carbon). To insure a sample with 0 wt.% carbon a sample was prepared from precursors containing no carbon ( $\text{Li}_3\text{PO}_4$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) [13]. In this case stoichiometric amounts of the powders were mixed in a jar mill for 2 h. After mixing, the powders were given the same two-step heat-treatment as for samples prepared from carbon precursors. This sample is designated as J-1.

All samples were first characterized by X-ray diffraction using  $\text{Cu K}\alpha$  radiation. The amount of any second phase(s) was estimated using Rietveld refinement (RIQAS software). The electronic conductivity was measured on sintered and polished pellets ( $\sim 12 \text{ mm}$  diameter and  $\sim 2 \text{ mm}$  thickness) using the two-point dc method [5]. Silver paste electrodes were applied to the top and bottom surfaces of the disk. A high impedance multimeter was used to measure the resistance at room temperature. Conductivity was calculated from the resistance and specimen dimensions. In addition,  $\text{Co}_2\text{P}$  powder (Alfa Aesar) was pressed into a pellet and then sintered at  $700^\circ\text{C}$  for 10 h under an  $\text{Ar} + 4 \text{ vol.}\% \text{ H}_2$  mixture, after which the electronic conductivity was determined. The carbon content of BM-3, BM-5 and BM-10 after final heat-treatment was determined using a combustion method (Galbraith Laboratories, Inc).

The first cycle discharge capacity of the  $\text{LiCoPO}_4$  cathode materials was determined using coin cells with metallic lithium as the anode. A typical cathode was prepared by mixing 78 wt.% active powders, 12 wt.% carbon and 10 wt.% polyvinylidene fluoride dissolved in *N*-methylpyrrolidinone. The mixture was coated onto an Al substrate. The cathodes were dried under vacuum at  $100^\circ\text{C}$  for 20 h. The electrolyte solution was 1 M  $\text{LiPF}_6$ :tetramethylene sulfone. Tetramethylene sulfone was used because of its high oxidative stability (around 5.8 V versus Li [23]). The  $\text{LiCoPO}_4$  cells were charged/discharged at room temperature between 3.5 and 5.3 V at a constant current density of  $50 \mu\text{A cm}^{-2}$  ( $\sim C/5$ , where the theoretical capacity  $\text{LiCoPO}_4 \sim 170 \text{ mAh g}^{-1}$ ). In addition, a  $\text{Co}_2\text{P}$  cathode (90 wt.%  $\text{Co}_2\text{P}$  and 10 wt.% binder) was prepared and charged/discharged at room temperature between 3.5 and 5.3 V at a constant current density of  $50 \mu\text{A cm}^{-2}$ .

### 3. Results and discussion

All  $\text{LiCoPO}_4$  samples (BM-3, BM-5 and BM-10) that were prepared with carbon were colored black, whereas the sam-

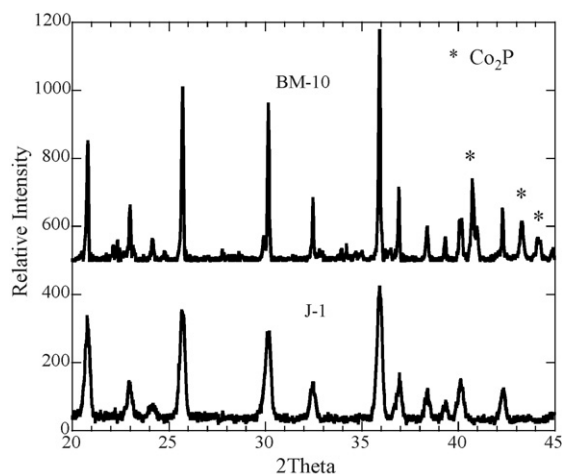


Fig. 1. X-ray diffraction patterns for samples J-1 and BM-10.

ple (J-1) prepared from precursors containing no carbon was purple.

X-ray diffraction patterns for samples J-1 and BM-10, over the  $2\theta$  range  $20\text{--}45^\circ$  are shown in Fig. 1. Rietveld refinement revealed that sample J-1 formed from non-carbon precursors was single-phase  $\text{LiCoPO}_4$  with an ordered olivine structure. Rietveld refinement revealed that sample BM-10 formed with 10 wt.% excess carbon was two-phase; consisting of a majority  $\text{LiCoPO}_4$  phase and a  $\text{Co}_2\text{P}$  second phase, indicated by the stars above these peaks in Fig. 1. Second phase  $\text{Co}_2\text{P}$  was also found for BM-3 and BM-5.  $\text{Co}_2\text{P}$  likely forms as a result of the carbothermal reduction of  $\text{LiCoPO}_4$  at particle surfaces during the high-temperature heat-treatment under a low oxygen partial pressure atmosphere. This result is in agreement with the results of Herle et al. [13], Arnold et al. [20], Kim et al. [19], Xu et al. [17], who have shown that for the case of Ni [13] and Fe [13,17,19,20] orthophosphates heated under low oxygen partial pressures in the presence of carbon from the precursors or intentionally added that metal phosphides formed along particle surfaces. The weight percent of  $\text{Co}_2\text{P}$  for BM-3, BM-5 and BM-10 determined by Rietveld refinement along with the carbon content after heat-treatment are listed in Table 1.

From Table 1, several important points are noted. Firstly, a comparison of the added carbon content to the final carbon content reveals that most of the added carbon has been consumed in reducing the  $\text{LiCoPO}_4$  surface layers to  $\text{Co}_2\text{P}$ . Secondly, as the carbon content increased the amount of  $\text{Co}_2\text{P}$  increased. The increase in the amount of metal phosphide with increasing carbon content is in good agreement with results of Arnold et al. [7] and Kim et al. [19] on  $\text{LiFePO}_4$ , who have shown that as

Table 1  
Composition of  $\text{LiCoPO}_4$  after heat-treatment

Sample ID	Added carbon (wt.%)	$\text{Co}_2\text{P}$ (wt.%)	Final carbon (wt.%)
J-1	0	0	0
BM-3	3	2	1
BM-5	5	4	2
BM-10	10	9	2

the amount of carbon increased the amount of  $\text{Fe}_2\text{P}$  increased. Thirdly, the total of the final carbon content plus  $\text{Co}_2\text{P}$  is greater than the initial added carbon content for BM-5 and BM-10. This result is consistent with the results of Wolfenstine et al. [4] on  $\text{LiCoPO}_4$ , who observed that using the same precursors as those used to prepare BM-3, BM-5 and BM-10, with no added carbon at slightly higher heat-treatment temperatures under the same low oxygen partial pressure atmosphere found  $\sim 1$  wt.%  $\text{Co}_2\text{P}$  and  $\sim 1$  wt.% carbon were present after heat-treatment. Thus, it is likely that the extra carbon in Table 1 comes from the carbon precursors.

The electronic conductivity of BM-3, BM-5 and BM-10 as function of  $\text{Co}_2\text{P}$  content is shown in Fig. 2. Also shown in Fig. 2 is the estimated electronic conductivity of single-phase  $\text{LiCoPO}_4$  (J-1) [5]. The electronic conductivity was plotted as a function of  $\text{Co}_2\text{P}$  instead of added carbon content since  $\text{Co}_2\text{P}$  is the dominant second phase remaining after heat-treatment. Plotting electronic conductivity against added carbon content would yield a similar curve. From Fig. 2 several important notes are noted. Firstly, the addition of the electronic conductive  $\text{Co}_2\text{P}$  phase ( $\sim 2 \text{ S cm}^{-1}$ ) to  $\text{LiCoPO}_4$  ( $\sim 10^{-15} \text{ S cm}^{-1}$  [5]) significantly increases its electronic conductivity. For example, the addition of 2 wt.%  $\text{Co}_2\text{P}$  increased the electronic conductivity of  $\text{LiCoPO}_4$  by a factor of greater than  $10^{10}$ . The results shown in Fig. 2 are in agreement with the results of Kim et al. [19] and Xu et al. [17], who have shown that as the amount of  $\text{Fe}_2\text{P}$  increased the electronic conductivity of  $\text{LiFePO}_4$  increased. For  $\text{LiCoPO}_4 + 9$  wt.%  $\text{Co}_2\text{P}$  (BM-10) the electronic conductivity  $\sim 4 \times 10^{-3} \text{ S cm}^{-1}$  is close to values obtained Herle et al. [13], Kim et al. [19] and Xu et al. [17] for  $\text{LiFePO}_4$  containing  $\text{Fe}_2\text{P}$ . Secondly, the electronic conductivity values for the BM-3, BM-5 and BM-10 are within the range of the commonly used cathodes ( $\text{LiCoO}_2 \sim 10^{-3} \text{ S cm}^{-1}$  [24] and  $\text{LiMn}_2\text{O}_4 \sim 10^{-5}$  to  $10^{-4} \text{ S cm}^{-1}$  [25]) in Li-ion batteries. Based on the increase in electronic conductivity for BM-3, BM-5 and BM-10 compared to J-1 it is expected that they would also exhibit a higher first cycle discharge capacity than sample J-1.

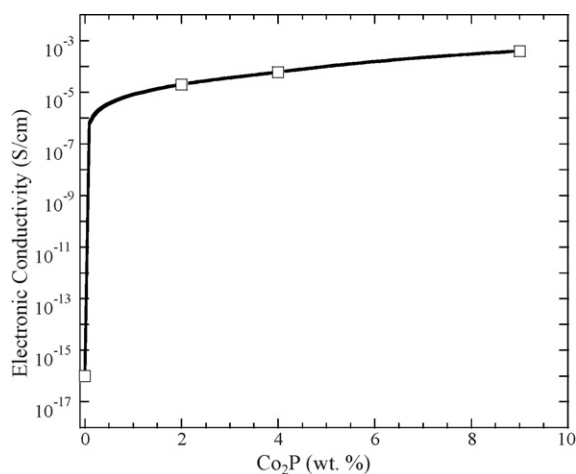


Fig. 2. Electronic conductivity vs. wt.%  $\text{Co}_2\text{P}$ . Data for pure  $\text{LiCoPO}_4$  is from [5].

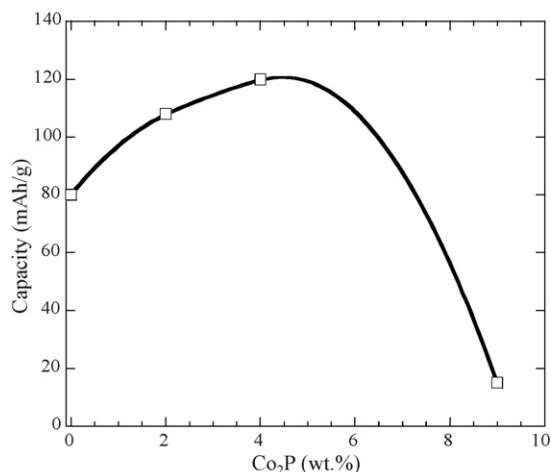


Fig. 3. First cycle discharge capacity vs. wt.%  $\text{Co}_2\text{P}$ .

The first cycle discharge capacity for J-1, BM-3, BM-5 and BM-10 plotted as a function of the amount of  $\text{Co}_2\text{P}$  is shown in Fig. 3. Plotting discharge capacity against added carbon content would yield a similar curve. From Fig. 3 it can be seen that capacity increases with increasing  $\text{Co}_2\text{P}$  content to  $\sim 4$ – $5$  wt.%, after which the capacity rapidly decreases with increasing  $\text{Co}_2\text{P}$  content. At  $\sim 4$ – $5$  wt.%  $\text{Co}_2\text{P}$  a maximum discharge capacity of  $\sim 120 \text{ mAh g}^{-1}$  is obtained. This is about a factor of  $\sim 1.5 \times$  higher compared to that obtained with no carbon ( $\sim 80 \text{ mAh g}^{-1}$ ). At the optimum  $\text{Co}_2\text{P}$  concentration  $\sim 70\%$  ( $120/170$ ) of the theoretical discharge capacity for  $\text{LiCoPO}_4$  could be obtained at a discharge rate of  $\sim C/5$ . The increase in discharge capacity is likely a result of the increase in the electronic conductivity (Fig. 2), associated with the conductive  $\text{Co}_2\text{P}$  on particles surfaces. It is also possible that part of the capacity increase is associated with the smaller particle size that results when second-phase carbon is added [4]. The trend shown in Fig. 3 that higher  $\text{Co}_2\text{P}$  contents lead to a decrease in capacity is in agreement with the results of Zhang et al. [21] on  $\text{LiFePO}_4$  with added carbon and the very recent results of Kim et al. [19] who investigated the effect of  $\text{Fe}_2\text{P}$  concentration, synthesized by the reduction of  $\text{LiFePO}_4$  by carbon, on the electronic conductivity and discharge capacity of  $\text{LiFePO}_4$ . Zhang et al. [21] observed an increase in discharge capacity of  $\text{LiFePO}_4$  with carbon additions up to  $\sim 10$  wt.% after which it decreased. At 15 wt.% added carbon the discharge capacity was less than 50% of the material with no added carbon. They suggested that the decrease in capacity at higher carbon contents was a result of: (1) reduction in the amount of crystalline  $\text{LiFePO}_4$  and the formation of an inactive  $\text{Fe}_2\text{P}$  phase. Kim et al. [19] observed that at discharge rates of  $\sim 1C$  that the discharge capacity of  $\text{LiFePO}_4$  increased from 0 wt.%  $\text{Fe}_2\text{P}$  to a maximum value at 8.3 wt.%  $\text{Fe}_2\text{P}$ , after which the capacity decreased with increasing  $\text{Fe}_2\text{P}$ . At 20 wt.%  $\text{Fe}_2\text{P}$  the discharge capacity was  $\sim 60\%$  of the pure material. Kim et al. [19] suggested that the increase in discharge capacity was a result of the increase in electronic conductivity associated with the  $\text{Fe}_2\text{P}$  phase, whereas the decrease in capacity at the higher  $\text{Fe}_2\text{P}$  concentrations was a result of the large amount of electrochemically inert  $\text{Fe}_2\text{P}$  phase present,

even though at these Fe<sub>2</sub>P concentrations the highest electronic conductivity values were exhibited. It is likely that a similar phenomenon is occurring with LiCoPO<sub>4</sub>. At higher Co<sub>2</sub>P volume fractions the presence of the electrochemically inert Co<sub>2</sub>P (the discharge capacity of Co<sub>2</sub>P in the range 5.3–3.5 V was ~0 mAh g<sup>-1</sup>) phase is to decrease capacity by: (1) reducing the amount of active LiCoPO<sub>4</sub> present and (2) preventing Li<sup>+</sup>-ions from entering/leaving LiCoPO<sub>4</sub>, even though the highest values of electronic conductivity are observed (Fig. 2). These results suggest that attempts to obtain high discharge capacities (>70% theoretical) for LiCoPO<sub>4</sub> by increasing electronic conductivity through the application of a surface coating with a high electronic conductor will not be successful, it will require an increase in bulk electronic conductivity, by such methods as aliovalent doping and an increase in Li-ion diffusivity, by reducing the particle size to the nanoscale.

#### 4. Conclusions

The effect of added carbon (3, 5 and 10 wt.%) on the electronic conductivity and discharge capacity of LiCoPO<sub>4</sub> was investigated. It was found that after heat-treatment the samples consisted of a LiCoPO<sub>4</sub> majority phase and Co<sub>2</sub>P second phase. The added carbon was consumed reducing the LiCoPO<sub>4</sub> surface layers to Co<sub>2</sub>P. As the amount of added carbon increased the amount of Co<sub>2</sub>P increased. The electronic conductivity increased as the amount of the high electronic conductive Co<sub>2</sub>P phase increased. For LiCoPO<sub>4</sub> + 9 wt.% Co<sub>2</sub>P an electronic conductivity value of ~4 × 10<sup>-3</sup> S cm<sup>-1</sup> was exhibited. This is at least a factor of 10<sup>10</sup> × greater than that for single-phase LiCoPO<sub>4</sub>. It was observed that the discharge capacity increased with increased Co<sub>2</sub>P content to ~4–5 wt.%, after which the capacity rapidly decreased with increasing Co<sub>2</sub>P content. At ~4–5 wt.% Co<sub>2</sub>P a maximum discharge capacity of ~120 mAh g<sup>-1</sup> is obtained. This is about a factor of ~1.5 × higher compared to that obtained with no carbon (~80 mAh g<sup>-1</sup>). The increase in discharge capacity is most likely is a result of the increase in the electronic conductivity due to the presence of Co<sub>2</sub>P. At higher Co<sub>2</sub>P volume fractions the presence of the electrochemically inert Co<sub>2</sub>P phase is to decrease capacity by: (1) reducing the amount of LiCoPO<sub>4</sub> present and (2) preventing Li<sup>+</sup>-ions from entering/leaving LiCoPO<sub>4</sub>, even though the highest values of electronic conductivity are observed. The results of this study suggest that increasing electronic conductivity by surface coating will not lead to high

discharge capacities (close to theoretical) for LiCoPO<sub>4</sub>. In order to achieve these high values of discharge capacity for LiCoPO<sub>4</sub> an increase in bulk electronic conductivity and Li-ion diffusivity is required.

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#### References

- [1] G.M. Ehrlich, in: D. Linden, T.B. Reddy (Eds.), Handbook of Batteries, third ed., McGraw-Hill, New York, 2002, p. 35.1.
- [2] P. Deniard, A.M. Dulac, X. Rocquefelte, V. Grogorova, O. Lebacqz, A. Pastural, S. Jobic, J. Chem. Phys. Solids 65 (2004) 229.
- [3] S. Okada, S. Sawa, M. Egashira, J. Yamaki, M. Tabuchi, H. Kageyama, T. Konishi, Yoshino, J. Power Sources 97 (2001) 430.
- [4] J. Wolfenstine, U. Lee, B. Poese, J.L. Allen, J. Power Sources 144 (2005) 226.
- [5] J. Wolfenstine, J. Power Sources 158 (2006) 1431.
- [6] N. Ravet, Y. Chouninard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, J. Power Sources 97–98 (2001) 503.
- [7] H. Huang, S.-C. Yin, L.F. Nazar, Electrochem. Solid State Lett. 4 (2001) A170.
- [8] S.-Y. Chung, J.T. Blocking, Y.-M. Chiang, Nat. Mater. 1 (2002) 123.
- [9] J. Molenda, Solid State Ionics 176 (2005) 1687.
- [10] S.Y. Chung, Y.-M. Chiang, Electrochem. Solid State Lett. 6 (2003) A278.
- [11] G.X. Wang, S.L. Bewaly, K. Konstantino, H.K. Liu, S.X. Dou, J.-H. Ahn, Electrochim. Acta 50 (2004) 443.
- [12] D. Wang, H. Li, S. Shi, X. Huang, L. Chen, Electrochim. Acta 50 (2005) 2955.
- [13] P.S. Herle, B. Ellis, N. Coombs, N.F. Nazar, Nat. Mater. 3 (2004) 147.
- [14] M.M. Doeff, Y. Hu, F. McLarnon, R. Kostecki, Electrochem. Solid State Lett. 6 (2003) A207.
- [15] Z. Chen, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A1184.
- [16] A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.
- [17] Y. Xu, Y. Lu, L. Yan, Z. Yang, R. Yang, J. Power Sources, in press.
- [18] S.L. Bewlay, K. Konstantinov, G.X. Wang, S.X. Do, H.K. Dou, Mater. Lett. 58 (2004) 1788.
- [19] C.W. Kim, J.S. Pak, K.S. Lee, J. Power Sources, in press.
- [20] G. Arnbold, J. Garche, R. Hemmer, S. Stroebble, C. Volger, M. Wohlfahrt-Mehrens, J. Power Sources 119 (2003) 247.
- [21] S.S. Zhang, J.L. Allen, K. Xu, T.R. Jow, J. Power Sources 147 (2005) 234.
- [22] S. Yang, Y. Song, K. Ngala, P.Y. Zavalij, M.S. Whittingham, J. Power Sources 119–121 (2003) 239.
- [23] K. Xu, C.A. Angell, J. Electrochem. Soc. 149 (2002) A920.
- [24] J. Molenda, A. Stoklosa, T. Bak, Solid State Ionics 36 (1989) 53.
- [25] Y. Shimakawas, Y. Numata, J. Tabuchi, J. Solid State Chem. 131 (1997) 138.