

Letter to the Editor

Chemical oxidation of LiCoPO₄

Recently, there has been interest in the use of lithium transition metal phosphates with an ordered olivine structure LiMPO₄ (M=Fe, Mn, and Co) as potential cathodes for Li-ion batteries [1–9]. In order for these materials to be used as cathodes it is important to understand their Li-ion insertion/deinsertion mechanism(s). One method to study this is chemical oxidation. For example, in the case of LiFePO₄, it has been shown that during chemical oxidation it exhibits a single-phase region (LiFePO₄) then a two-phase region (LiFePO₄ and FePO₄) and eventually a single-phase region (FePO₄) [1]. This is a similar mechanism to what is observed using electrochemical oxidation [1]. Very recently it has been shown that both chemical and electrochemical oxidation of LiMnPO₄ follows the same mechanism as LiFePO₄ [8]. The only difference between the results for LiFePO₄ and LiMnPO₄, was that only FePO₄ was observed 24 h after chemical oxidation, whereas both LiMnPO₄ and MnPO₄ were observed after 8 days of chemical oxidation. It was suggested that the complete transformation from LiMnPO₄ to MnPO₄ was not observed because of kinetic limitations [8]. Based on the above it might be expected that chemical and electrochemical oxidation of LiCoPO₄ should follow the same reaction mechanism as was observed for LiFePO₄ and LiMnPO₄. However, very preliminary results have shown that the phase(s) observed at the end of electrochemical oxidation (i.e., charging) for LiCoPO₄ are not similar (i.e., no CoPO₄) [5,10] to those observed for LiFePO₄ [1] and LiMnPO₄ [8] thus, suggesting a potentially different reaction mechanism for delithiation.

It is the purpose of this note to investigate the chemical oxidation of LiCoPO₄ to gain insight into the delithiation mechanism for LiCoPO₄.

LiCoPO₄ powders were obtained using a two-step solid-state reaction method. In the first step stoichiometric amounts CoO and LiH₂PO₄ were mixed in a jar mill for two hours and then heated at 375 °C for 20 h in air. The powders were then crushed and ground and pressed into a pellet. The pellet was fired in air at 775 °C for 48 h. After which the powders were crushed and ground and sieved to less than 45 μm. The powders were characterized by X-ray diffraction using Cu Kα radiation. The X-ray diffraction pattern revealed that the material was single-phase LiCoPO₄ (<5% second-phase) with an ordered olivine structure.

Chemical oxidation of LiCoPO₄ was undertaken using the same procedure that was used for LiFePO₄ and LiMnPO₄ [8,9,11]. Chemical oxidation of LiCoPO₄ was performed using two equivalents of nitronium tetrafluoroborate (NO₂BF₄, Aldrich) in acetonitrile that was continually stirred at room temperature in a glove box (≈1 ppm O₂ and 1 ppm H₂O) [10]. Nitronium tetrafluoroborate should be successful in removing (oxidizing) Li from LiCoPO₄ since the redox potential of NO⁺/NO is 5.1 V [11], versus Li⁺/Li, compared to 4.7–4.8 V for the Co³⁺/Co²⁺ redox potential [3–6]. After the nitronium tetrafluoroborate treatment the powders were washed and filtered several times with acetonitrile. The powders were then dried at 70 °C for 24 h under vacuum. The Li and Co content (atomic emission spectroscopy using a Perkin-Elmer 5100 PC Flame Atomic Absorption Spectrometer) and phases present (X-ray diffraction) were determined as a function of time in the nitronium tetrafluoroborate/acetonitrile solution.

The Li/Co ratio of the powders as a function of time in the nitronium tetrafluoroborate/acetonitrile solution is shown in Fig. 1. Also shown in Fig. 1 is data for LiMnPO₄ [8]. From Fig. 1, several important points are noted. Firstly, it can be seen that chemical extraction of Li from both LiCoPO₄ and LiMnPO₄ is very similar, in that initially there is rapid Li removal followed by a gradual slowing down. Secondly, after 7 days for LiCoPO₄ and 8 days for LiMnPO₄ not all the Li

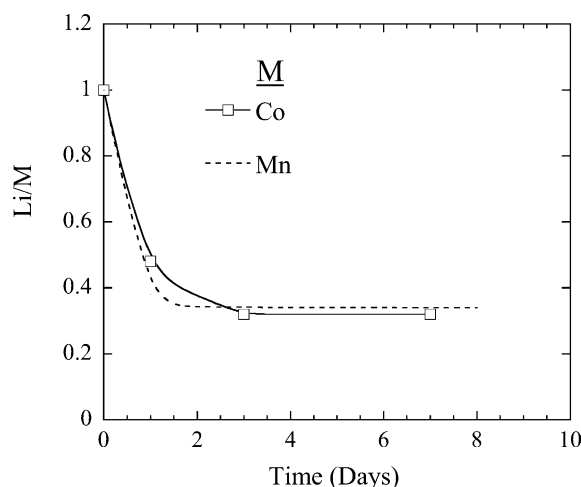


Fig. 1. The Li/M ratio as a function of time in the nitronium tetrafluoroborate/acetonitrile solution for LiCoPO₄ and LiMnPO₄ [8].

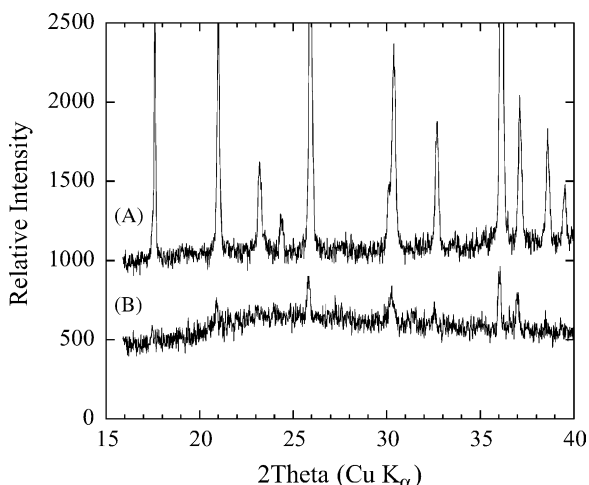


Fig. 2. X-ray diffraction patterns of [A] initial LiCoPO_4 and [B] after 7 days in the nitronium tetrafluoroborate/acetonitrile solution ($\text{Li/Co} \approx 0.32$).

has been removed. The Li/Metal ratio of these two materials after 7–8 days is very similar; $\text{Li/Co} \approx 0.32$ and $\text{Li/Mn} \approx 0.34$.

X-ray diffraction patterns for the initial LiCoPO_4 (A) and after 7 days in the nitronium tetrafluoroborate/acetonitrile solution (B) are shown in Fig. 2. From Fig. 2 a comparison of curves A and B reveals the following: (1) no new crystalline peaks appear, (2) there is an amorphous peak ($2\theta \approx 25^\circ$), (3) very slight shift in the peaks to lower 2θ values, (4) the peaks have become broader and (5) lower in intensity after chemical oxidation. It should be noted that no new crystalline phases were present in powders that were in the nitronium tetrafluoroborate/acetonitrile solution for 1 and 3 days. The above result is in contrast to that for LiMnPO_4 where at the same Li to metal ratio (≈ 0.34) and time of etching (8 days) two crystalline phases exist; LiMnPO_4 and MnPO_4 [8]. A possible explanation for this difference might be kinetic limitations, as was suggested for the difference between LiMnPO_4 and LiFePO_4 . Since, LiMnPO_4 has a smaller particle size, higher Li-ion diffusivity [12] and lower redox potential for Li-ion removal (4.1 V for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couple [1,8,9] compared to 4.7–4.8 V for the $\text{Co}^{3+}/\text{Co}^{2+}$ redox couple [3–6]) LiMnPO_4 would be expected to transform faster and thus, maybe LiCoPO_4 did not have sufficient time to transform from the initial single-phase material to the two-phase material. Kinetic limitations cannot be the reason for this difference because, both LiCoPO_4 and LiMnPO_4 have the same initial Li/Metal ratio = 1, were subjected to almost the same time for chemical oxidation (7–8 days) and both had the same final composition, Li/Metal ≈ 0.32 – 0.34 , after chemical oxidation, if kinetic limitations existed the final Li/Metal ratio would be different. The fact that a difference in the phases that result from chemical oxidation of LiCoPO_4 compared to LiMnPO_4 is not unexpected since, it is known that crystalline FePO_4 [1] and

MnPO_4 [8] exist, whereas no data could be found in the literature for the existence of crystalline CoPO_4 . At present, because of limited data the exact delithiation mechanism for LiCoPO_4 cannot be determined. More data on the structure and phases that form during electrochemical removal of Li from LiCoPO_4 are needed. The results of this study suggest that chemical oxidation of LiCoPO_4 is different from what was observed for LiFePO_4 and LiMnPO_4 , suggesting that their electrochemical oxidation behavior will be different, which is in agreement with preliminary electrochemical results.

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References

- [1] K. Phadhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [2] A. Yamada, M. Hosoya, S.-C. Chung, Y. Kudo, K. Hinokuma, K.-Y. Liu, Y. Nishi, *J. Power Sources* 119–121 (2003) 232.
- [3] S. Okada, S. Sawa, M. Egashira, J. Yamaki, M. Tabuchi, H. Kageyama, T. Konishi, A. Yoshino, *J. Power Sources* 97–98 (2001) 430.
- [4] P. Deniard, A.M. Dulac, X. Rocquefelte, V. Grigorova, O. Lebacqz, A. Pasturel, S. Jobic, *J. Phys. Chem. Solids* 65 (2004) 229.
- [5] K. Amine, H. Yasuda, M. Yamachi, *Electrochem. Solid State Lett.* 3 (2000) 178.
- [6] J.M. Loris, C. Perez-Vicente, J.L. Tirado, *Electrochem. Solid State Lett.* 5 (2002) A234.
- [7] G. Li, H. Azuma, M. Tohda, *Electrochem. Solid State Lett.* 5 (2002) 135.
- [8] C. Delacourt, P. Poizot, M. Morcrette, J.-M. Tarascon, C. Masquelier, *Chem. Mater.* 16 (2004) 93.
- [9] A. Yamada, Y. Kudo, K.-Y. Liu, *J. Electrochem. Soc.* 148 (2001) 1153.
- [10] K. Tadanaga, F. Mizuno, A. Hayashi, T. Minami, M. Tasumisago, *Electrochemistry* 71 (2003) 1192.
- [11] A.R. Wizansky, P.E. Rauch, F.J. Disalvo, *J. Solid State Chem.* 81 (1989) 203.
- [12] K. Rissouli, K. Benkhoulja, J.R. Ramos-Barrado, C. Julien, *Mater. Sci. Engr. B* 98 (2003) 185.

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