Short communication

LiNiPO$_4$–LiCoPO$_4$ solid solutions as cathodes

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Abstract

LiNiPO$_4$–LiCoPO$_4$ solid solutions were investigated as potential cathodes for use in Li-ion batteries. Cyclic voltammetry and discharge curves reveal that the discharge capacity of the LiNiPO$_4$–LiCoPO$_4$ solid solutions is associated entirely with the Co^{3+}/Co^{2+} redox couple at a potential of 4.7–4.8 V. The effect of Ni is to reduce the length of the 4.7–4.8 V plateau.
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1. Introduction

Recently, there has been interest in the use of lithium transition metal phosphates with an ordered olivine structure, LiMPO$_4$ (M = Fe, Mn, and Co), as potential cathodes for Li-ion batteries [1–9]. The main problem with the above phosphates is their poor rate capability [1–3,6,8–10]. This is attributed to low Li-ion diffusion and/or low electronic conductivity [1–10]. Previous attempts to increase the rate have primarily focused on decreasing particle size [8,9], carbon coating of the particle surface [7,11] and lattice doping with aliovalent cations [10]. There is another possible method to improve rate, which has received less attention, which entails increasing Li-ion diffusion [12]. This involves the formation of a solid solution between two lithium transition metal phosphates (i.e., LiMnPO$_4$–LiFePO$_4$) where the conductivity (Li-ion diffusion) of one end member (i.e., LiFePO$_4$) is higher than that of the other end member (i.e., LiMnPO$_4$) so that the resulting solid solution (i.e., LiMnPO$_4$–LiFEPO$_4$) will have enhanced conductivity compared to the lower conductivity end member [2,12].

The potential of the M^{3+}/M^{2+} redox couple versus Li of the above materials is as follows; 3.5 V for LiFePO$_4$, 4.1 V for LiMnPO$_4$ and 4.8 V for LiCoPO$_4$ [1–9]. In addition, there is another member of the LiMPO$_4$ series, LiNiPO$_4$, which has been postulated to have a higher redox potential ($\approx$5.2–5.4 V [1,4,13]) than LiCoPO$_4$. Previous studies on

LiNiPO$_4$ have shown that no Li can be discharged when it was charged to 5.2 V [1,3].

It is the purpose of this short paper to investigate the effects of: (1) adding LiCoPO$_4$ and (2) charging to higher potentials (>5.2 V) than previously investigated [1,3], on the discharge behavior of LiNiPO$_4$. LiCoPO$_4$ was chosen for the following reasons: (1) it has been recently shown that the electrical conductivity of a LiNi$_{0.5}$Co$_{0.5}$PO$_4$ solid solution was an order of magnitude higher than that for LiNiPO$_4$ [12] and (2) of the lithium transition metal phosphates; LiFePO$_4$, LiMnPO$_4$ and LiCoPO$_4$, LiCoPO$_4$ has the highest redox potential, thus a LiNiPO$_4$–LiCoPO$_4$ solid solution will have the highest energy density of the three possible solid solutions (i.e., LiNiPO$_4$–LiFePO$_4$) since, the theoretical capacity for LiFePO$_4$, LiMnPO$_4$ and LiCoPO$_4$ is about the same, $\approx$170 mAh/g [1–9].

2. Experimental

The materials investigated in this study were: (1) LiNiPO$_4$, (2) LiNi$_{0.8}$Co$_{0.2}$PO$_4$, (3) LiNi$_{0.5}$Co$_{0.5}$PO$_4$, (4) LiNi$_{0.2}$Co$_{0.8}$PO$_4$ and (5) LiCoPO$_4$. Powders of these materials were obtained using a two-step solid-state reaction method. In the first step stoichiometric amounts of NiO, CoO and LiH$_2$PO$_4$ 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.

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The electrochemical behavior of the $LiNiPO_4$–$LiCoPO_4$ cathode materials was accomplished using coin cells with metallic lithium as the anode. Cells were subjected to cyclic voltammetry and galvanostatic cycling. Cyclic voltammetry was used only as a guide to whether Li insertion/de-insertion occurred. For cyclic voltammetry all cells were scanned at a rate of 0.2 mV/s. The $LiCoPO_4$ cells were cycled between 3.5 and 5.3 V, for $LiNiPO_4$ the cells were cycled between 3.5 and 6.0 V and for the $LiNiPO_4$–$LiCoPO_4$ solid solutions the cells were cycled between 3.5 and 5.8 V. For the case of galvanostatic cycling the $LiCoPO_4$ cells were charged to 5.3 V, for $LiNiPO_4$ the cells were charged to 6.0 V and for the $LiNiPO_4$–$LiCoPO_4$ solid solutions the cells were charged to 5.8 V. All cells were discharged to 3.5 V. All charging and discharging was at a constant current density of 50 μA/cm^2. 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 °C for 20 h. The electrolyte solution was 1 M $LiPF_6$:ethylene carbonate/dimethyl carbonate (1:1 by volume) for $LiCoPO_4$. For $LiNiPO_4$ and the $LiNiPO_4$–$LiCoPO_4$ solid solutions the electrolyte was 1 M $LiPF_6$: tetramethylene sulfone. Tetramethylene sulfone was used because of its high oxidative stability (around 5.8 V versus Li [14]).

3. Results and discussion

X-ray diffraction patterns for the $LiNiPO_4$, $LiNi_{0.5}Co_{0.5}PO_4$ and $LiCoPO_4$ powders after heating at 775 °C are shown in Fig. 1. From Fig. 1 it can be seen that the patterns are similar. The X-ray diffraction patterns for $LiNi_{0.8}Co_{0.2}PO_4$, and $LiNi_{0.2}Co_{0.8}PO_4$ were similar to those shown in Fig. 1. The diffraction patterns for all five materials can be indexed to a single-phase material (the amount of second phase ma-
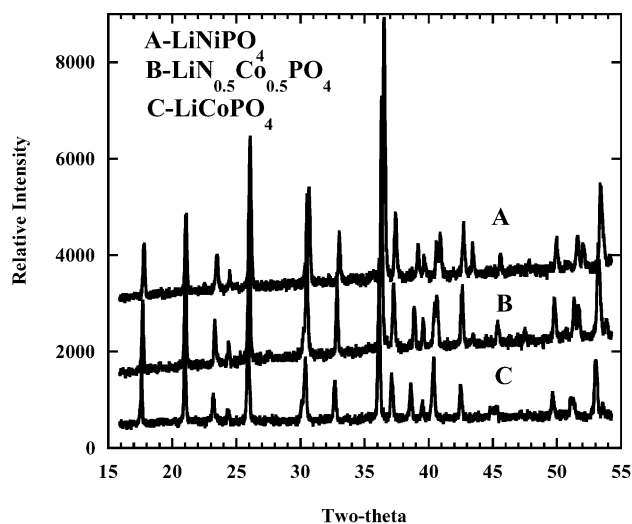

Fig. 2. Cyclic voltammogram for $LiNiPO_4$ at a scan rate of 0.2 mV/s.

terial, $NiO/Co_3O_4/Li_3PO_4$, was estimated to be less than 5% for all materials) having an ordered olivine structure [12].

Figs. 2–4 show the cyclic voltammograms for $LiNiPO_4$, $LiCoPO_4$ and $LiNi_{0.5}Co_{0.5}PO_4$. From Fig. 2 it can be seen for $LiNiPO_4$ that there are no significant reduction or oxidation peaks in the range 3.5 to 6.0 V. This is in good agreement with previous results at lower charging potentials [1,3]. The cyclic voltammogram for $LiNi_{0.8}Co_{0.2}PO_4$ also exhibited no reduction or oxidation peaks in the range 3.5 to 5.8 V. From Fig. 3 it can be seen that in contrast $LiCoPO_4$ exhibited a significant reduction peak around 4.6 V and an oxidation peak around 5.1 V. This result is in good agreement with previous cyclic voltammetry investigations on $LiCoPO_4$ [3,5]. The cyclic voltammogram for $LiNi_{0.5}Co_{0.5}PO_4$ is shown in Fig. 4. From Fig. 4 it can be seen that the cyclic voltammogram for $LiNi_{0.5}Co_{0.5}PO_4$ is similar to that for $LiCoPO_4$ (Fig. 3), in that there is a large reduction peak around 4.7 V and an oxidation peak around 5.2 V. The cyclic voltammogram for $LiNi_{0.2}Co_{0.8}PO_4$ was similar to that exhibited by $LiNi_{0.5}Co_{0.5}PO_4$ and $LiCoPO_4$, in that a reduction and oxidation peak was observed around
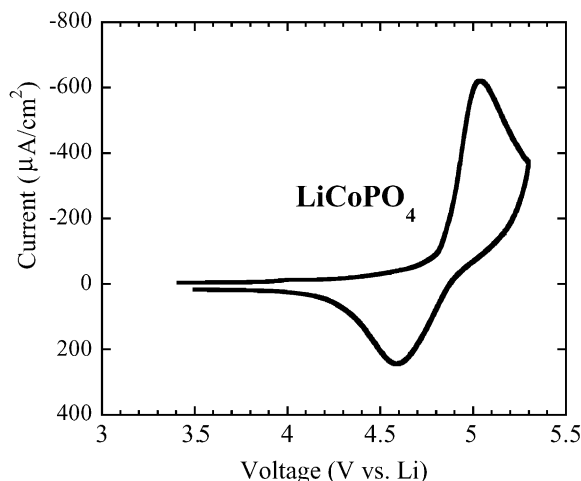

Fig. 1. X-ray diffraction patterns for (A) $LiNiPO_4$, (B) $LiNi_{0.5}Co_{0.5}PO_4$ and (C) $LiCoPO_4$.

Fig. 3. Cyclic voltammogram for $LiCoPO_4$ at a scan rate of 0.2 mV/s.

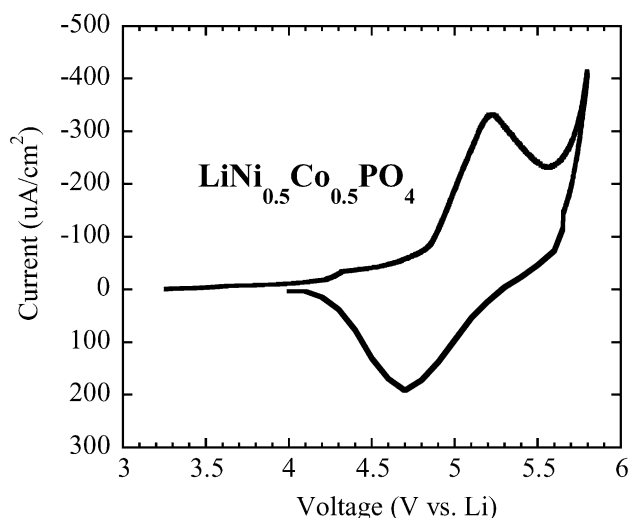Fig. 4. Cyclic voltammogram for LiNi$_{0.5}$Co$_{0.5}$PO$_4$ at a scan rate of 0.2 mV/s.

4.6 and 5.1 V, respectively. The cyclic voltammetry results suggest that even after charging to as high as 5.8–6.0 V, LiNiPO$_4$ and LiNi$_{0.8}$Co$_{0.2}$PO$_4$, will exhibit no discharge capacity, whereas LiNi$_{0.5}$Co$_{0.5}$PO$_4$, LiNi$_{0.2}$Co$_{0.8}$PO$_4$ and LiCoPO$_4$ will have capacity on discharge with a plateau voltage around 4.6–4.7 V.

The first discharge curves after initial charging for LiNiPO$_4$, LiNi$_{0.8}$Co$_{0.2}$PO$_4$, LiNi$_{0.5}$Co$_{0.5}$PO$_4$, LiNi$_{0.2}$Co$_{0.8}$PO$_4$ and LiCoPO$_4$ are shown in Fig. 5. From Fig. 5 several important points are noted. Firstly, the discharge capacity for LiNiPO$_4$ and LiNi$_{0.8}$Co$_{0.2}$PO$_4$ is almost nothing (<5 mAh/g). Secondly, no plateaus above 5.0 V are observed for LiNiPO$_4$ or any of the LiNiPO$_4$–LiCoPO$_4$ solid solutions, where the Ni^{3+}/Ni^{2+} redox couple would be expected ($\approx$5.2–5.4 V [1,4,13]). Thirdly, a discharge plateau for LiNi$_{0.5}$Co$_{0.5}$PO$_4$, LiNi$_{0.2}$Co$_{0.8}$PO$_4$ and LiCoPO$_4$ is exhibited and is at the same potential, 4.7–4.8 V. The plateau
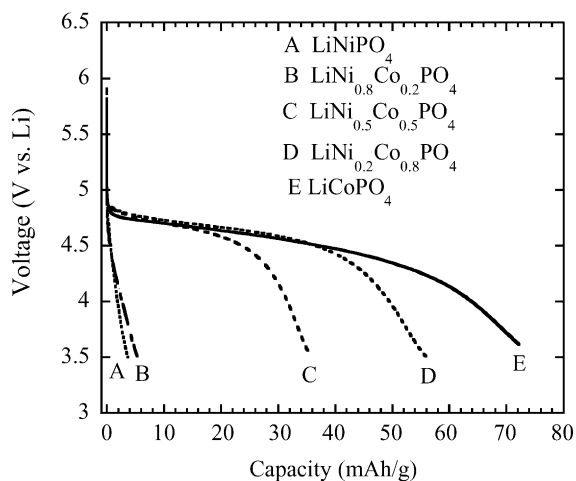
at 4.7–4.8 V is in good agreement with previous results for the Co^{3+}/Co^{2+} redox couple in LiCoPO$_4$ [3–6]. Thus, it appears that Ni additions do not effect the Co^{3+}/Co^{2+} redox potential. Fourthly, the discharge capacity for LiCoPO$_4$ of 74 mAh/g is in good agreement with previous results for LiCoPO$_4$ of 70–100 mAh/g [3–6]. Fifthly, the discharge capacity decreases almost linearly as the amount of Co decreases (Ni increases) for the Co-rich solid solutions. For example, the capacity of LiNi$_{0.2}$Co$_{0.8}$PO$_4$ is around 58 mAh/g versus the predicted value of 59 mAh/g (0.8×74 = 59) and for LiNi$_{0.5}$Co$_{0.5}$PO$_4$ is about 35 mAh/g versus the predicted value of 37 mAh/g ($0.5 \times 74 = 37$).

The cyclic voltammetry and discharge results reveal that the discharge capacity of the LiNiPO$_4$–LiCoPO$_4$ solid solutions is associated entirely with the Co^{3+}/Co^{2+} redox couple at a potential of 4.7–4.8 V. The effect of Ni is to reduce the length of the 4.7–4.8 V plateau and hence, discharge capacity. The addition of LiCoPO$_4$ to LiNiPO$_4$ did not allow the Ni^{3+}/Ni^{2+} redox couple to be achieved even after to charging to as high as 5.8–6.0 V. It is possible that the Ni^{3+}/Ni^{2+} plateau was not observed because the conductivity of the LiNiPO$_4$–LiCoPO$_4$ solid solutions is still not sufficient. One way to increase the conductivity would be to form LiNiPO$_4$–LiMnPO$_4$ or LiNiPO$_4$–LiFePO$_4$ solid solutions whose electrical conductivity is at least one to two orders of magnitude higher than for LiNiPO$_4$–LiCoPO$_4$ [12]. However, it is anticipated that even these solid solutions still will not have adequate conductivity to observe the Ni^{3+}/Ni^{2+} redox potential. More likely methods to observe the Ni^{3+}/Ni^{2+} redox potential involve decreasing the particle size to nano-scale and/or carbon coating and/or lattice doping.

4. Conclusions

LiNiPO$_4$–LiCoPO$_4$ solid solutions were investigated as potential cathodes for use in Li-ion batteries. Cyclic voltammetry and discharge curves reveal that the discharge capacity of the LiNiPO$_4$–LiCoPO$_4$ solid solutions is associated entirely with the Co^{3+}/Co^{2+} redox couple at a potential of 4.7–4.8 V. The effect of Ni is to reduce the length of the 4.7–4.8 plateau. The Ni^{3+}/Ni^{2+} redox couple was not observed for LiNiPO$_4$ or any of the LiNiPO$_4$–LiCoPO$_4$ solid solutions even after charging to as high as 5.8–6.0 V.

Fig. 5. First discharge curves for (A) LiNiPO$_4$, (B) LiNi$_{0.8}$Co$_{0.2}$PO$_4$, (C) LiNi$_{0.5}$Co$_{0.5}$PO$_4$, (D) LiNi$_{0.2}$Co$_{0.8}$PO$_4$ and (E) LiCoPO$_4$.

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. Lebacq, 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) A135.

[8] C. Delacourt, P. Poizot, M. Morcrette, J.-M. Tarascon, C. Masquelier, Chem. Mater. 16 (2004) 93.

[9] A. Yamada, S.-C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.

[10] S.-Y. Chung, J.T. Blocking, Y.-M. Chiang, Nat. Mater. 1 (2002) 123.

[11] N. Ravet, Y. Chouninard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, J. Power Sources 97–98 (2001) 503.

[12] K. Rissouli, K. Benkhouja, J.R. Ramos-Barrado, C. Julien, Mater. Sci. Eng. B 98 (2003) 185.

[13] G.T. Fey, W. Li, J.R. Dahn, J. Electrochem. Soc. 141 (1994) 2279.

[14] K. Xu, C.A. Angell, J. Electrochem. Soc. 149 (2002) A920.