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Ni³⁺/Ni²⁺ redox potential in LiNiPO₄

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Recently, there has been interest in the use of lithium transition metal phosphates with an ordered olivine structure LiMPO₄ (M = Fe, Mn, Co and Ni) as potential cathodes for Li-ion batteries [1–3]. For the case of LiFePO₄, LiMnPO₄ and LiCoPO₄ there is good agreement between theoretical predictions and experimental values of the M³⁺/M²⁺ redox potential in these materials [1–8]. For the case of LiNiPO₄ theoretical calculations suggest that the Ni³⁺/Ni²⁺ redox potential is above 5 V [4,8]. Previous attempts to experimentally confirm this prediction have failed as a result of: (1) low stability electrolytes and/or (2) low rate capability of this material, which is of its result low electrical conductivity and slow Li-ion diffusion. It is the purpose of this note to determine the Ni³⁺/Ni²⁺ redox potential in LiNiPO₄ and compare it to theoretical predictions.

In order to overcome the problems with low electrolyte stability, a 1 M LiPF₆:tetramethylene sulfone electrolyte was used. Tetramethylene sulfone was used because of its high oxidative stability, around 5.8 V versus Li [9]. In order to overcome the low electrical conductivity of LiNiPO₄ a two-step approach was used. In the first step the LiNiPO₄ powder was prepared using the method of Herle et al. [10]. They observed at least a two to three order of magnitude increase in electrical conductivity for LiNiPO₄ when the heat-treatment atmosphere was changed from flowing air to flowing argon when carbon-containing precursors were used [10]. They suggested based on X-ray diffraction and transmission electron microscopy data that the increase in electrical conductivity was a result of the formation of a nano-network of metal phosphides and/or metal phosphocarbides and/or amorphous carbon at grain boundaries that formed as a result of the reducing conditions under the argon atmosphere when carbon-containing precursors were used. In the second step the powders were coated with a conductive carbon coating, which has been shown to be very successful in increasing the electrical conductivity of LiFePO₄ and LiMnPO₄ [6,11–13].

The LiNiPO₄ powders were synthesized using a solid-state reaction method [10]. Stoichiometric amounts of Li₂CO₃ (Alfa Aesar), NiC₂O₄·2H₂O (Alfa Aesar) and NH₄H₂PO₄ (Alfa Aesar) were mixed in a jar mill for two hours. In the first step the powders were heated at 375 °C for 20 h. They were then crushed and ground and pressed into a pellet. In the second step the pellet was fired at 775 °C for 48 h. Both heat-treatments were conducted under high purity flowing argon ($PO_2 \approx 10^{-5}$ atm). The powders at this stage were black whereas powders heated under air were yellow. X-ray diffraction confirmed that the powders were mostly single-phase LiNiPO₄. Some small Ni₃P peaks were observed, in agreement with the results of Herle et al. [10]. The conductive carbon surface coating was obtained by pyrolysis of propane gas at 800 °C for 2 h. Based on the weight gain the amount of carbon was estimated to be about 18 wt.%. The coated powders were then mixed with 12 wt.% carbon and 10 wt.% polyvinylidene fluoride dissolved in *N*-methylpyrrolidinone and coated onto an Al substrate. The cathodes were dried under vacuum at 100 °C for 20 h. The cathodes were placed in coin cells with metallic lithium as the anode. The electrolyte solution was 1 M LiPF₆:tetramethylene sulfone. To investigate the Ni³⁺/Ni²⁺ redox potential cyclic voltammetry was undertaken. For cyclic voltammetry cells were scanned at a rate of 0.2 mV s⁻¹ between 3.5 and 5.8–6.0 V.

The cyclic voltammogram for LiNiPO₄ (solid line) prepared under high purity argon gas with the addition of the carbon coating is shown in Fig. 1. Also shown in Fig. 1 are data for LiNiPO₄ (dotted line) prepared under air [14]. From Fig. 1 several important points are noted. Firstly, it can be seen for LiNiPO₄ prepared under air (dotted line) that there are no significant reduction or oxidation peaks in the range 3.5–6.0 V. This is in good agreement with previous results for LiNiPO₄ prepared under air [3]. In addition, no oxidation or reduction peaks were observed for LiNiPO₄ prepared under high purity

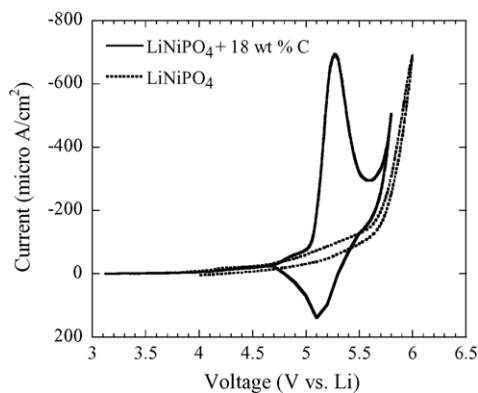


Fig. 1. Cyclic voltammogram of: (1) LiNiPO_4 [14] prepared under air (dotted line) and (2) LiNiPO_4 prepared under argon + 18 wt % C (solid line) at a scan rate of 0.2 mV s^{-1} .

argon in the absence of a carbon coating. Secondly, it can be observed that LiNiPO_4 prepared under high purity argon gas with the addition of the carbon coating exhibits both a significant oxidation peak $\sim 5.3 \text{ V}$ and reduction peak $\sim 5.1 \text{ V}$. The magnitude of the oxidation peak is about $2.8\times$ that for the reduction peak. These results suggest that the $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox potential in LiNiPO_4 is between 5.1 and 5.3 V, confirming theoretical predictions that it is above 5 V [4,8]. Furthermore, the experimental value is in excellent agreement with recent theoretical prediction of Zhou et al. [8], who predict a $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox potential in LiNiPO_4 of $\sim 5.1 \text{ V}$. The observation that no oxidation/reduction peaks were exhibited when LiNiPO_4 was heated under argon, even though a significant increase in electrical conductivity was observed, $100\text{--}1000\times$ compared to the air sample [10], suggests that this material has a very low intrinsic electrical conductivity and hence, additional treatments such as; carbon coating are required for LiNiPO_4 to exhibit Li insertion/deinsertion. This result is in good agreement with the electrical conductivity results of Rissouli et al. [15], who observed that the electrical conductivity of LiNiPO_4 was $100\text{--}1000\times$ lower than that for LiCoPO_4 and LiMnPO_4 . The fact the oxidation peak is larger than the reduction peak suggests it is harder to insert Li and than to remove Li thus, making it difficult for LiNiPO_4 to exhibit a reasonable discharge capacity and cycle life, in agreement with previous results [14,16–18]. Alternatively, it may be a result of the formation of an amorphous phase during oxidation of LiNiPO_4 which does not readily intercalate lithium. This viewpoint is supported by the lack of a mineral phase of formula NiPO_4 , whereas in contrast, FePO_4 is a naturally occurring mineral [1,2].

The results of this study suggest that the $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox potential in LiNiPO_4 is between 5.1 and 5.3 V, in agreement with theoretical predictions. LiNiPO_4 has very

low electrical conductivity, making it difficult to observe Li insertion/deinsertion.

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