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Minakshi, M., Singh, P., Appadoo, D., & Martin, D. E. (2011). Synthesis and characterization of olivine LiNiPO₄ for aqueous rechargeable battery. *Electrochimica Acta*, 56(11), 4356–4360.

<https://doi.org/10.1016/j.electacta.2011.01.017>

Document Version: Author's Version

Published Version: <https://doi.org/10.1016/j.electacta.2011.01.017>



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<http://dx.doi.org/10.1016/j.electacta.2011.01.017>

Minakshi, M., Singh, P., Appadoo, D. and Martin, D.E. (2011)
Synthesis and characterization of olivine LiNiPO₄ for aqueous rechargeable battery. *Electrochimica Acta*, 56 (11). pp. 4356-4360.

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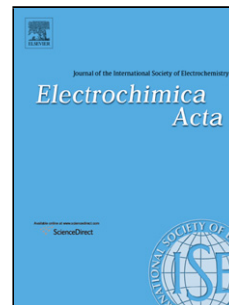
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Accepted Manuscript

Title: Synthesis and Characterization of Olivine LiNiPO_4 for Aqueous Rechargeable Battery

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PII: S0013-4686(11)00078-8
DOI: doi:10.1016/j.electacta.2011.01.017
Reference: EA 16631

To appear in: *Electrochimica Acta*

Received date: 16-11-2010
Revised date: 17-12-2010
Accepted date: 14-1-2011

Please cite this article as: M. Minakshi, P. Singh, D. Appadoo, D.E. Martin, Synthesis and Characterization of Olivine LiNiPO_4 for Aqueous Rechargeable Battery, *Electrochimica Acta* (2010), doi:10.1016/j.electacta.2011.01.017

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Synthesis and Characterization of Olivine LiNiPO_4 for Aqueous Rechargeable Battery

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Abstract

LiNiPO_4 belong to a family of olivine type compounds, with members LiMPO_4 where $M = \text{Fe, Mn, Co or Ni}$ are transition metals. The lithium nickel phosphate was prepared and characterized in order to evaluate a new potential cathode material for our ongoing research in aqueous rechargeable batteries. Annealing the final product is critical in obtaining the stoichiometric LiNiPO_4 pure phase; conventional cooling to a room temperature leads to an indication of Li_3PO_4 & NiO secondary phases as impurities. The synchrotron infrared radiation (SR-IR) as a source for IR spectroscopy pins down the differences in the chemical bonding for annealed and conventional cooled LiNiPO_4 samples. The cyclic voltammetric and galvanostatic studies showed annealed LiNiPO_4 is electrochemically active from which lithium ions can be de-intercalated during oxidation process leading to an amorphous NiPO_4 and a minor product of nickel (II) hydroxide ($\beta\text{-NiOOH}$). During subsequent reduction, lithium ions are not fully intercalated, however, the structure is reversible and adequate for multiple cycles. The high potential in LiNiPO_4 looks to be very attractive in terms of high energy density, given the efficiency is improved.

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Introduction

Since the demonstration of lithium intercalation – de-intercalation process in the ordered olivine structure with general formula LiMPO_4 ($M = \text{Fe, Mn, Co or Ni}$), lithium transition metal phosphates have been extensively investigated as possible candidates for cathode materials in lithium ion batteries that use non-aqueous electrolytes. The phosphate materials built with $(\text{PO}_4)^{3-}$ anions offer advantages in practical applications due to its low cost, environmental benign, safe and stable over layered and spinel structures [1-4]. The olivine framework is more stable in the charged state and no phase transition is necessary to balance the loss in lithium, these features improved their electrochemical performances than the layered oxide counterpart [4-6]. The olivine compounds LiMPO_4 contain tetrahedral “anion” structure units $(\text{PO}_4)^{3-}$ with strong covalent bonding, generating oxygen octahedral occupied by other M metal ions. The PO_4 unit tends to reduce the covalency of the $M - \text{O}$ bond, modifying the redox potential for the $M^{2+}/^{3+}$ couple and thus producing a practical voltage while lithium insertion and re-insertion occurs [7-8]. Among the LiMPO_4 reported in the literature [7-10], lithium iron phosphate (LiFePO_4 ; [7]) and lithium manganese phosphate (LiMnPO_4 ; [10]) have been recognised as promising cathode material for rechargeable battery applications. This is mainly because a large reversible capacity of 164 mAh/g was achieved over a wide composition range of $\text{Li}_{1-y}\text{Mn}_y\text{PO}_4$ and $\text{Li}_{1-y}\text{Fe}_y\text{PO}_4$, even at Mn & Fe contents as high as $y = 0.75$ [11]. Comparative studies of the LiMPO_4 family [12-13] reported that it was difficult to de-intercalate Li^+ from Co and Ni phosphate within the voltage stability window of existing non-aqueous electrolyte; for the high potential value of the redox couples $\text{Co}^{3+}/^{2+}$ and $\text{Ni}^{3+}/^{2+}$ [12]. However, efforts in improving the electrolyte have recently made it possible to explore the LiCoPO_4 compound to about 5 V [9, 13]. The

information available about the electrochemical performance of LiNiPO_4 is very limited [14-16] due to the difficulty in obtaining a pure phase of lithium nickel phosphate. It is reported [17-18] that stringent synthesis conditions are required to synthesis LiNiPO_4 . Few studies [14-20] on this material have also shown that lithium nickel phosphate is not electrochemically active; no lithium can be subsequently intercalated if it is charged over 5.2 V. With these reasons, LiNiPO_4 cathode was scarcely researched and the available literature [14-20] is limited only to non-aqueous electrolytes.

The impetus for this work is to synthesise pure phase LiNiPO_4 using conventional synthesis method and to understand their reduction/oxidation reactions in the stable aqueous electrolyte. The emphasis is not only the fundamental understanding of the redox mechanism but also the possible use of this material for the battery applications. In the current work, we report on the synthesized LiNiPO_4 pure powder yielded with bright yellow colour exhibiting orthorhombic structure for integration into battery device technology. Herein, we have primarily investigated the LiNiPO_4 cathode with Sn as an anode in aqueous LiOH electrolyte. The effect of replacing zinc (Zn) with tin (Sn) anode was investigated by our group [21] for aqueous secondary batteries. The Sn-based aqueous battery involves reversible lithium intercalation/de-intercalation, passivation-free anodic reaction resulting in long term cycling behaviour. The chemical stability of Sn in our aqueous LiOH electrolyte is found to be stable unlike the solid electrolyte interphase (SEI) layer that limits the cycling as what observed for lithium ion batteries using Sn anode in non-aqueous electrolyte [22]. Hence, we have chosen Sn as an anode and the Sn| LiNiPO_4 cell shows potential candidate for aqueous rechargeable battery investigated for the first time in this paper.

Experimental

The olivine LiNiPO_4 as a polycrystalline powder was synthesized by a solid state reaction between Li_2CO_3 (Sigma Aldrich), NiO (Ajax Chemicals) and $\text{NH}_4\text{H}_2\text{PO}_4$ (Sigma Aldrich) raw materials. Stoichiometric amounts of reactants were mixed with ethanol in a mortar and pestle. After mixing the ingredients for 30 min, the mixture was transferred into an oven maintained at 80°C for 1 h. Then the dried powder was collected in a crucible and given a two-step heat treatment in a box furnace containing ambient atmosphere. In the initial step the powder was heated at 375°C for 12 h, and then it was crushed and ground. This thermal treatment causes the departure of gases present according to the relation:



The calcined ground powder was sintered at 800°C for 24 h and then two different approaches were made on cooling the final product. The former is annealing – slow cooling for 25 h (ramp rate $0.5^\circ\text{C}/\text{min}$) to room temperature and the latter by rapid cooling for 5 h ($2.5^\circ\text{C}/\text{min}$) to room temperature, both were performed in air; bright yellow and green powders were achieved respectively. Phase purity was determined by X-ray powder diffraction and they were all indexed as orthorhombic in the space group Pmna .

The experimental procedures for the slow scan cyclic voltammetric studies were similar to those reported earlier [23]. We fabricated the LiNiPO_4 cathode for electrochemical charge-discharge test with the following procedure; a pellet was prepared by mixing 75 wt % LiNiPO_4 with 15 wt % acetylene black (A-99, Asbury, USA) and 10 wt % poly (vinylidene difluoride) (PVDF, Sigma Aldrich) binder in a mortar and pestle and pressed at 78 MPa. An electrochemical (battery) cell was constructed with the disk-like pellet (8 mm in diameter, 0.5 mm in thick, and 0.10 g)

as the cathode, metallic tin as the anode (with identical dimensions to the cathode), and filter paper used as the separator. Sn powder was purchased from Ajax Chemicals. Analytical reagent grade LiOH.H₂O from Sigma Chemicals Company was used as received. The electrolyte used was a saturated solution of lithium hydroxide (LiOH) with a pH of 10.5.

For galvanostatic experiments, the cell was discharged/charged galvanostatically at 0.5 mA/cm² by using an 8 channel battery analyser from MTI Corporation, USA, operated by a battery testing system (BTS). The charge and discharge cut-off voltage were of 1.7 and 0.5 V respectively. An EG&G Princeton Applied Research Versa Stat III model was used to scan the potential at 25 μ V/s (microV/s) in all cyclic voltammetric experiments. Hg/HgO purchased from Koslow Scientific is used as the standard reference electrode.

Structural characterization was performed by X-ray powder diffraction. The X-ray patterns were obtained by Siemens X-ray diffractometer (Cu-K α radiation), at room temperature. The 2 θ range was 15°-45° at a scan rate of 1.0°/min. Powder morphology was studied by Scanning Electron Microscopy (SEM) using a Philips Analytical XL series 20 (20 KV). For infrared (IR) analysis, IR absorption spectra between 400 and 750 cm⁻¹ were measured at the Australian Synchrotron using IR synchrotron radiation as the source coupled to an IFS 125/HR spectrometer. LiNiPO₄ powder was mixed with KBr (potassium bromide) powder and pressed into 12 mm diameter disks (pellets) for transmission studies. The sample was crushed to create minute particles of less than 50 μ m in diameter before 5 mg of each sample was mixed with 95 mg of KBr. Spectra were recorded using a 3.15 mm aperture, a resolution of 1 cm⁻¹. For each sample an average of 200 scans were recorded.

Results and Discussion

The X-ray diffraction pattern of LiNiPO_4 sample recorded after annealing the final product at 800°C is shown in Fig. 1a. The crystal structure of sample obtained from the XRD pattern was identified to be a pure LiNiPO_4 phase (database card 032-0578) with an ordered olivine structure with crystallographic space group Pnma . The LiNiPO_4 adopting the Pnma space group, in which Ni^{2+} ions occupy the centres of slightly distorted NiO_6 octahedra, and P ions are located at the centres of the PO_4 tetrahedra. Both the lithium and nickel occupy octahedral sites LiO_6 and NiO_6 respectively. The important characteristic of the XRD spectrum is that all the peaks are well assigned to LiNiPO_4 phase without any presence of impurities. It is generally believed [17-18] that the synthesis of LiNiPO_4 requires stringent atmosphere conditions without which Ni_3P peaks [24] were observed as an impurity. In this work, pure single phase is obtained without any difficulty while using NiO and $\text{NH}_4\text{H}_2\text{PO}_4$ as precursors and thermal treated under air atmosphere at 800°C followed by annealing the product. However, the XRD pattern in Fig. 1b indicates that in the case of non-annealed samples (conventional cooling the final product), formation of an olivine structure with secondary phases of Li_3PO_4 (Card No. 015-0760) and NiO (Card No. 044-1159) as impurities are seen. It is interesting to note that the colour of the powders changes from bright yellow to green for annealed and non-annealed samples respectively. Our studies indicate that only annealed samples yielding a bright yellow colour exhibited a single phase of olivine- type LiNiPO_4 . The correlation between the coloration of the nickel compounds and its structure was studied by G. R. Rossman et al [25]. Ni^{2+} ions in the NiO_6 octahedra produces green colour. A bright yellow colour resulted when Ni^{2+} is in the NiO_6 site distorted from octahedral symmetry, pre-requisite for olivine structure. Colouration of annealed

LiNiPO₄ sample reveals the difference in the structural features of the obtained product. The variations in the local structure and chemical bonding for annealed and non-annealed LiNiPO₄ have been studied by synchrotron infrared (SR-IR) spectroscopy. The sample after annealing the final product at 800° C exhibits a typical IR spectrum for well crystallized olivine type LiNiPO₄ as shown in Fig. 2. The IR features (above 400 cm⁻¹) two fundamental vibrations (ν_2 and ν_4) of the (PO₄)³⁻ group in an olivine structure [26-28]. It involves mainly O-P-O symmetric and antisymmetric bending mode with a small contribution of P vibration; such as ν_2 and ν_4 in the regions 400-470 cm⁻¹ and 575-665 cm⁻¹ respectively [26-29]. Using synchrotron IR radiation as a source these bending vibrations have been recorded with better signal to noise ratio due to the much higher brightness and smaller effective source size of IR synchrotron. The high frequency band of the FTIR absorption spectra of LiNiPO₄ located at 650 and 663 cm⁻¹ are attributed to the stretching mode of NiO₆ distorted octahedra [30]. The most noticeable features in the vibrational pattern for an annealed spectrum (fig. 2a) are the higher in intensity and the appearance of the NiO₆ distorted octahedra at the higher frequencies.

The Scanning electron microscopy images (SEM) images of the LiNiPO₄ samples are shown in Fig. 3. The compact in morphology, uniform particle size distribution forming a network that leads to high surface area are observed for annealed sample in Fig. 3a. In a more detailed analysis, the grains for annealed samples at higher magnifications (in Fig. 3c) exhibits orthorhombic like structure where as for non-annealed no such face is obviously identified. Hence, the LiNiPO₄ used for electrochemical characterization in the following sections are confined only to annealed samples which seemed to be an important part of the LiNiPO₄ preparation route.

To investigate the oxidation-reduction reactions of $\text{Ni}^{3+}/\text{Ni}^{2+}$, cyclic voltammetry and galvanostatic charge/discharge tests were undertaken. The typical cyclic voltammogram for LiNiPO_4 in aqueous lithium hydroxide electrolyte is shown in Fig. 4. The working electrode (LiNiPO_4) was scanned between -0.3 and 0.2 V at $25\mu\text{V/s}$ (microV/s) scan rate. On each occasion, the potential was started at -0.3 V, moving initially in the anodic direction to 0.2 V and then reversing it to the starting potential of -0.3 V. As can be seen in the Fig. 4, the LiNiPO_4 exhibits a significant oxidation peak A_1 at -94 mV and a corresponding reduction peak C_1 at -231 mV. The area under the peak A_1 is about 2x that for the peak C_1 . The ratio of the peaks A_1 and C_1 was 0.45 suggesting that the reaction was only 45% reversible. The use of LiNiPO_4 as a cathode material for lithium ion battery using non-aqueous solutions is scarcely realised because of the limitations such as obtaining pure phase [17-18], voltage instability window [12] and their poor practical discharge capacity [15-16]. By contrast, to the available reports in the literature [14-20], our results show that the $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox reaction is significant and found to be 45% reversible in aqueous solutions.

To determine the mechanism through which LiNiPO_4 undergoes electron transfer reactions in aqueous LiOH electrolyte, XRD analysis were carried out on the pristine, oxidised and reduced LiNiPO_4 samples. The notable feature of the XRD pattern (in Fig. 5) for the oxidised sample is a nucleation of new peaks marked with symbols “O” and “●” are seen. The emergence of new peaks (●) is assumed to be lithium extracted NiPO_4 as there are no consistent literature data for comparison. As indexed in the XRD pattern, the minor reflection at $2\theta = 33^\circ$ was in good agreement with those reported for the compound nickel (II) hydroxide (Card No. 06-0141). The oxidised product of LiNiPO_4 in the aqueous LiOH electrolyte involves delithiated

NiPO_4 and a formation of nickel hydroxide. The crystallinity of the electrode during oxidation was affected, as deduced from the sharpness of the x-ray diffraction peaks of the oxidised material (Fig. 5 compare with Fig. 1a). The peak intensity is 10x smaller than the pristine sample (in Fig. 1a). The lower peak intensity may relate to the utilization of LiNiPO_4 leading to amorphous in nature resembling the major final product as NiPO_4 . The XRD patterns of the products formed on subsequent electro-reduction together with that of the pristine LiNiPO_4 are shown in Fig. 6. The process is almost reversible, indicating that LiNiPO_4 is reproduced on reduction of NiPO_4 . A careful examination of Fig. 6b indicates that there is an evidence of the presence of tiny peaks at $2\theta = 32, 37.5$ and 40° which are related to NiPO_4 . Thus, the redox reaction of LiNiPO_4 in LiOH aqueous electrolyte involves de-intercalation of Li^+ but the intercalation process is not reversible. It is important to note this is for the first time that lithium intercalation mechanism is observed for the lithium nickel phosphate in aqueous electrolyte. However, the observed delithiation mechanism is quite similar to that reported for non-aqueous electrolytes [31]. In order to study this for possible use in battery applications, galvanostatic study has been performed. A typical charge-discharge curve of $\text{Sn} | \text{LiNiPO}_4$ cell is shown in Fig. 7. An initial open-circuit voltage of about 1 V versus Sn is measured for LiNiPO_4 electrode. The cell voltage profile display the typical curve currently observed for LiNiPO_4 cathode in LiOH electrolyte. The efficiency of the redox reaction observed in cyclic voltammetry (in Fig. 4) is in agreement with the galvanostatic studies suggesting it is harder to intercalate lithium than to extract lithium, resulting in a lower discharge capacity of 55 mAh/g. At this point, it is difficult to draw more conclusion on the discharge capacity, as a part of the charge capacity could be devoted to $\beta\text{-NiOOH}$ which is irreversible for subsequent discharge. The variation in discharge capacity with cycle number is shown in Fig. 8.

The capacity reaches a stable value of ~50 mAh/g after 5 cycles, losing 10% of its initial value, and then it is retained for multiple cycles. Thus, it confirmed that the LiNiPO_4 cathode is reversible in aqueous electrolyte.

Figure 9 shows the changes in the cyclic voltammogram when the LiNiPO_4 cathode is subjected to multiple cycling in the potential between -0.3 and 0.2 V. The anodic and cathodic peak currents decreased up to 10% for the first few cycles and tended to stabilise. This suggest that lithium can be extracted /inserted from/into LiNiPO_4 structure with a charge balance of $\text{Ni}^{3+}/\text{Ni}^{2+}$ over a number of cycles. The peak due to hydrogen evolution is indicated as C_2 in the figure 9. The strong PO_4 framework and the stability of the aqueous electrolyte improved the reversibility, but the formation of nickel hydroxide or the poor conductivity of this material is not sufficient enough to achieve practical discharge capacity.

Conclusions

We have demonstrated for the first time that lithium extraction/insertion mechanism can be achieved for LiNiPO_4 in aqueous LiOH electrolyte. In the as-synthesized LiNiPO_4 powder, variation of colour from green to bright yellow is related to changes in NiO_6 octahedra. The LiNiPO_4 synthesized in air without any stringent synthesis conditions yielding yellow colour product shows sample purity with a single phase compound. The IR spectroscopic measurements provided information on the variations in the bonding between NiO_6 octahedral and $(\text{PO}_4)^{3-}$ tetrahedral groups in the annealed and non-annealed LiNiPO_4 samples. The LiOH based $\text{Sn}|\text{LiNiPO}_4$ cell can be charged and discharged however the efficiency was found to be only 45%. The electrochemical oxidation of LiNiPO_4 resulted in the formation of an amorphous delithiated NiPO_4 and a minor product of $\beta\text{-NiOOH}$. The subsequent reverse reduction of NiPO_4 forms a crystalline LiNiPO_4 . The retention of

capacity during cycling indicates that the material has potential for battery application if the voltage and efficiency are improved.

Acknowledgement

The author (M. M) wishes to acknowledge the Australian Research Council (ARC). This research was supported under ARC's Discovery Projects funding scheme (DP1092543) and from the Australian Synchrotron Company Limited through the grant no AS103/HRIR3003. The views expressed herein are those of the authors and are not necessarily those of the Australian Research Council.

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Figure Captions

Fig. 1 XRD patterns of as prepared LiNiPO_4 olivine (a) annealed and (b) non-annealed samples (conventional cooling). Lines are indexed in the orthorhombic system.

Fig. 2 The far IR spectra of the as-synthesized LiNiPO_4 (a) annealed and (b) non-annealed samples.

Fig. 3 Scanning electron micrographs of as prepared LiNiPO_4 olivine (a) annealed (b) non-annealed and (c) annealed sample at a higher magnification (4x of Fig. 3a) exhibits orthorhombic like structure.

Fig. 4 A typical cyclic voltammogram of annealed lithium nickel phosphate (LiNiPO_4) in aqueous lithium hydroxide electrolyte (scan rate: $25 \mu\text{V} \cdot \text{s}^{-1}$; potential limit: 0.2 to -0.3 V and back).

Fig. 5 XRD pattern of annealed LiNiPO_4 electrode after oxidation in aqueous LiOH electrolyte. "O" corresponds to (delithiated) NiPO_4 peaks.

Fig. 6 XRD pattern of annealed LiNiPO_4 electrodes (a) before electrochemical treatment and (b) subsequent reduction after oxidation in aqueous LiOH electrolyte. "O" corresponds to (delithiated) NiPO_4 peaks reduced in intensity during lithiation.

Fig. 7 Typical galvanostatic (charge-discharge) curves for annealed olivine LiNiPO_4 in aqueous LiOH electrolyte at a current density of 0.5 mA/cm^2 . Metallic Sn is used as an anode.

Fig. 8 Sn- LiNiPO_4 battery using LiOH electrolyte illustrating the cyclability.

Fig. 9 Cyclic voltammogram of annealed lithium nickel phosphate (LiNiPO_4) in aqueous lithium hydroxide electrolyte (scan rate: $25 \mu\text{V} \cdot \text{s}^{-1}$; potential limit: 0.2 to -0.3 V and back) on successive cycling. Cycle numbers are indicated in the figure.

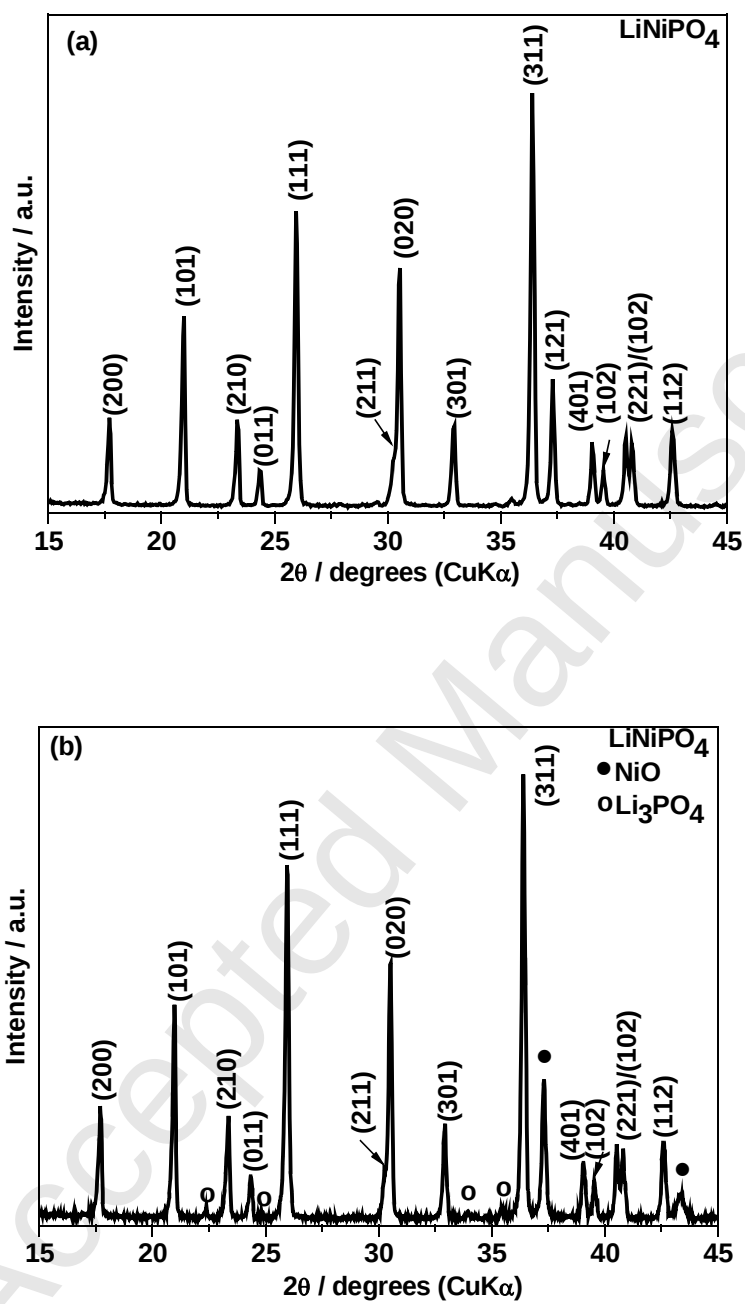


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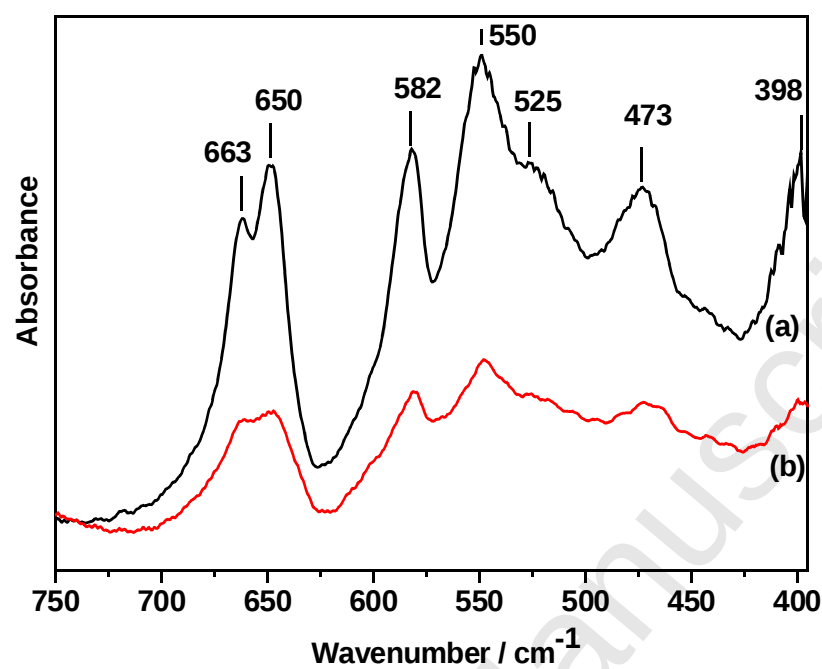


Fig. 2 The far IR spectra of the as-synthesized LiNiPO₄ (a) annealed and (b) non-annealed samples.

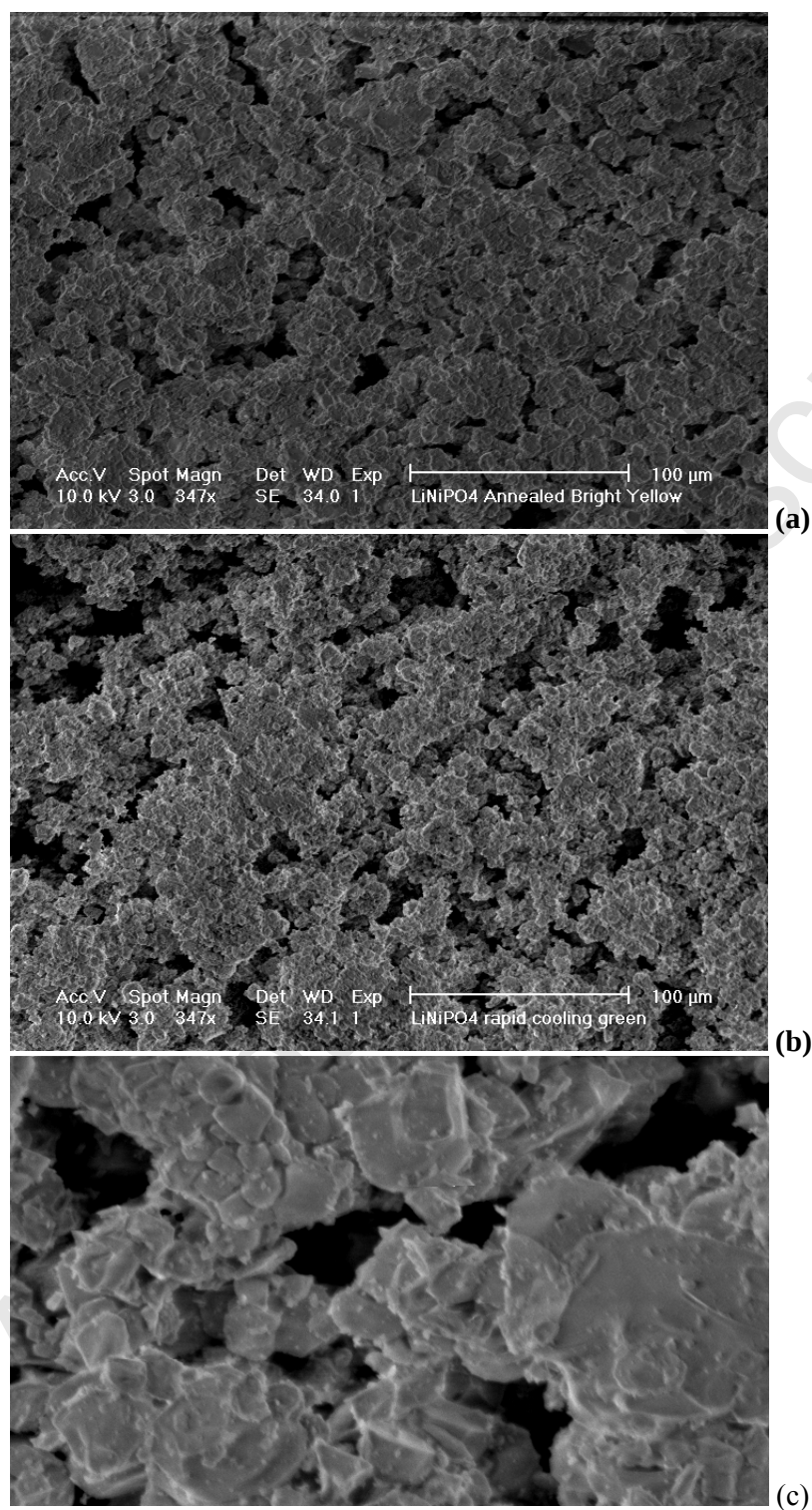


Fig. 3 Scanning electron micrographs of as prepared LiNiPO_4 olivine (a) annealed (b) non-annealed and (c) annealed sample at a higher magnification (4x of Fig. 3a) exhibits orthorhombic like structure.

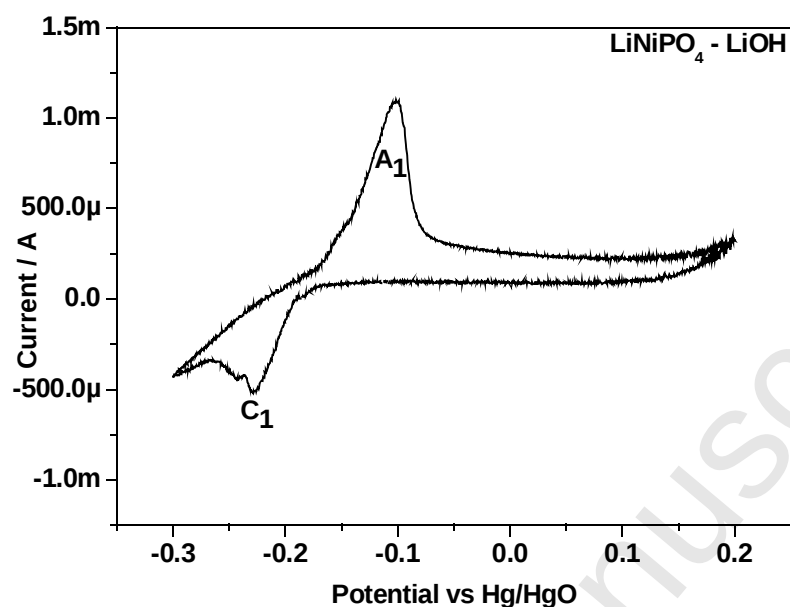


Fig. 4 A typical cyclic voltammogram of annealed lithium nickel phosphate (LiNiPO_4) in aqueous lithium hydroxide electrolyte (scan rate: $25 \mu\text{V} \cdot \text{s}^{-1}$; potential limit: 0.2 to -0.3 V and back).

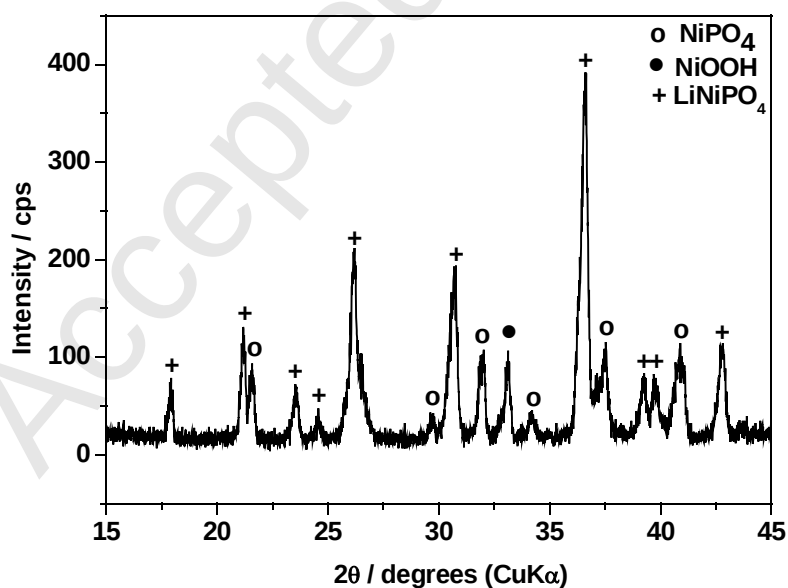


Fig. 5 XRD pattern of annealed LiNiPO_4 electrode after oxidation in aqueous LiOH electrolyte. “O” corresponds to (delithiated) NiPO_4 peaks.

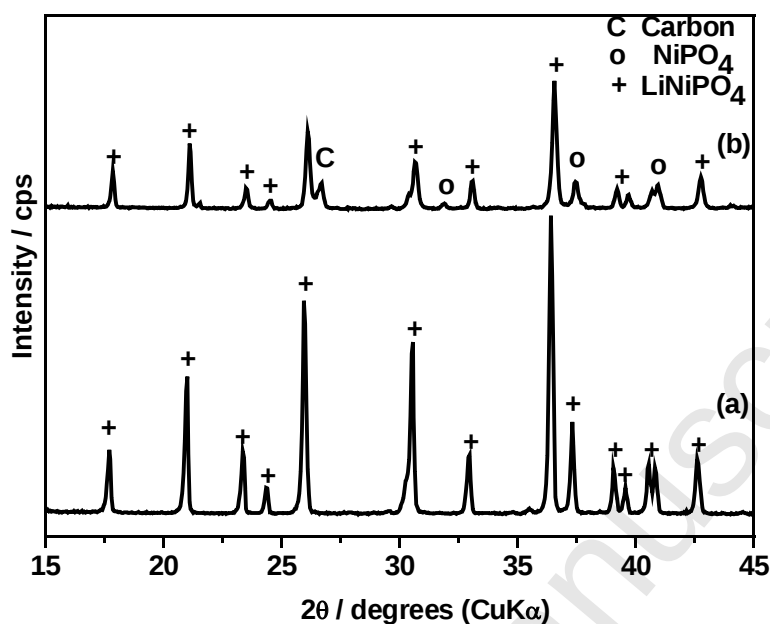


Fig. 6 XRD pattern of annealed LiNiPO_4 electrodes (a) before electrochemical treatment and (b) subsequent reduction after oxidation in aqueous LiOH electrolyte. “O” corresponds to (delithiated) NiPO_4 peaks reduced in intensity during lithiation.

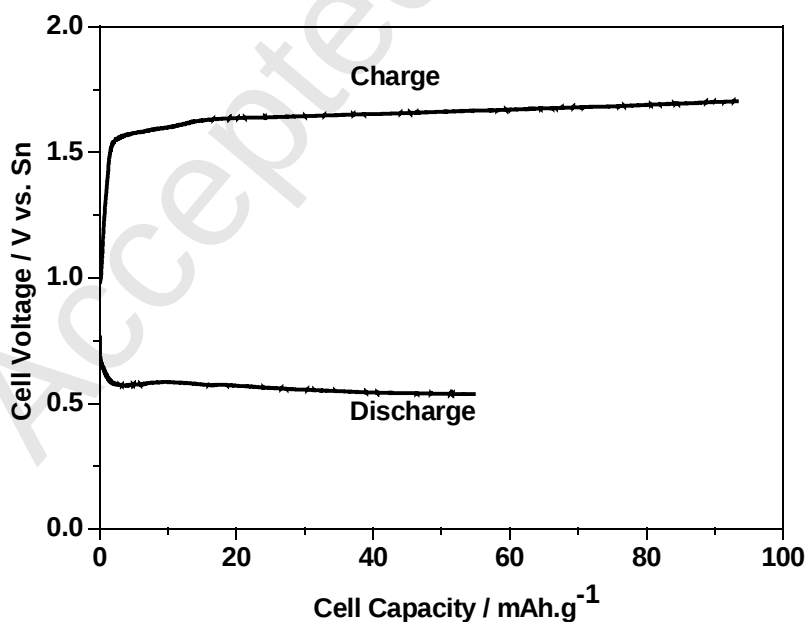


Fig. 7 Typical galvanostatic (charge-discharge) curves for annealed olivine LiNiPO_4 in aqueous LiOH electrolyte at a current density of 0.5 mA/cm^2 . Metallic Sn is used as an anode.

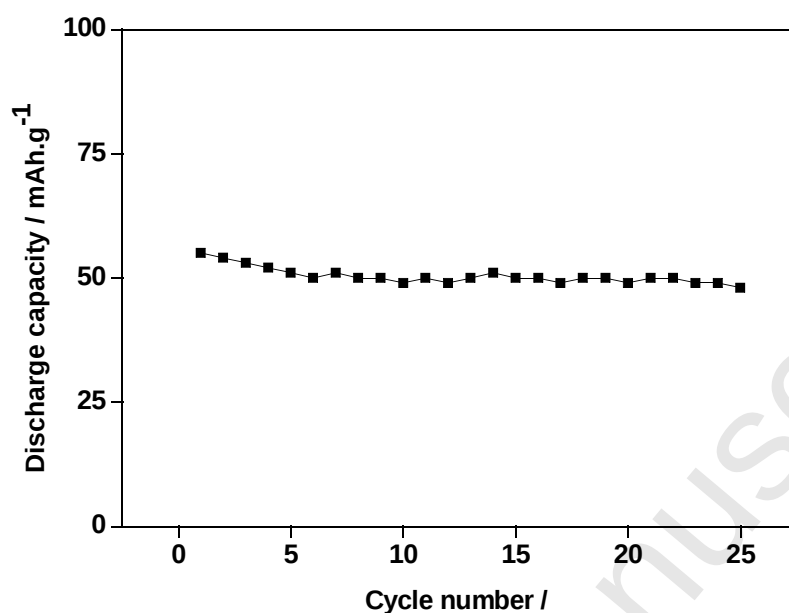


Fig. 8 Sn-LiNiPO₄ battery using LiOH electrolyte illustrating the cyclability.

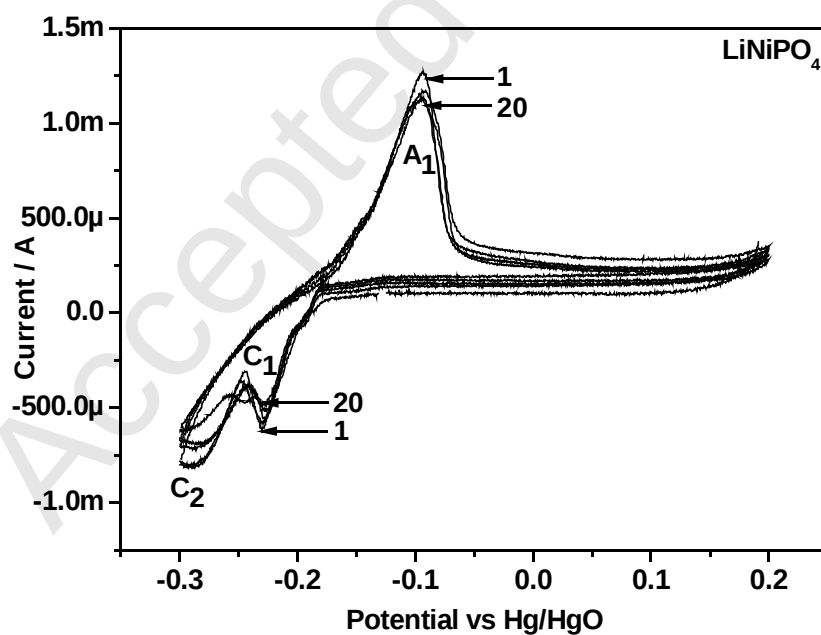


Fig. 9 Cyclic voltammogram of annealed lithium nickel phosphate (LiNiPO₄) in aqueous lithium hydroxide electrolyte (scan rate: 25 μV. s⁻¹; potential limit: 0.2 to -0.3 V and back) on successive cycling. Cycle numbers are indicated in the figure.