

# Characterization of Nanocathode Material for Rechargeable Lithium Ion Battery

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**Abstract**— Li-ion batteries are one of the most commercialized solutions to store electrochemical energy, but until now their broad use is limited to small electronic devices. During the past few years, much attention was focused on cathode materials with either high voltage or high capacity coupled with high stability. In the present work, we focused on the synthesis and characterization of LiNiPO<sub>4</sub> and lanthanum-doped LiNiPO<sub>4</sub> prepared by Pechini-type precursor method. The X-ray diffraction analysis confirms the formation of compounds LiNiPO<sub>4</sub> and lanthanum-doped LiNiPO<sub>4</sub> with orthorhombic structure. The Fourier transform infra-red analysis has been made to confirm the formation of Li<sub>1-y</sub>La<sub>y</sub>NiPO<sub>4</sub> (y = 0.05, 0.07, 0.09 mol%). From AC impedance analysis, it is found that the undoped LiNiPO<sub>4</sub> has ionic conductivity of 8.13×10<sup>-9</sup> S cm<sup>-1</sup> and the La-doped sample (Li<sub>0.93</sub>La<sub>0.07</sub>NiPO<sub>4</sub>) has maximum conductivity of 3.83×10<sup>-8</sup> S cm<sup>-1</sup> at ambient temperature. This value is one order greater than that of the undoped LiNiPO<sub>4</sub>.

**Keywords**— Cathode Material; Lanthanum; Lithium Ion Battery; Nickel Phosphate; Rare Earths

## I. INTRODUCTION

Currently the energy economy is in constant hazard due to the dependence on non-renewable fossil fuels. In recent years, substantial interest is being paid to exploit cathode materials for lithium ion batteries with high capacity, safety and dependability. Lithium orthophosphates LiMPO<sub>4</sub> (M=Fe, Mn, Co, Ni, etc.) have been a lot of interest as cathodes for use in Li-ion batteries [1]. These olivine phosphate cathode materials have been intensively studied as high energy and high potential cathodes for lithium ion batteries due to their non toxic, cost effectiveness, environmental friendly, stable even at over charge and better thermal stability during charging and discharging [2]. However, one of the main problems of olivine phosphate cathode materials lies in its poor rate capability, which is attributed to its low electronic and ionic conductivity and slow kinetics of lithium ion diffusion through the LiMPO<sub>4</sub> - MPO<sub>4</sub> interfaces [3]. Various approaches have been attempted to overcome this problem. Particle size reduction by modifying synthesis conditions, carbon coating and lattice doping with polyvalent metal ions are considered as effective ways to improve the electrochemical properties of lithium metal phosphates [4-8]. Chung et al [7] showed that controlled cation non-stoichiometry combined with solid-solution doping by metals polyvalent to Li<sup>+</sup> increases the electronic conductivity of Li<sub>0.99</sub>D<sub>0.01</sub>FePO<sub>4</sub> (D = Nb, Zr, Mg, Ti). Rare earth materials such as yttrium, lanthanum, europium, etc. have been used as dopants in the preparation of LiMPO<sub>4</sub>

(M=Fe, Mn, Co, Ni, etc.) cathode materials to improve their ionic conductivity. The research of Jiezi Hu et al [9] has shown that substitution of rare earth ions at Li site of (LiY)FePO<sub>4</sub> improves the ionic conductivity. LUO et al [10] added a small amount of lanthanum ions in LiFePO<sub>4</sub> by solid state synthesis, and found that these ions doping could improve its capacity delivery and cycle performance. Prabu et al carried out investigation on the undoped LiNiPO<sub>4</sub> and yttrium-doped LiNiPO<sub>4</sub> [11] and europium-doped LiNiPO<sub>4</sub> [12] cathode materials prepared by the Pechini-type polymerizable precursor method and found that the ionic conductivity of LiNiPO<sub>4</sub> (9.34×10<sup>-9</sup> S cm<sup>-1</sup>) is enhanced by around two orders of magnitude by doping yttrium and one order of magnitude by doping europium at room temperature.

In the present study an effort has been made to investigate the effect of the rare earth material lanthanum (La) on the structural, vibrational, and electrical properties of the LiNiPO<sub>4</sub> cathode material prepared by Pechini-type precursor method.

## II. EXPERIMENTAL

### A. Preparation of La-doped LiNiPO<sub>4</sub>

Cathode materials, bare LiNiPO<sub>4</sub> and LiNiPO<sub>4</sub> doped with different concentrations of lanthanum in mol% have been prepared by the Pechini-type precursor method using high purity raw materials. To prepare LiNiPO<sub>4</sub>, LiNO<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (Loba Chemie) are dissolved in double distilled water. In case of lanthanum doped LiNiPO<sub>4</sub> then lanthanum nitrate hexahydrate (LaNO<sub>3</sub>.6H<sub>2</sub>O) is added in different molar concentrations as reduced in lithium nitrate part. Citric acid (Loba Chemie) and Ethylene glycol (Spectrum) in the molar ratio of (0.2:0.2) have been added to the above salt solution for gelation with vigorous stirring. The solution is evaporated on a hot plate; the black powder recovered is ground into fine powder and calcinated at 800 °C by keeping it in silica crucible for 8 hours in muffle furnace to form yellow powder. The following compositions of cathode material have been prepared.

Li<sub>1-y</sub>La<sub>y</sub>NiPO<sub>4</sub> (y = 0, 0.05, 0.07, 0.09 mol%)

These samples are characterized using X-Ray diffraction (XRD), Fourier transform infra-red (FTIR) and complex impedance spectroscopy techniques. The results obtained from the instruments are explained with relevant literature, and presented in this paper.

### B. Characterization Techniques

The prepared undoped  $\text{LiNiPO}_4$  and La-doped  $\text{LiNiPO}_4$  powders are yellow in color. The diffraction patterns for the cathode materials are recorded on X'PERT-PRO X-ray diffractometer equipped with  $\text{CuK}\alpha$  radiation ( $\lambda=0.154$  nm) with a scan step time [s] 3.1750. Infra-red (IR) spectra is recorded in transmission mode by using SHIMADZU IR Affinity 1 spectrophotometer at ambient temperature. For conductivity measurements, the powder has been pressed (~1.2 ton pressure) to form a pellet (~1 mm thick and 10 mm diameter). AC measurements have been carried out using impedance analyzer HIOKI 3532 LCR HiTESTER at room temperature in the frequency range of 42 Hz to 1 MHz.

## III. RESULTS AND DISCUSSION

### A. XRD Analysis

The XRD is used to analyze structure parameters such as, unit cell parameters and unit cell volumes. The knowledge of such parameters especially for new materials is essential to find their technical applications. Figure 1 shows the X-ray diffraction patterns of undoped  $\text{LiNiPO}_4$  and  $\text{LiNiPO}_4$  doped with various concentrations of La. The diffraction patterns of all the samples have shown single phase  $\text{LiNiPO}_4$  with an orthorhombic olivine structure with the space group  $\text{P}_{mnb}$ . It can be observed from the patterns that all diffraction peaks are very strong, which indicated that the sample has good crystal structure [11]. The major diffraction peak values are well matched with the reported values (JCPDS file, 032-0578).

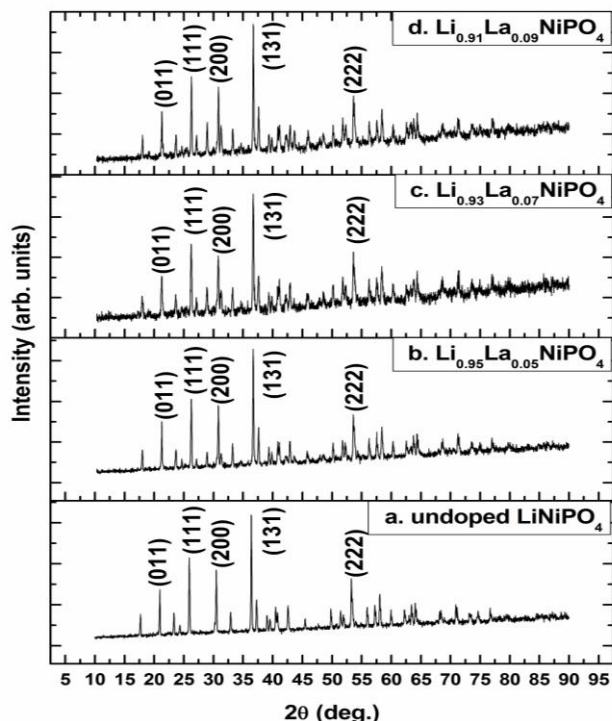


Figure 1 XRD patterns of (a) undoped  $\text{LiNiPO}_4$  and (b - d) La-doped  $\text{LiNiPO}_4$

The unit cell parameters (lattice constants) and unit cell volumes for the series of  $\text{Li}_{1-y}\text{La}_y\text{NiPO}_4$  ( $y=0, 0.05, 0.07, 0.09$  mol%) are calculated by using the software of cellcalc. These values are consolidated in Table 1 and displayed in Figure 2 (a) & (b). Doping effect will sometime increase or decrease lattice parameters depending on the nature of doping ion and amount of doping [5,10,11,13,14]. It is seen that doping of lanthanum does not change the crystal structure but decreases the lattice parameter along a-axis and increases along c-axis in  $\text{LiNiPO}_4$  as the position of  $\text{Li}^+$  in the lattice is partially replaced by  $\text{La}^{3+}$ , which is favorable for the transmission of Li ions along c-axis [11]. This is because; the radius of  $\text{Li}^+$  (0.076 nm) is smaller than that of  $\text{La}^{3+}$  (0.1016 nm).

Table 1 Lattice parameters and volume of the unit cell for all compounds

| Compound  | a (Å) | b (Å)  | c (Å) | Volume of the unit cell (Å) <sup>3</sup> |
|---|-------|--------|-------|--|
| $\text{LiNiPO}_4$                               | 5.869 | 10.034 | 4.681 | 275.6                                    |
| $\text{Li}_{0.95}\text{La}_{0.05}\text{NiPO}_4$ | 5.860 | 10.027 | 4.686 | 275.3                                    |
| $\text{Li}_{0.93}\text{La}_{0.07}\text{NiPO}_4$ | 5.861 | 10.044 | 4.682 | 275.6                                    |
| $\text{Li}_{0.91}\text{La}_{0.09}\text{NiPO}_4$ | 5.855 | 10.017 | 4.684 | 274.7                                    |

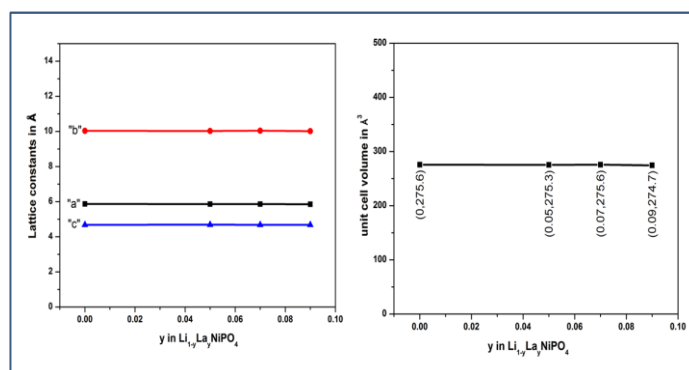


Figure 2 Variation of (a) unit cell parameters and (b) unit cell volume as a function of  $y$  in  $\text{Li}_{1-y}\text{La}_y\text{NiPO}_4$

### B. FTIR Analysis

Figure 3 shows the FTIR spectra for undoped  $\text{LiNiPO}_4$  and  $\text{LiNiPO}_4$  doped with various concentrations of La with wavenumber ranging from 400 to 4000  $\text{cm}^{-1}$  recorded at room temperature. The bands observed in the region 1400–400  $\text{cm}^{-1}$  are characteristic of phosphate ion  $[\text{PO}_4]^{3-}$  which are in free-state existing in tetrahedral (Td) symmetry.

The peak at 393  $\text{cm}^{-1}$  is essentially due to the translation modes of the Ni-O bonds. The peaks at 471-478  $\text{cm}^{-1}$  are attributed to vibrations of Li-O bonds. The intensity of this peak decreases considerably upon Li extraction from the olivine lattice [15]. The peak at 548  $\text{cm}^{-1}$  is attributed to the component originating to the  $\nu_2(\text{PO}_4)$  mode and the peaks at 648-656  $\text{cm}^{-1}$  are accredited essentially to the components originating to the  $\nu_4(\text{PO}_4)$  mode,  $\nu_2$  and  $\nu_4$  involve the symmetric and antisymmetric bending modes of O-P-O bonds [16]. The peaks observed between 964-1150  $\text{cm}^{-1}$  are related to stretching mode of the tetrahedral  $\nu_3(\text{PO}_4)$ ,  $\nu_3$  involves the antisymmetric stretching mode of P-O bonds [1]. The characteristic peaks at 471, 648, 964  $\text{cm}^{-1}$  observed for the undoped  $\text{LiNiPO}_4$  are found

to be shifted to 478, 656, 972  $\text{cm}^{-1}$  respectively for the La-doped  $\text{LiNiPO}_4$ . Changes in the intensity of peaks have been observed from the FTIR patterns of the La-doped  $\text{LiNiPO}_4$  with respect to undoped  $\text{LiNiPO}_4$ . Thus the FTIR analysis confirms the formation of La-doped  $\text{LiNiPO}_4$ .

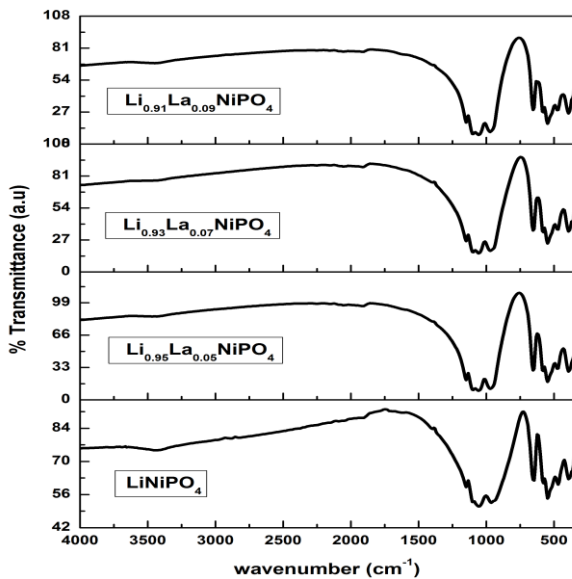


Figure 3 FTIR spectra for undoped  $\text{LiNiPO}_4$  and  $\text{LiNiPO}_4$  doped with various concentrations of La

### C. Impedance Analysis

The Cole-Cole plots or Nyquist plots ( $Z'$  versus  $-Z''$ ) for the series of samples  $\text{Li}_{1-y}\text{La}_y\text{NiPO}_4$  ( $y=0, 0.05, 0.07, 0.09$  mol%) prepared by Pechini-type precursor method at room temperature are shown in Figure 4. These plots consist of depressed semicircles for La-doped  $\text{LiNiPO}_4$  and a high frequency semicircle and a low frequency spike for undoped  $\text{LiNiPO}_4$ . These semicircles are due to parallel combination of bulk resistance ( $R_b$ ) and bulk capacitance ( $C_b$ ) of the materials. The depressed semicircle is an indication of the non-ideal nature of material and the spike is due to the effect of blocking electrodes. The equivalent circuit for the impedance plot of  $\text{LiNiPO}_4$  is given as inset of Figure 4. Bulk resistance values ( $R_b$ ) are obtained from the low frequency intercept of the semicircle on the real  $Z'$ -axis using the "EQ" software developed by Boukamp for the analysis of impedance data [17]. The ionic conductivity ( $\sigma$ ) values are calculated using the equation:

$$\sigma = L/R_b A \dots\dots (1)$$

where  $L$ ,  $A$ ,  $R_b$  are the thickness, area and bulk resistance of the pellet, respectively.

The conductivity values for all the samples at 303 K are presented in Table 2. The conductivity of the undoped  $\text{LiNiPO}_4$  at room temperature is found to be  $8.13 \times 10^{-9}$  S/cm which agrees well with that of the same sample reported by Prabu et al. [11]. In Pechini-type precursor method, the samples  $\text{LiNiPO}_4$  doped with different concentrations of La on Li site have shown improved conductivity over an order. The reason is that lanthanum doping can reduce the grain size, decrease the  $\text{Li}^+$  diffusion resistance. Also, the impregnation

of lanthanum leads to creation of vacancies of lithium ions which is beneficial to the diffusion of lithium ions and lanthanum can reduce the interaction force between  $\text{Li}^+$  and  $\text{Li}^+$ , which makes the  $\text{Li}^+$  intercalation/de-intercalation easier. Similar effect is reported by LUO et al [10] in lanthanum-doped  $\text{LiFePO}_4$ , Prabu et al [11] in yttrium-doped  $\text{LiNiPO}_4$  and Tian et al [18] in yttrium-doped  $\text{LiFePO}_4$ . The sample with 0.07 mol% La-doped  $\text{LiNiPO}_4$  on Li site has maximum conductivity of  $3.83 \times 10^{-8}$  S/cm at 303 K. It is noted that lanthanum doping improves the conductivity of  $\text{LiNiPO}_4$ .

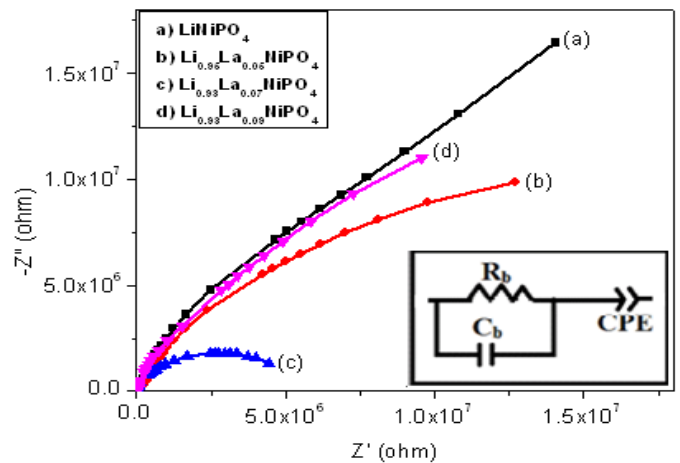


Figure 4 Nyquist plots for all samples at room temperature (303 K)

Table 2 Conductivity values of all the cathode materials at room temperature

| $\text{Li}_{1-y}\text{La}_y\text{NiPO}_4$ | Conductivity (S/cm)   |
|---|-----------------------|
| y   |                       |
| 0   | $8.13 \times 10^{-9}$ |
| 0.05                                      | $1.38 \times 10^{-8}$ |
| 0.07                                      | $3.83 \times 10^{-8}$ |
| 0.09                                      | $7.19 \times 10^{-9}$ |

### IV. CONCLUSION

Nanocathode materials based on  $\text{LiNiPO}_4$  and La-doped  $\text{LiNiPO}_4$  on Li sites have been prepared by Pechini-type precursor method and investigated for structural, vibrational, and electrical properties. The X-ray diffraction patterns of the samples confirm single phase formation and orthorhombic crystal structure. FTIR spectra of the samples show characteristic peaks for  $[\text{PO}_4]^{3-}$  ion, Li-O symmetric bending and Ni-O bending, shifts and changes in the intensity of the characteristic absorption peaks for the La-doped  $\text{LiNiPO}_4$  with respect to undoped  $\text{LiNiPO}_4$  confirming the formation of La-doped  $\text{LiNiPO}_4$ . Complex impedance spectroscopy reveals that the 0.07 mol% of La-doped on Li-site of  $\text{LiNiPO}_4$  has improved the conductivity over an order. It can be seen that the sample  $\text{Li}_{0.93}\text{La}_{0.07}\text{NiPO}_4$  shows better conductivity ( $3.83 \times 10^{-8}$  S/cm at 303 K) than all other samples. This optimized sample  $\text{Li}_{0.93}\text{La}_{0.07}\text{NiPO}_4$  proves to be a better choice for cathode material in Li-ion batteries.

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