

Influence of europium doping on conductivity of LiNiPO_4

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Abstract: Europium doped LiNiPO_4 and undoped LiNiPO_4 were prepared by Pechini method. Compound formation temperature was confirmed from thermogravimetry and differential thermal analysis (TG/DTA). Powder X-ray diffraction (XRD) pattern confirmed the formation of pure LiNiPO_4 compound with an orthorhombic structure. The conductivity and modulus analyses of the samples were carried out at different temperatures and frequencies using the complex impedance spectroscopy technique. The conductivity parameters such as ion hopping frequency and the charge carrier concentration term were calculated using Almond and West formalisms. An increase of one order of magnitude in the ionic conductivity has been observed for 1.0% Eu-doped LiNiPO_4 (mole fraction). The complex modulus studies suggest the presence of non-Debye type of relaxation in the materials.

Key words: LiNiPO_4 ; ionic conductivity; impedance spectroscopy; doping; hopping

1 Introduction

Recently, lithium metal phosphates LiMPO_4 ($M=\text{Fe}$, Mn , Co , and Ni) with olivine-type structure have attracted considerable attention as perspective intercalation materials for lithium-ion batteries because of their low cost, improved safety and good capacity retention [1–3].

Unfortunately, besides all their advantages, olivine phased compounds have one serious deficiency, i.e., their very low electrical conductivity. Many efforts have been undertaken to improve electrical properties by structure modification, introduction of carbon additives [4,5] or by selective doping with supervalent metal ions such as Mg^{2+} , Al^{3+} , Cr^{3+} , Zr^{4+} , Ti^{4+} , Nb^{5+} , W^{6+} [6–9], which can greatly improve the conductivity. It is observed, so far no study has been made on the conductivity mechanisms of europium-doped LiNiPO_4 cathode material by means of impedance spectroscopy. The goal of this work is to study the conductivity processes in europium-doped LiNiPO_4 at temperatures from 303 K to 423 K using impedance measurements at frequencies from 10 Hz to

1 MHz in order to deduct useful information about the Li ion mobility in the orthorhombic structure.

2 Experimental

The Pechini method, as described in Ref. [10], has been employed for the preparation of 1.0% (mole fraction) europium-doped LiNiPO_4 cathode material. The synthesis procedure adopted for the preparation of europium-doped LiNiPO_4 cathode material is schematically shown in Fig. 1. Stoichiometric amounts of LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ of analytical grade, have been used as starting materials together with citric acid and ethylene glycol. Pyrolysis of the mixture obtained was performed at 350 °C for 2 h in a hot plate that yielded homogeneous black powder precursors that have been ground into fine powders and has been calcinated at 800 °C for 8 h.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) studies have been performed using Perkin Elmer Diamond TGA/DTA instrument at a heating rate of 5 °C/min in air. XRD patterns have been obtained using a XPERT-PRO X-ray diffractometer

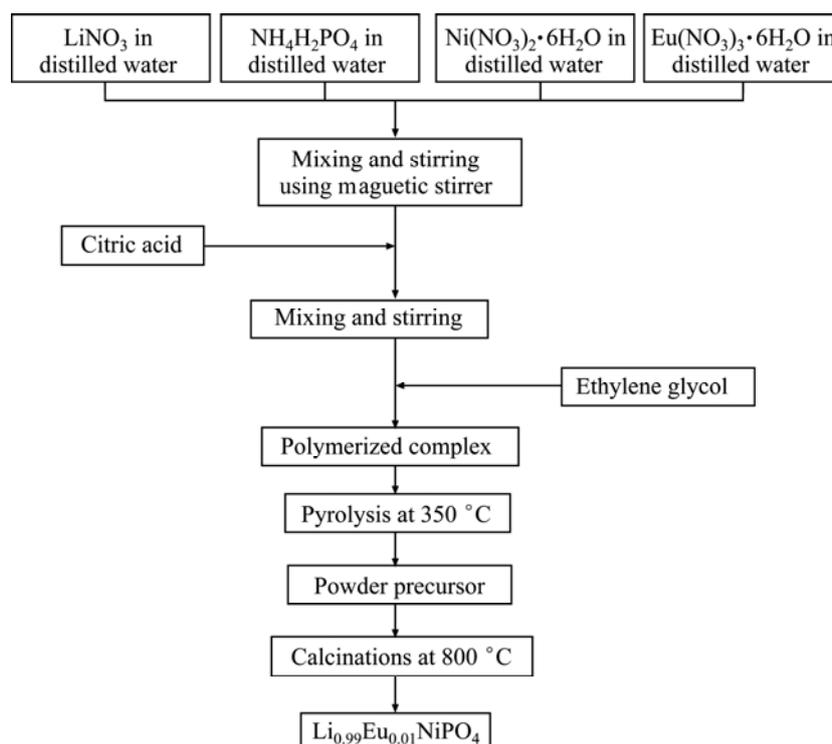


Fig. 1 Schematic diagram of synthesis of europium-doped LiNiPO_4 cathode material

PW3050/60 with Cu K_α radiation having a wavelength of 1.5417 \AA at room temperature. A pressure around 1.76 kN (1.2 t) was applied to forming a pellet with 1 mm in thickness and 10 mm in diameter. The pellet has been sintered at $600 \text{ }^\circ\text{C}$ for 3 h . The pellets were coated with conductive silver paint. Complex impedance spectroscopy (CIS) measurements have been carried out using a Solatron 1260 frequency response analyzer combined with a Solatron 1296 electrochemical interface. The impedance spectra were recorded over the frequency range of 10 Hz to 1 MHz in different temperature ranges.

3 Results and discussion

3.1 Thermal response

In order to obtain the information about the exact temperature of the formation reaction of the olivine structured LiNiPO_4 and europium doped LiNiPO_4 powders, combined thermal analysis (TG/DTA) on the precursor complex has been studied in the temperature range from room temperature to $850 \text{ }^\circ\text{C}$. The results are shown in Fig. 2.

Thermogravimetric analyses of both samples exhibit a gradual and an initial mass loss up to about $630 \text{ }^\circ\text{C}$ due to the initial evaporation of water (below $200 \text{ }^\circ\text{C}$) and a subsequent decomposition of precursors ($200\text{--}630^\circ\text{C}$) from the in-situ formed metastable complex. In other words, the decomposition of citric acid with evolution of NO_2 and NH_3 gases followed by the final

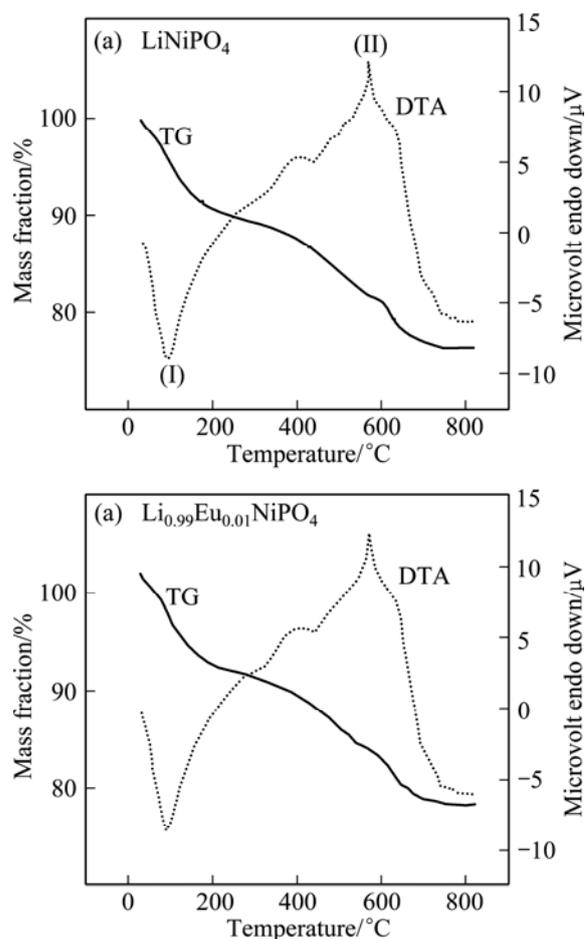


Fig. 2 TG–DTA curves of LiNiPO_4 (a) and Eu-doped LiNiPO_4 (b)

decomposition which shows larger exothermic peak observed at 572 °C in the DTA curve, which results in the formation of LiNiPO_4 and europium-doped LiNiPO_4 . Herein, the compound formation process starts at a temperature as low as 450 °C and gets completed around 630 °C. It is indicated that no exothermic reaction or mass-loss appears after 630 °C.

3.2 X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of LiNiPO_4 and 1.0% europium-doped LiNiPO_4 powders are shown in Fig. 3. The diffraction peaks of both samples are in full accordance with the ordered LiNiPO_4 olivine structure indexed to the orthorhombic $Pnma$ space group with (JCPDS file number 88–1297). It can be seen from the patterns that all diffraction peaks are very strong after europium doping, which indicates that the samples have good crystal structure.

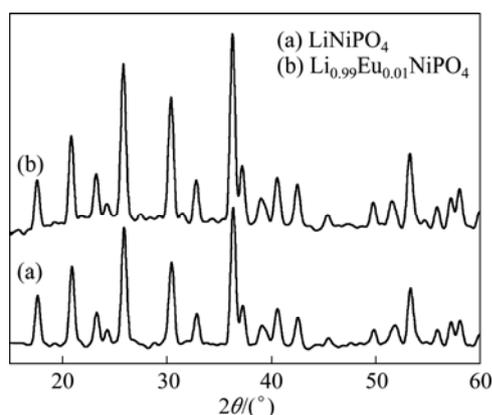


Fig. 3 XRD patterns of LiNiPO_4 (a) and Eu-doped LiNiPO_4 (b)

3.3 Conductance spectra analysis

The conductance spectra of LiNiPO_4 and europium-doped LiNiPO_4 measured at various temperatures are given in Fig. 4. The pattern of variation indicates low-frequency plateau and high-frequency dispersion. The hopping frequency is found to shift towards the higher frequency as temperature increases. This behavior suggests that electrical conduction in the material takes place via hopping mechanism governed by the Jonscher's power equation [11]:

$$\sigma(\omega) = \sigma_{\text{DC}} + A\omega^n \quad (1)$$

where $\sigma(\omega)$ is the conductivity at a particular frequency; σ_{DC} is the DC conductivity of the sample; ω is the angular frequency; A is a constant; n is the ratio of backhop rate to site relaxation time.

The frequency independent conductivity at low frequency region corresponds to DC conductivity of the sample [12]. The room temperature conductivity of LiNiPO_4 is found to be 9.34×10^{-9} S/cm. The conductivity increases by doping europium in LiNiPO_4 .

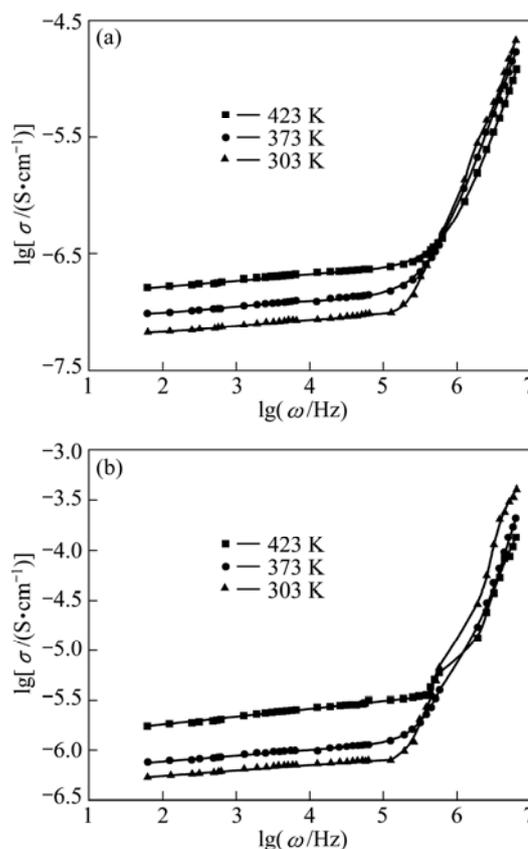


Fig. 4 Conductance spectra of LiNiPO_4 (a) and Eu-doped LiNiPO_4 (b) at various temperatures

A conductivity value of 7.02×10^{-8} S/cm is observed for europium doped LiNiPO_4 which is about one order of magnitude higher than LiNiPO_4 .

According to the jump relaxation model reported by FUNKE [13], the power law exponent (n) relates the ratio of backhop rate to the site relaxation time.

The backhop is the backward motion of a hopping ion to its initial site, which is caused by the coulomb repulsive interaction between mobile ions. The conductance spectra of all the samples have been fitted with Eq. (1) and the parameter (n) has been extracted and given in Table 1. The decrease in n in the case of doping europium has been observed and it may be due to the formation of free sites for Li ion migration, which in turn reduces the backhop rate and hence n decreases.

Ionic hopping rate (ω_p) has been calculated from the conductance spectra for all the samples at different temperatures using the formula proposed by ALMOND and WEST [14].

$$\sigma(\omega) = 2\sigma_{\text{DC}} \quad (2)$$

The hopping rate (ω_p) has been calculated from the conductance spectra for all the samples at different temperatures given in Table 1. The magnitude of the carrier-concentration term (K) can be obtained from the following formula [15]:

Table 1 Transport parameters of doped and undoped LiNiPO₄

Sample	Temperature/K	$\sigma/(S \cdot cm^{-1})$	n	ω_p/Hz	τ_c/s	β	$K/(S \cdot cm^{-1} \cdot kHz^{-1})$
LiNiPO ₄	303	9.34×10^{-9}	0.98	1.34×10^5	5.08×10^{-6}	0.85	0.160×10^{-10}
	373	1.08×10^{-7}	0.83	2.84×10^5	3.85×10^{-6}	0.76	1.42×10^{-10}
	423	1.90×10^{-7}	0.75	4.29×10^5	2.13×10^{-6}	0.71	1.87×10^{-10}
Li _{0.99} Eu _{0.01} NiPO ₄	303	7.02×10^{-8}	0.93	2.07×10^5	4.29×10^{-6}	0.76	1.03×10^{-10}
	373	8.68×10^{-7}	0.75	3.26×10^5	3.71×10^{-6}	0.74	9.91×10^{-10}
	423	2.29×10^{-6}	0.62	4.84×10^5	1.27×10^{-6}	0.66	12.6×10^{-10}

$$K = \sigma T / \omega_p \tag{3}$$

The charge carrier concentration term remains almost constant over the temperature range studied for all the samples as shown in Table 1. This reveals that all the lithium ions which are responsible for the conductivity are in a mobile state.

3.4 Modulus spectra analysis

In 1970’s many researchers opted to study the dielectric response caused by ion relaxation using the reciprocal quantity, $M^* = \epsilon^* = M' + jM'' = j\omega C_0 Z^*$, known as the electric modulus [16, 17], in which the electrode polarization artifacts are suppressed where M' and M'' are the real and imaginary parts of modulus; Z^* is complex impedance; C_0 is the vacuum capacitance of the empty measuring cell; $\omega (\omega = 2\pi f, \text{ where } f \text{ is the frequency})$ is the angular frequency; $j = (-1)^{1/2}$. Typical features of modulus spectrum include a broad, asymmetric peak in the imaginary part and a sigmoidal step in the real part. This feature is due to the storage of mechanical stress associated with relaxation processes of the conducting species. Figure 5 shows the frequency dependence of M'' at various temperatures for europium-doped and undoped LiNiPO₄. The broadened nature of the peaks can be interpreted with the distributions of relaxation time.

The maximum of modulus spectra $M''(\omega_{max})$ shifts towards the higher frequencies with increase in temperature. This behavior suggests that the dielectric relaxation is activated thermally in which hopping process of charge carriers takes place [18]. Also, shifting of the peak frequencies in the forward direction with temperature implies that the relaxation time decreases with increase in temperature. The angular frequency ω_{max} corresponding to $M''(\omega_{max})$ gives the relaxation time (τ_c) under the condition of $\omega_{max}\tau_c = 1$. Values of relaxation time (τ_c) for both samples are given in Table 1. The non-exponential conductivity relaxation can be described by a Kohlrausch Williams Watt (KWW) function $\Phi(t)$, which represents the distribution of relaxation time in ion conducting materials [19]. The electric modulus can be represented as:

$$M^* = M_\infty \left[1 - \int_0^\infty dt \exp(-i\omega t) \left(\frac{d\Phi}{dt} \right) \right] \tag{4}$$

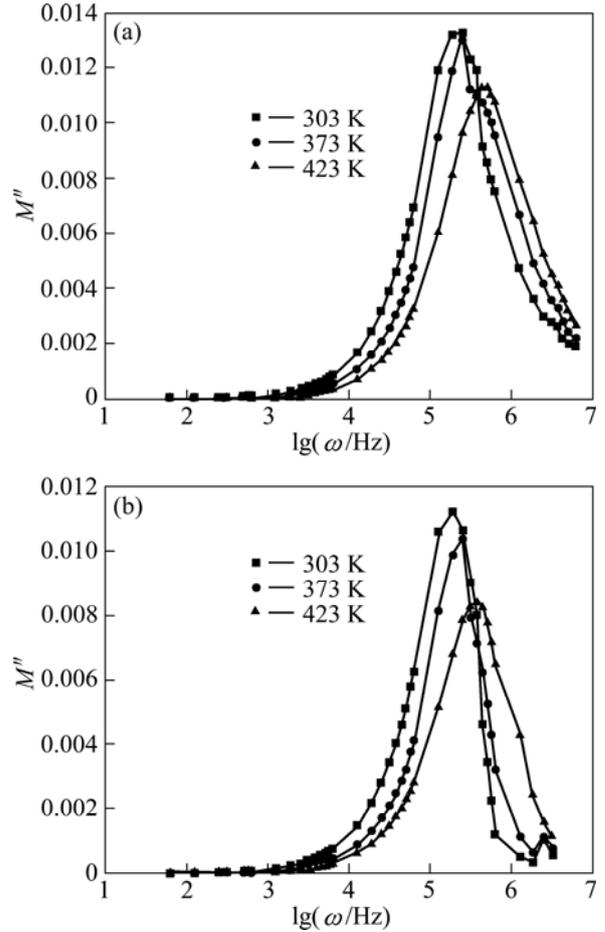


Fig. 5 Modulus spectra for samples of LiNiPO₄ (a), Eu-doped LiNiPO₄ (b)

And

$$\Phi(t) = \Phi_0 \exp \left[- \left(\frac{t}{\tau\sigma} \right)^\beta \right] \tag{5}$$

where Φ_0 is the conductivity relaxation time and β is the Kohlrausch exponent. The parameter β is most often interpreted as a result of correlated motions between ions. This means that the jump of a mobile ion in a material cannot be treated as an isolated event. The parameter β corresponding to the studied sample was established as a function of temperature using modulus formalism. Using the modulus formalism, i.e., M'' spectrum, the corresponding full width half height (FWHH) is wider

than the breadth of the Debye peak (1.14 decades) and thus results in a value of $\beta=1.14/\text{FWHM}$. The parameter β has been calculated for all the samples tabulated in Table 1. The low β value, i.e., high FWHM, of both samples reveals non-Debye nature of this material. The non-Debye property of the materials arises due to the presence of unequal potential barriers for the conduction species [20–24].

4 Conclusions

Europium-doped and undoped LiNiPO_4 have been prepared by Pechini technique. TG–DTA analysis and XRD pattern confirm the formation of the sample. The conductivity and modulus properties of the materials have been investigated with the help of complex impedance spectroscopy technique. From conductance spectra, conductivity parameters such as hopping frequencies and the charge carrier concentration term have been calculated using the Almond and West formalism. The ionic conductivity of LiNiPO_4 is enhanced by around one order of magnitude by doping europium. The distribution of relaxation time, which causes the non-Debye nature of the material, has been explained from the broad nature of the modulus spectra.

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Eu 掺杂对 LiNiPO_4 导电性的影响

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摘 要: 采用 Pechini 方法制备了掺杂 Eu 和未掺杂 Eu 的 LiNiPO_4 化合物, 通过热重分析和差热分析(TG/DTA) 来确定 LiNiPO_4 的生成温度。粉末 X 射线衍射谱证实所得到的化合物为具有正交结构的纯 LiNiPO_4 。采用复合阻抗谱技术分析样品在不同的温度和频率下的电导率和模量谱。采用 Almond 和 West 公式计算导电性能参数, 如离子跃迁频率、电荷载体浓度。掺杂 1.0% Eu 的 LiNiPO_4 的离子电导率增加了一个数量级。电模量谱分析表明 LiNiPO_4 化合物中存在非德拜类型的弛豫。

关键词: LiNiPO_4 ; 离子导电性; 阻抗谱; 掺杂; 跃迁

(Edited by YANG Hua)