Electrochemical studies on LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ cathode material synthesized by polyol method

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Abstract: LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ was prepared by polyol method using 1, 2 propanediol as a polyol medium. The cathode properties were analyzed through electrochemical impedance spectroscopy, cyclic voltammetry and charge-discharge studies. Electrochemical impedance spectroscopy revealed the presence of sluggish kinetic behavior in the LiNi$_{0.85}$Zn$_{0.15}$PO$_4$. The charge transfer resistance was decreased upon doping of Zn$^{2+}$ in LiNiPO$_4$. Cyclic voltammetry results have shown a reversible one-stage process of intercalating and de-intercalating lithium from and into LiNi$_{0.85}$Zn$_{0.15}$PO$_4$. The discharge capacity of LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ is found to be 4mAh g$^{-1}$.

Keywords: Lithium Nickel Phosphate, Electrochemical studies, Polyol method, Doping.

1. Introduction

In recent years, considerable interest is being paid to develop cathode materials for Li-ion batteries with high capacity, safety and reliability. LiMPO$_4$ (M= Fe, Co, Mn, and Ni) olivine structured materials are examined as an attractive cathode materials due to their higher theoretical capacity and/or energy density than that of other commercial cathodes[1,2,3]. Among these materials, LiNiPO$_4$ is expected to have a high energy density due to its 5.1 V discharge plateau. Though this material is working at high voltage, it suffers from poor electronic conductivity and electrochemical performance. The lower electrical conductivity of LiNiPO$_4$ causes miserable Li$^+$ intercalation/deintercalation. Electrochemical performance of LiNiPO$_4$ is improved by different synthesis methods[5], metal doping on the lattice[6], carbon coating on the particle surface and materials prepared from carbon containing precursors[7]. The solid solutions of LiNiPO$_4$-LiCoPO$_4$ do not have adequate conductivity to observe Ni$^{3+}$/Ni$^{2+}$ potential[8]. Graphite carbon foams coated on LiNi$_y$PO$_4$ (y=0.8, 1.0) shows redox couple in the range of 5.1 and 5.2V and the specific capacity of this composite increases by reducing the nickel content in LiNiPO$_4$[9]. The electronic conductivity of LiNiPO$_4$ is found to be increased upon 10% doping of Cu$^{2+}$, Mg$^{2+}$ and Al$^{3+}$[10]. Further, the specific capacity is also improved by Mg$^{2+}$ doped graphite carbon foams LiNi$_{1-y}$Mg$_y$PO$_4$ composites[11]. Addition of Zn$^{2+}$ to LiFePO$_4$ causes improvement in the electronic conductivity and Li-ion diffusion coefficient of the material[12]. The electrical conductivity of LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ is higher than that of bare LiNiPO$_4$ and other compositions[13]. So, the present work aims to study the electrochemical performance of LiNi$_{0.85}$Zn$_{0.15}$PO$_4$.

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2. Experimental

Bare LiNiPO$_4$ and LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ were prepared by polyol method using 1,2propanediol as a polyol medium. The preparation is discussed elsewhere[3]. For testing the electrochemical properties of the as-prepared electrodes, Swagelok cell was used. The cells contained the as-prepared electrode as the working electrode, lithium foil as the counter and reference electrode, a porous polypropylene as the separator, and 0.5 M Lithium nanoflouro 1,2 butane sulfonate in a 2:1 mixture of propylene carbonate (PC) and dimethaxy ethane(DME) as the electrolyte. The electrodes for lithium-ion batteries tests were fabricated by mixing the 75wt% active material, 15 wt% activated carbon and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) homogenously. The slurry was uniformly pasted onto Al foil (for cathode) and dried in an oven at 80-100 °C overnight under vacuum. Electrodes are kept in an argon filled glove box. The cells were assembled in an argon filled glove box (MIKROUNA) with O$_2$ and H$_2$O levels less than 0.1 ppm. The electrochemical impedance measurements were conducted with Biologic Electrochemical Workstation model SP-300.

3. Results and discussion

3.1 Electrochemical impedance spectroscopy

EIS is an important technology to study the lithium ion batteries. Figure 1a and 1b show the Nyquist plots of LiNiPO$_4$ and LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ that are obtained from the swadgelock cell before and after 5 cycles. The plots give a similar profile composed of a semicircle in the high frequency region and an inclined line in the low frequency region. An equivalent circuit as shown in the inset figure is used to fit the impedance spectrum. The impedance parameters of R$_s$, R$_ct$, CPE and W represent the solution resistance, charge transfer resistance, double layer capacitance and Warburg impedance respectively. The charge transfer resistance value decreases from 1302 Ω for undoped LiNiPO$_4$ to 57 Ω for LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ due to an improvement in electrochemical kinetics of LiNiPO$_4$. Decrease of charge transfer resistance corresponds to the mutual solubility of Zn$^{2+}$ and Ni$^{2+}$ ions. After few cycles, the charge transfer values are increased. Especially for undoped LiNiPO$_4$, it is increased (4358 Ω) suddenly even after 4$^{th}$ cycle. This may be due to the presence of slow lithium ion kinetics in undoped and doped LiNiPO$_4$ during cycling. The abrupt increase of charge transfer resistance of the LiNiPO$_4$ is considered as the main reason for the capacity fading which is expected to reflect in charge-discharge studies.

![Figure 1a: Electrochemical impedance spectra of bare LiNiPO$_4$ after and before cycling](image1)

![Figure 1b: Electrochemical impedance spectra of LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ before and after cycling](image2)
3.2 Cyclic voltammetry studies

Figures 2a and 2b show the cyclic voltammetry curves for bare LiNiPO$_4$ and LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ prepared by polyol method. From the CV curves at the scan rate of 0.5 mV/sec, it can be seen that both materials have a redox Ni$^{2+}$/Ni$^{3+}$ reaction coupled with the lithium ion extraction/insertion in the olivine structure. There is no significant oxidation and reduction peak identified in the first cycle. The material shows one anodic peak at 4.29 V and one distinct cathodic peak at 3.37 V in the subsequent cycles (4th, 5th and 6th cycles) signifying a reversible one-stage process of intercalating and de-intercalating lithium from and into LiNiPO$_4$. Similar results are also observed [14] for LiNiPO$_4$ by CAM sol-gel method under air atmosphere. The redox potential is found to be 3.8 V and 3.5V for oxidation and reduction respectively. LiNiPO$_4$ prepared under air and argon atmosphere do not show any redox couple in CV analysis.

The material synthesized from both argon atmosphere and carbon coating shows the redox couple at 5.3 V (anodic) and 5.1 V (cathodic)[15]. The role of carbon is still not fully understood. Despite that, their data underline that some kind of carbon support is required for LiNiPO$_4$ to exhibit lithium insertion/deinsertion[1]. But, the present study shows that polyol method is one of the best methods to produce the phase pure LiNiPO$_4$ which also shows the redox couples.

It is noted from the figure 2b, Zn$^{2+}$ doped sample shows the redox couple in the range of 4.01–4.4 V (anodic potential) and 3.4 & 3.7 V (cathodic potential). This indicate that the insertion/extraction process of Li-ions through Ni$^{2+}$/Ni$^{3+}$ redox reactions become more reversible with cycling upon doping of Zn$^{2+}$. The CV response also infers that the voltage difference between the Li$^+$ intercalation-de-intercalation is less (~0.6 V), thus accounting for the high degree of reversibility in Li$^+$ intercalation-deintercalation process[16].
3.3 Charge-discharge studies

Figure 3a: Charge-discharge curves of pristine LiNiPO$_4$ measured at C/20.

Figure 3a shows the galvanostatic charge-discharge profiles for bare LiNiPO$_4$ at low current rate (C/20) for 4 cycles. The observed voltage profile of the LiNiPO$_4$ electrode evolves around the 4.6 V vs Li$^+$/Li in charged state with a depressed trend in the discharged state. Under such a low rate condition, pure LiNiPO$_4$ material demonstrates very low capacity. The first delivered capacity, i.e. 1.1 mA.h g$^{-1}$ is far from the theoretical value of 167 mA h/g even if at a low current rate of C/20. No plateaus above 4.6 V are observed for LiNiPO$_4$. Similar results are also observed by wolfenstine et al who observed the capacity of about <5mA h g$^{-1}$ [2]. Surprisingly, LiNiPO$_4$ does not charge above 4.6 V even low current at C/20 rate. The observed capacity is found to be nearly zero when it is charged up to 5.1V at 1C rate. Figure 3b shows the discharge curves for LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ at C/20 rate in the voltage range of 2.8 V-4.6 V vs. Li$^+$. Similar result is also observed by wolfenstine et al who observes the capacity of about < 5 mA.h g$^{-1}$ for 20% cobalt doped LiNiPO$_4$. The disappointing capacity of the transition metal doped LiNiPO$_4$ mainly results from low intrinsic electronic conductivity and sluggish kinetics of Li-ion transport [17].

Figure 3b: Charge-discharge curves of LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ measured at C/20.

4. Conclusions

LiNiPO$_4$ and LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ were prepared by polyol method. The electrochemical performance of undoped LiNiPO$_4$ and LiNi$_{0.85}$Zn$_{0.15}$PO$_4$ electrodes was investigated by using EIS, CV and galvanostatic charge-discharge studies. Electrochemical impedance spectroscopy results reveal that the electrical conductivity is enhanced upon Zn$^{2+}$ doping. Cyclic voltammogram measurements provide strong evidence that the Zn$^{2+}$ doping can improve cycling reversibility. At discharge current of C/20, undoped LiNiPO$_4$ has initial discharge capacity of 1mAh g$^{-1}$ whereas Zn$^{2+}$ doped sample possess the capacity of 4 mAh g$^{-1}$. 
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References


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