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

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Abstract : $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ was prepared by polyol method using 1, 2 propanediol as a polyol medium. The cathode properties were analyzed through electrochemical impedance spectroscopy, cyclic voltametry and charge-discharge studies. Electrochemical impedance spectroscopy revealed the presence of sluggish kinetic behavior in the $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$. The charge transfer resistance was decreased upon doping of Zn^{2+} in LiNiPO_4 . Cyclic voltammety results have shown a reversible one-stage process of intercalating and de-intercalating lithium from and into $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$. The discharge capacity of $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ 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 $\text{Ni}^{3+}/\text{Ni}^{2+}$ potential[8]. Graphite carbon foams coated on LiNi_yPO_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 $\text{LiNi}_{1-y}\text{Mg}_y\text{PO}_4$ 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 $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ is higher than that of bare LiNiPO_4 and other compositions[13]. So, the present work aims to study the electrochemical performance of $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$.

2. Experimental

Bare LiNiPO_4 and $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ 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_2O 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 $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ 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} , CPE2 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 $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ 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 4th 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.

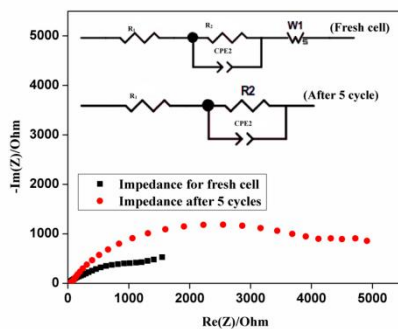


Figure 1a: Electrochemical impedance spectra of bare LiNiPO_4 after and before cycling

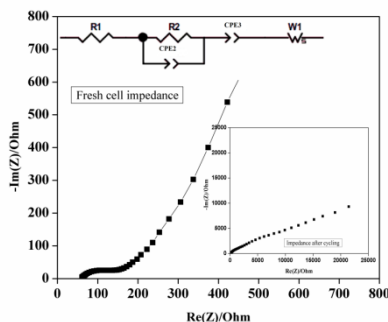


Figure 1b: Electrochemical impedance spectra of $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ before and after cycling

3.2 Cyclic voltammetry studies

Figures 2a and 2b show the cyclic voltammetry curves for bare LiNiPO_4 and $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ 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 $\text{Ni}^{2+}/\text{Ni}^{3+}$ 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.

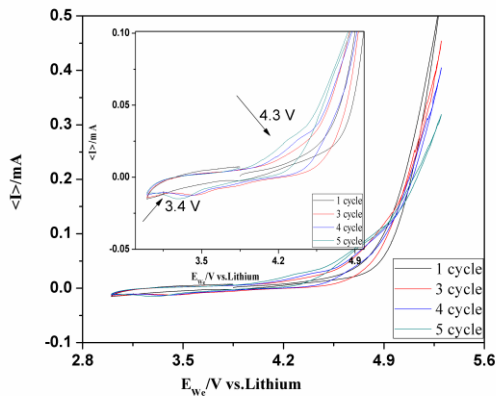


Figure 2a: Cyclic voltammetry curves of bare LiNiPO_4

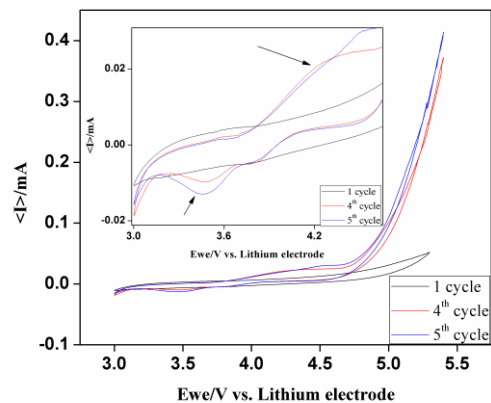


Figure 2b: Cyclic voltammetry curves of $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$

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^+ through $\text{Ni}^{2+}/\text{Ni}^{3+}$ 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

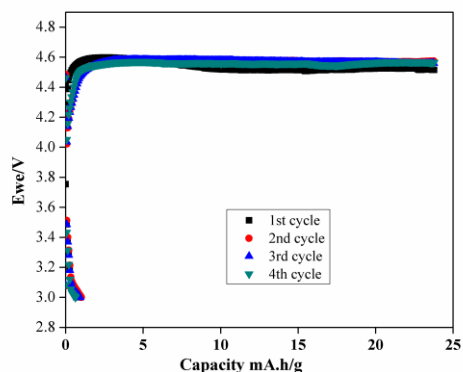


Figure 3a: Charge-discharge curves of pristine LiNiPO_4 measured at $C/20$.

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 $<5 \text{ mA h g}^{-1}$ [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 $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ at $C/20$ rate in the voltage range of 2.8 V-4.6 V vs. Li^+ up to 10 cycles. The observed discharge capacity is 4 mA.h g^{-1} . Similar result is also observed by wolfenstine et al who observes the capacity of about $<5 \text{ mA.h g}^{-1}$ 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].

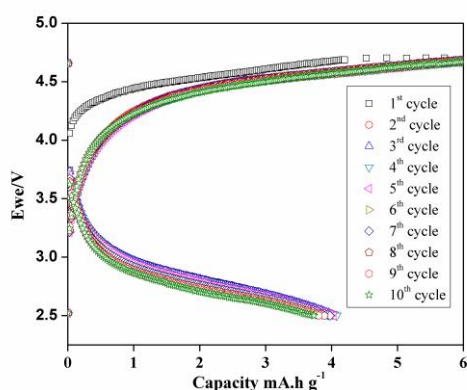


Figure 3b: Charge-discharge curves of $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ measured at $C/20$.

4. Conclusions

LiNiPO_4 and $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ were prepared by polyol method. The electrochemical performance of undoped LiNiPO_4 and $\text{LiNi}_{0.85}\text{Zn}_{0.15}\text{PO}_4$ 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 1 mA.h g^{-1} whereas Zn^{2+} doped sample possess the capacity of 4 mA.h g^{-1} .

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