



Structural and electrochemical properties of ZrO₂ doped PVP-Na⁺ based nanocomposite polymer films

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ABSTRACT

Polymer based nanocomposite polymer films are prepared with polyvinyl pyrrolidone (PVP) and sodium metaphosphate (NaPO₃) into which zirconium oxide (ZrO₂) is dispersed by different wt% compositional ratios using solution cast technique. The prepared polymer films are characterized by different analytical methods. XRD studies have revealed the semicrystalline phase of the prepared nanocomposite films. The interlinking band formation and their complex nature with dopant ions are analyzed by FTIR and Raman studies. DSC analysis have revealed the glass transition temperature, $T_g = 42.5$ °C at which the phase transformation changes from glassy to rubbery amorphous phase on heating. The AC conductivity is measured in the frequency ranging from 42 Hz to 5 MHz. The ionic conductivity is found to be maximum (1.02×10^{-3} S/cm) for the film prepared with wt% composition of PVP + NaPO₃: ZrO₂ (60:40:4%) at room temperature. Electrochemical studies are also carried out on the prepared polymer films for solid state battery application.

1. Introduction

In the past researchers have made remarkable efforts on nanocomposite polymers (NCP's) owing to their excellent performance in physical and electrochemical studies. They are widely used in many potential applications like rechargeable batteries, electrochemical cells and grid sources etc [1]. At present, the energy consumption is the main source for the main kind for household purposes. To overcome these problems a wide interest has taken place on electrolyte materials for the development of batteries and energy storage devices. Solid polymer based batteries exhibit several advantages like easy film formation and flexibility. They are good at physical and mechanical stability over liquid electrolyte based batteries. The next step of the liquid electrolytes is executed by solid polymer electrolytes due to their advantages like high ionic conductivity and better performance at their operating voltages [2]. Although the battery technology has improved for the past few years, the search for new materials having better performance with high energy density and extended cycles of rechargeability is promoted. However the uses of non-toxic and non-hazardous surrogate materials have not yet been systematically developed.

First PEO-based sodium polymer batteries have been developed in which sodium based salts are dissolved in the host polymer. Later the research has been carried out on the other polymers such as poly (vinyl alcohol) (PVA), poly (vinyl pyrrolidone) (PVP), poly (methyl

methacrylate) (PMMA), poly (ethylene glycol) (PEG) etc, to enhance the ionic conductivity. The reason behind the enhancement of ionic conductivity in the NCP's is the solubility of cation in the host polymer matrix. Although sodium-ion battery carries several advantages, safety and environmental issues associated with sodium-ion battery cannot be ignored [3]. In the present scenario sodium based rechargeable batteries can be considered an essential power sources due to their excellent properties such as good mechanical behavior, light weight, easy fabrication and long durability [4]. Steep growth takes place on sodium-ion conducting solid polymer electrolytes due to their fast growing demand and usage in several applications like mobile rechargeable batteries, portable optoelectronic devices etc [5,6]. By adding sodium salt to the host polymer the ionic conductivity can be improved and it shows significant properties which can be used for energy devices. Some inorganic nanofillers are added to the polymer matrix to enhance the ionic conductivity which will increase the durability of a battery [7]. The brittle nature can be minimized by doping nanofillers like Cr₃O₂, TiO₂, ZrO₂, Al₂O₃ and plasticizers such as ethylene carbonate (EC) and propylene carbonate (PC) to the NCP's. By the complete dispersion of salt, the effective transfer of ions takes place through the polymer matrix [8,9]. They also possess high ionic transfer of ions more than electrons and it is well supported and explained by Wagner's polarization technique [10,11].

The first rechargeable sodium battery was developed in 1970s.

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Initially the researcher used a dry solid polymer electrolyte in the battery system. This electrolyte resembles a plastic-like film and acts as a separator that does not conduct electricity but allows an exchange of ions between anode and cathode. The fabrication of solid state battery is an easy process. When compared to lithium it is safer and flexible than the lithium battery. Therefore, research continues to develop a solid Na^+ polymer battery that performs at room temperature. Nowadays Na^+ polymer batteries are used in mobile batteries and rechargeable microbatteries. With the implementation of solid electrolyte, it is noticed that the characteristics and performance are similar to the solid type when these polymer electrolytes are replaced by the porous separator to enhance ionic conductivity. From this point of view different types of sodium batteries have been developed. Ansari et al. prepared low cost, dendrite-blocking polymer- Sb_2O_3 separators for lithium and sodium batteries [12]. Feerra et al. has developed the high-performance $\text{Na}_{0.44}\text{MnO}_2$ slabs for sodium-ion batteries which were obtained through urea-based solution combustion synthesis [13]. Palomares et al. has prepared the Na-ion batteries. With recent advances they have become popular as low cost energy storage systems [14]. Zhang et al. has developed the synthesis, structure and sodium mobility of sodium vanadium nitridophosphate. It resulted in a zero-strain and safe high voltage cathode material for sodium-ion batteries [15]. Guerfi et al. has developed high rechargeable sodium metal-conducting polymer batteries [16]. Wang et al. has prepared a Prussian blue analog for rechargeable batteries [17].

In the present study, polyvinyl pyrrolidone is chosen as a polymer matrix due to two valid characteristics. One is that, PVP has excellent behavior in the formation of polymer films, adhesive behavior and the other due to good optical quality and mechanical strength. Due to its properties it is used as electrolyte membrane as well as in secondary batteries and microelectronics [18,19]. Sodium metaphosphate (NaPO_3) is widely used in the preparation of electrolyte membranes for long life batteries at high temperature. Since NaPO_3 has low lattice energy and bulkier anion, it helps in easy dissociation of the cations and thereby it facilitates complexation. Due to this reason, NaPO_3 has been selected as a salt in the present work. Zirconium oxide (ZrO_2) is used as nanofiller in the preparation of polymer electrolytes to improve mechanical integrity and softness of the films because zirconium ions produce vacancies in which drifting of ions takes place freely which give rise to ionic conductivity.

The novelty behind this work is to prepare the nanocomposite polymer films having uniform thickness from 50 to 180 μm with cost effective technique. The film thickness will be measured by using wedge method. The prepared films have large internal area with high tensile strength and improvement in physical and electrochemical properties. The results showed that the sodium based nano polymer films could be used in microbatteries. The prime novelty of this work is to get ready and portray the sodium based electrolyte films with cost effective solution-casting technique, which will enhance physical, electrical and mechanical integrity. This strategy can be utilized in making battery-powered gadgets. The primary target of the present examination is to get ready with strong nanocomposite polymer films utilizing PVP with various wt% proportions of NaPO_3 and by doping the nanoparticles like ZrO_2 . The arranged nanocomposite films were characterized by different characterization techniques and furthermore to discover the electrochemical execution of the manufactured cells. From the study, it is affirmed that numerous researchers took a shot at auxiliary batteries. However a couple of scientists have reported about the electrochemical investigations of their work. The energy improvement of the cell is the main criteria for designing the efficient energy storage devices. The present execution of the cell demonstrates higher effectiveness which is equivalent to the lithium batteries and is accessible in the market. Numerous specialists have thought about the exhibitions of their cells in their work. In the present work batteries manufacturing and the cell parameters have been widely examined and announced. The present study also covers the making of polymer-

sodium based batteries. The calculated ionic conductivity for the combination of (PVP + NaPO_3) electrolytes is obtained at 10^{-6} S/cm and this may not be useful for energy storage device applications. Until now there is no report on ceramic filler which is doped on sodium based polymer electrolytes which have been prepared by cost effective solution cast technique. By doping the nanofiller (ZrO_2) in (PVP + NaPO_3) system, the enhancement of ionic conductivity takes place of the order 10^{-3} S/cm. In the present work, ZrO_2 nanofiller was used as a dopant material to improve the physical and electrochemical properties such as mechanical integrity, ductility, tensile strength, long durability and high transportation of ions etc of the prepared PVP: Na^+ polymer electrolytes.

2. Experimental

2.1. Materials and methods

The chemicals like PVP (molecular weight: 36,000), sodium metaphosphate (NaPO_3) with 98% purity and zirconium oxide (ZrO_2) were used for the preparation of sodium based polymer electrolyte films. The above mentioned chemicals were brought from Sigma Aldrich chemicals, India. The nanocomposite polymer films were prepared by using solution-cast technique. Initially all the chemicals were dried under vacuum oven at 40 °C for 1 h to remove any moisture traces present in the chemicals. After, proper ratios of chemicals were weighing accurately through an electronic balance. The chemicals PVP and NaPO_3 are taken in different wt% ratios (90: 10, 80: 20, 70: 30 and 60: 40) in a conical flask, later double deionized water which act as a solvent (30 ml) is poured in the chemical that contains conical flask and allowed to stir the solution for about 48 h. While dispersing ZrO_2 nanoparticles in different weight ratios in the prepared chemical solution of PVP+ NaPO_3 : x wt% ZrO_2 (x = 1%, 2%, 3% and 4%), this homogeneous mixture was allowed for continuous stirring upto 24 h. Later they obtained solution and poured it into Petri dishes where the solution was let to be evaporated in a hot air oven in order to remove the moisture and solvent solution. Finally, the obtained samples were peeled off and placed in vacuum desiccators.

2.2. Characterization

XRD technique is used to identify the crystalline nature of the films and it is examined by Philips analytical X'pert diffractometer. Morphological surfaces of the nanocomposite polymer films were examined by the FE-SEM, Carl Zeiss, Ultra 55 model. The chemical complex nature between the dopant and the polymer was confirmed by using FTIR of Perkin Elmer Alpha-E Spectrophotometer. The phase transformation point of the prepared films was identified by using DSC, Q-2920, TA. The interlinking band formation in NCP's was characterized by a Nano finder 30 SOLAR TII laser Raman spectroscopy. Electrical measurements of the nanocomposite films were measured by the AC impedance spectroscopy in the frequency ranging from 42 Hz to 5 MHz. Cyclic voltammetry, polarization studies and electrochemical measurements were performed by using 600E electrochemical analyzer by fabricating the sodium-ion rechargeable battery with the prepared combination of $\text{Na}^+(\text{PVP} + \text{NaPO}_3 + \text{ZrO}_2)/\text{I} + \text{C} + \text{electrolyte}$.

3. Results and discussion

3.1. XRD analysis

XRD pattern of the prepared nanocomposite based $\text{NaPO}_3 + \text{ZrO}_2$ was shown in Fig. 1. Pure PVP showed a wide peak at 21.5° which lies in the diffraction angle ranging from 10° to 90° indicating its semi-crystalline structure. PVP based $\text{NaPO}_3 + \text{ZrO}_2$ nanocomposite films exhibited crystalline peaks at 21.5°, 30.1°, 31.5°, 34.5° and 35.5° for the composition 90:10:1%, the crystalline peaks at 15.5°, 17.2°, 25.2° and

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