

Influence of Al₂O₃ Nanofiller on Morphological and Discharge Studies of PVP: CH₃COOK Films

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Abstract

Nanocomposite polymer (NCP) films were prepared by doping potassium acetate with polyvinyl pyrrolidone (PVP) by complete dispersion of aluminum oxide (Al₂O₃) with different wt% proportions by using solution-casting method. The acquired NCPs films were characterized systematically. The crystalline structure of the prepared NCPs films was confirmed by XRD. The little agglomeration and grain sizes involved in the films were analyzed by SEM. The energy bandgap values were observed to be at 3.16 eV for the wt% ratio of PVP: CH₃COOK: Al₂O₃ (80:20:1%). The most extreme ionic conductivity was found to be 1.08×10^{-3} S/cm for the prepared PVP+CH₃COOK: Al₂O₃ (80:20:1%) film. From the charge discharge characteristics, it was concluded that the film with wt% ratio of PVP+CH₃COOK: Al₂O₃ (80:20:1%) possesses long durability when compared to other wt% ratios.

Keywords: Nanocomposite polymer films, solution cast technique, XRD, SEM, optical absorption, AC ionic conductivity, cyclic voltammetry

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INTRODUCTION

The present day researchers have shown much interest in the development of nano-composite polymer (NCP) films due to their magnificent trademark nature and great potential at physical and electrical properties. They showed much influence on electrochemical properties by doping with the nanofillers in the host polymer. Due to this reason, NCPs have been utilized in numerous potential applications such as secondary batteries, electrochemical cells and bio-sensors [1]. Nowadays, utilization of excess power sources has been the common platform. As a result shortage of power sources are arising. To beat these issues a wide interest has taken upon the NCP materials for the development of primary and secondary batteries. NCP films based batteries show much efficiency, long durability and furthermore possess great physical and mechanical properties over the alkaline batteries. Fluid electrochemical cells have lot of impediments, for example, unsteady at high temperatures, overflow of fluid at ambient temperatures and development of rust at electrodes [2]. In spite of the fact that

the battery innovation has enhanced couple of years, the scan for new materials having better execution with great efficiency and expanded cycles of rechargeability started [3]. Anyway, the employments of non-poisonous and non-risky materials have not yet been deliberately reported. In that perspective the researchers have been focused around potassium based rechargeable batteries because potassium based batteries will give high potential and electrochemical performance. Along with these, they are treated as the elective source to lithium and sodium batteries [4, 5].

In the present examination, PVP polymer is taken as the host, due to its astounding conduct of attributes. PVP is mostly utilized in electronic and pharmaceutical enterprises because of its numerous potential applications. It is utilized as an optoelectronic display material in microelectronics. Potassium acetate is a natural earth abundant element, and it is broadly utilized in the implant of many applications like solar cells, sensors and electrolyte layers as long as life batteries [6]. Due to the low dispersal grid constants,

CH₃COOK is easily soluble in natural solvents and in distilled water. Aluminum oxide (Al₂O₃) is utilized as nanofiller in the arrangement of polymer electrolytes to enhance mechanical conduct and level of roughness of the films, since aluminum particles create opening in which floating of particles takes place randomly, which rises the ionic conductivity.

EXPERIMENTAL SETUP

Inorganic chemicals like potassium acetate (CH₃COOK) with 98% purity, PVP with average molecular weight of M.W.: 36,000 g/mol and Aluminum oxide (Al₂O₃) were bought from the Sigma Aldrich chemicals, India. NCP films were synthesized by adding inorganic salt (potassium acetate) with nanofiller in the host PVP polymer by different wt% ratios of (95:5:1), (90:10:1), (85:15:1) and (80:20:1) using solution cast technique. During the titration, deionized water is used as solvent in the process. Later the solution is allowed for stirring up to 48 hours to get complete complexation. Finally, the obtained solution was taken into polypropylene dishes and kept in a hot air oven at 60°C. The NCP films obtained from dishes were peeled off and placed in a desiccator.

RESULTS AND DISCUSSION

XRD Analysis

Figure 1 demonstrates the XRD pattern of PVP and Al₂O₃ doped (PVP+CH₃COOK:Al₂O₃) films with various wt% proportions such as (95:5:1), (90:10:1), (85:15:1) and (80:20:1).

In XRD pattern, a wide peak has been observed at 24.5° which indicates the semicrystalline nature. The films with different wt% proportions showed the peaks at 2θ = 28.5°, 30.1°, 44.5° and 47.2°. This clearly indicates the distribution of nanoparticles in the films. The similar behavior in the XRD pattern, which was observed, indicates the complete dispersion of salt has taken in all the prepared films. Figure 1 shows few twists in the peaks, which this may be due to the clusters of salt coordinating with the PVP. From the XRD pattern, it is clearly observed that as increasing the wt% composition in the polymer the intensity of the

peaks gets sharpens. As a result, its FWHM is increased. Among all the wt% composition films, less intensity spectral peak is observed for (80:20:1) % film. This may be due to the phase change from semicrystalline to amorphous nature, and also with the substitution of the crystalline particles in the polymer chains [7, 8]. By increasing the salt concentration, the crystalline nature of the films decreases and few disturbances in the peaks also have been observed. This may be due to the doping of nanofiller in the PVP polymer. Hence, XRD confirms that the coordination or complex nature of polymer mix with the salt.

SEM Studies

The morphological images of different wt% ratios of NCP [PVP+CH₃COOK: Al₂O₃]: x% were shown in Figure 2(a)–(e). SEM picture of pure PVP is shown in Figure 2(a) and the rest of the pictures with different wt% compositions were shown in Figure 2(b)–(e).

All the SEM images were analyzed at the resolution of 10 μm. When compared to other ratios the polymer surface of the films with little crystalline like structures were seen in Figure 2(b)–(d). These little types of chunks formed because of the scattering of salt and the nanofiller, which were lies in the polymer framework [9]. In any case, at higher wt% organization, no stage division was seen because of the disintegration of salt and the nanofiller for the creation (80:20) which was appeared in Figure 2(e). These images explain that the salt chunks and the dopant nanofiller were embedded uniformly in the PVP polymer. As a result, porosity nature had been expanded which prompt the expansion in the ionic conductivity.

AC Ionic Conductivity Studies

Nyquist plots of PVP and Al₂O₃ doped NCP films with different wt% proportions (95:5:1), (90:10:1), (85:15:1) and (80:20:1) were shown in Figure 3. The conductivity of the films was measured by sandwiching the sample between the two silver plates and connected to probes of LCR Heister. While measuring the conductivity a constant load is applied across the sample and the obtained frequency is balanced to an extent that the Cole-Cole plots have been acquired and screened. While

expanding the frequency range, the Cole-Cole plots demonstrate a semi-circle bend at high frequency area later demonstrate the spike shape at the low frequency circle [10, 11]. At any case in Figure 3, a spike like spectra has been seen which results the development of twofold layer capacitance at the electrode-electrolyte interface. The ionic conductivity is figured by the accompanying connection,

$$\sigma_{ac} = ixl/R_bxA \quad (1)$$

Where, "R_b" is the bulk resistance,

The ionic conductivity and its values were calculated from the above formula and the values are introduced in Table 1.

Among all the wt% composition ratios the conductivity observed to be high for the organization of (80:20:1%) film which is found to be 1.08×10^{-3} S/cm. The conductivity of the films increases due to the salvation of the ions in the polymer chains. This intend to decrement in the crystalline nature. One of the reasons for higher wt% ratio of the film is due to the non-porosity nature formation in the films. As a result, the glass transition of the

film becomes low, which tends to the increase in the ionic conductivity abruptly. Further, on increasing the salt concentration the ionic conductivity may be decreased. This may be due to the disintegration of ions and the charge carriers and their mobility has been decreased [12, 13]. This indicates the reality in the exchange of potassium particles occur openly in the polymer network, which has the higher ionic conductivity.

Charge/Discharge Performance

The fabrication of the cell was done with the combination of anode (K⁺)/electrolyte (NCP)/(I+C+electrolyte traces) cathode and the galvanostatic charge/release execution of the wt% ratio of (80:20:1%) done for the arrangement was shown in Figure 4.

At first, a quick decline in the applied voltage has been screened. This might be because of the depolarization formed between the electrolytes. From the Figure 4, it is seen that as increasing the current the OCV is decreased exponentially from 2.9 to 0.2 V. This may be due to the dispersion of salt and the nanofiller

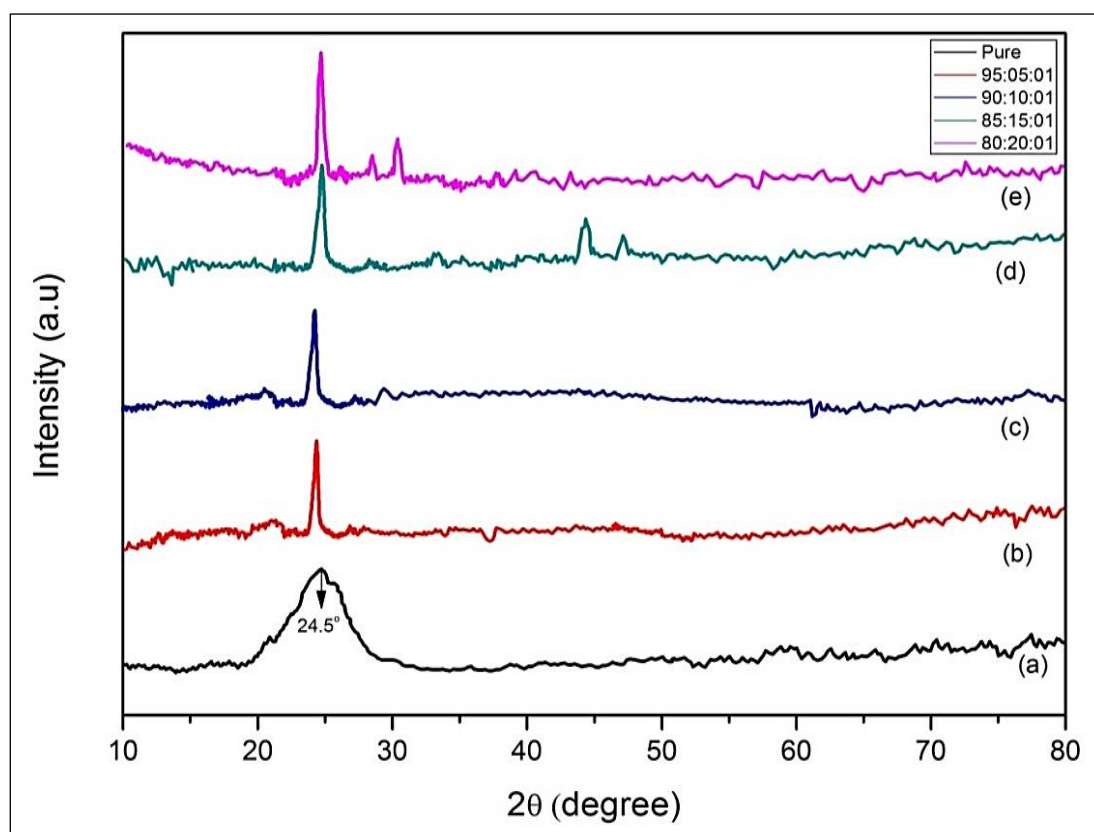


Fig. 1: XRD Pattern of NCP Films.

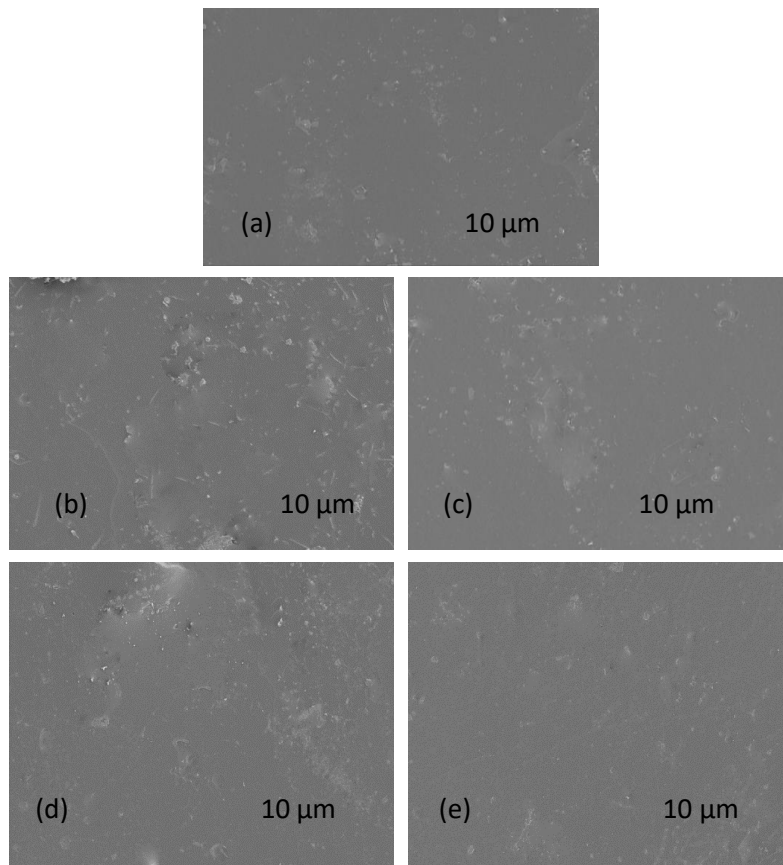


Fig. 2: SEM Images of NCP Films.

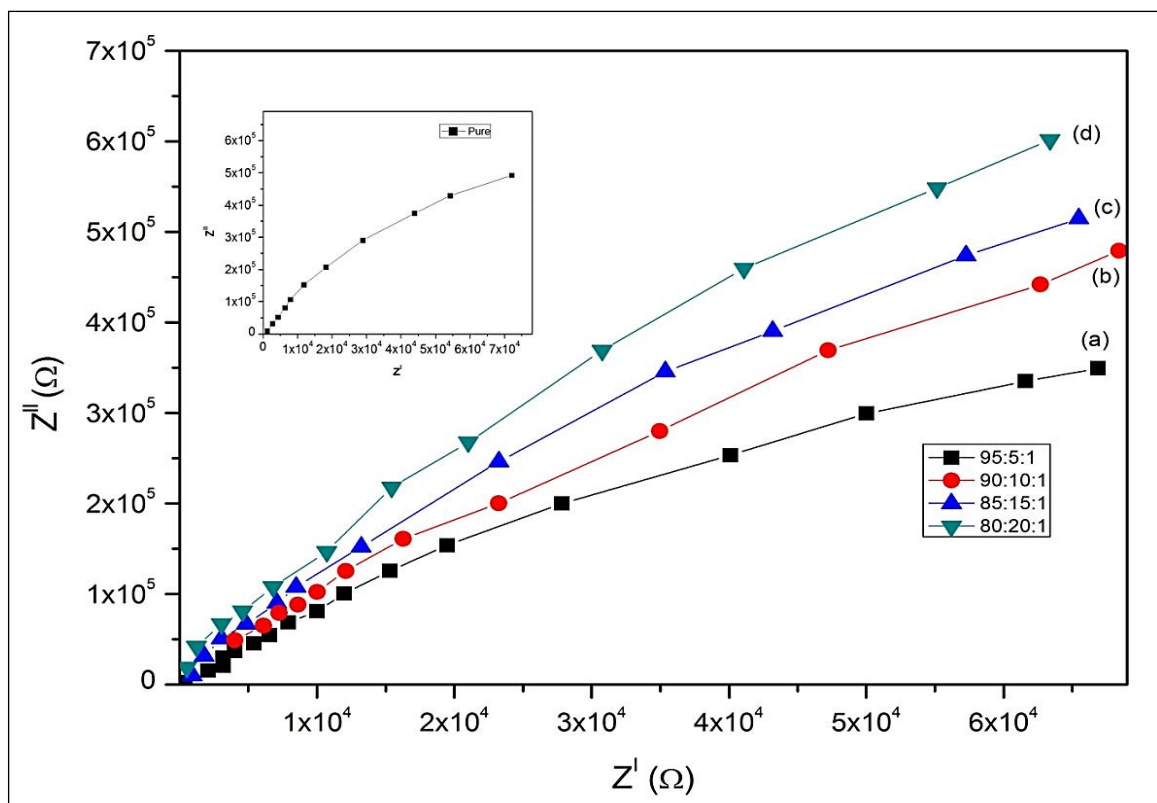


Fig. 3: AC Ionic Conductivity of NCP Films.

Table 1: AC Conductivity of NCP Films.

NCP films	Conductivity at RT (Scm^{-1})	Conductivity at 373 K (Scm^{-1})
Pure PVP	1.02×10^{-9}	1.13×10^{-8}
PVP+CH ₃ COOK:Al ₂ O ₃ (95:5:1%)	4.32×10^{-8}	2.12×10^{-5}
PVP+CH ₃ COOK: Al ₂ O ₃ (90:10:1%)	3.12×10^{-6}	3.42×10^{-5}
PVP+CH ₃ COOK: Al ₂ O ₃ (85:15:1%)	2.24×10^{-5}	2.10×10^{-4}
PVP+CH ₃ COOK: Al ₂ O ₃ (80:20:1%)	6.24×10^{-5}	1.08×10^{-3}

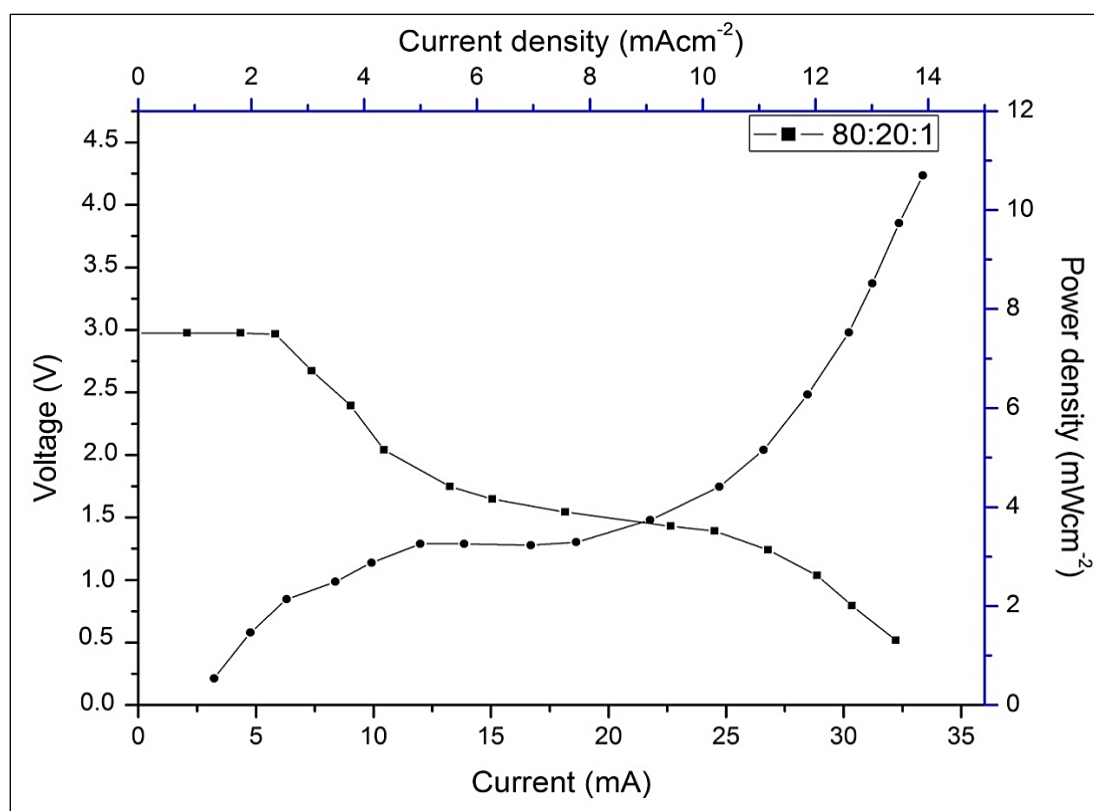


Fig. 4: Charge-Discharge Performance of NCP Films.

in the PVP polymer that have bring down molecule size and everything happens because of the substantial surface territory of the particles [14, 15]. The current density and power density are stabilized as increasing the current up to 32 mA. This may be due to the charge polarization formation at the electrolyte surfaces. On comparing the results with the other wt% ratios of the films, the NCP film (80:20:1%) possesses high ionic conductivity with stable execution of the cell.

CONCLUSIONS

Nanocomposite polymer films are prepared by doping potassium acetate in host polymer of polyvinyl pyrrolidone by dispersing aluminum oxide with different wt% compositional ratios using solution cast technique. From the different wt% composition studies the higher

value of ion conductivity Al₂O₃ is found to be $1.08 \times 10^{-3} \text{ Scm}^{-1}$ at 373 K for composition 80PVP-20CH₃COOK+1% Al₂O₃. Charge-discharge characteristics are measured for the obtained high ionic conductivity film and the results are reported.

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