2021

Vol.6 No.3:7873

The effect of doping VO²⁺ ions on thermal, structural and morphological, properties of PVP polymer electrolytes

K. Sreekanth¹, T. Siddaiah¹, N.O. Gopal¹, Y. Madhava Kumar¹, Ch. Ramu^{1*}

¹Department of Physics, Vikrama Simhapuri University PG centre, Kavali, India

*Corresponding author: Ch. Ramu, Department of Physics, Vikrama Simhapuri University PG centre, Kavali – 524201, India; Tel: 94949301638; Email: chramu8@gmail.com

Received date: March 22, 2021; Accepted date: September 4, 2021; Published date: September 14, 2021

Citation: Ch. Ramu (2021) The effect of doping VO²⁺ ions on thermal, structural and morphological, properties of PVP polymer electrolytes. Polym Sci Vol 6:3

Abstract

In this work, films of polyvinyl pyrrolidone (PVP) polymer electrolyte complexes with different concentrations of VO²⁺ ions (1 to 5 mol%) were prepared by solution casting technique. The thermal, structural and morphological properties of pure and VO²⁺ doped PVP polymer films were investigated using TGA, XRD and SEM. Based on dTG and TGA data shows three different stages of weight loss and the thermal stability of all the investigated samples were improved. The increased amorphous nature of PVP polymer film due to doping has been identified from XRD pattern. The SEM elucidates the surface morphology of the pure and VO²⁺ ions doped PVP films indicates a continuous microstructure is relatively rough of the polymer film, which suggests the amorphous nature.

Keywords: Polymer electrolytes, PVP, TGA, XRD, and SEM

Introduction

Modern technology development mainly depends on improvements in electrochemical devices such as energy storage batteries, solar cells, colour filters, smart windows, super capacitors, fuel cells, catalysts, sensors, and electro chromic devices [1-5]. Solid polymer electrolytes, compared to conventional liquid once, can be easily fabricated with several advantages like safety, leakage-free nature, low cost and easy fabrication into flexible geometries [6-8], and good contact in electrode-electrode interfaces in different electrochemical devices [9,10]. Room temperature ionic conductivity is the crucial property of polymer electrolytes for the realization of their technological applications. So, intense research has been focused both from a fundamental point of view toward an understanding of ion-transport and the applications point of view toward enhancing the performance of devices based on polymer electrolytes. Another advantage of PVP is reasonable ionic conductivity, flexibility, processibility, and dimensional stability under ambient conditions. These requirements have been achieved for several polymers by adopting various methods of preparation.

Polyvinyl Pyrrolidone (PVP) is a synthetic, biodegradable polymer with excellent characteristics for the fabrication of solid-state batteries and optoelectronic devices, such as dielectric constant, thermal stability, excellent solubility in various solvents, moderate electrical conductivity, resistivity, high charge transport mechanism and it is low cost. It is also a conjugated polymer with high amorphous content that can provide faster ionic mobility than other semi-crystalline polymers. The increased dielectric properties, predominating amorphous nature, and low scattering loss is due to the existence of carbonyl groups (C=O) results in marked Lewis base character in the side chain of PVP leading to the formation of various complexes with different inorganic salts [11]. PVP has a high Tg with excellent environmental stability. Furthermore, it provides outstanding thermal stability, mechanical strength, electrochemical stability, and high ionic conductivity. The low light scattering loss because of the amorphous nature of the PVP is why the best results in many optical applications [3].

Based on the importance and relevance of PVP polymer as a suitable matrix, transition metal ions can be used as a dopant to magnify its electrical conductivity and optical absorption. Further, it should be noted that the addition of transition metal particles inside the polymer system to change the different applications, such as storage of optical data, microelectronics, solid-state lonics, photo electronics shielding of electromagnetic radiation, various flexible elements for resistive heating, laser systems, optical lenses and integrated waveguides [12-15].

The study of transition metal ions in amorphous materials is one of the interesting studies from a theoretical and experimental point of view. Among the transition metal oxides, V_2O_5 is of great interest for modern and developing technology, i.e. applications in microelectronics, solid-state lonics, and optoelectronics [16-18]. The addition of transition metal ions has also been found to have a significant effect on the structural, optical, electrical and magnetic properties of the polymer. The study aims at developing a new type of polymer electrolyte system doped with VO^{2+} ions, which can be used in the production of electrochemical devices. The prepared solid polymer electrolytes a systematic study of the thermal, structural and morphological properties of pure polymer films and films doped with VO^{2+} ions was investigated using TGA, XRD and SEM.

Experimental

Electrolytes preparation

PVP (Aldrich) with molecular weight 3,60,000 was used as polymer host Cr₂ (SO₄)₃.nH₂O (MOLY CHEM Ltd, India) was used as an ion provider. All samples were prepared using the solution casting technique in which double distilled water was used as a solvent. Stock solutions of 5% PVP and various concentrations (1, 2, 3, 4 and 5 mol%) of Cr₂ (SO₄)₃.nH₂O were prepared separately. All the solutions with continuous stirring individually at room temperature using a magnetic stirrer for an hour to obtain complete dissolution. The aqueous solutions of pure PVP and one of the various concentrations of Cr₂ (SO₄)₃.nH₂O were mixed and stirred well to form a homogeneous and clear solution. The stirred solutions were then cast into plastic Petri dishes and evaporate at room temperature until polymer films were acquired at the bottom of the dishes. The thickness of the prepared samples was obtained by the capacitance method and found to be around 150 μ m. The resultant solution was slowly evaporated at room temperature to get the polymer film and the resulting film was kept in a vacuum desiccators.

Electrolytes Characterization

The thermal properties of the polymer electrolytes were determined to employ thermo gravimetric analysis (TGA). The thermal measurements were performed using a SEIKO thermal analysis system (TGA-20) from 30 to 600° C at the heating rate of 10° C/min in the presence of a nitrogen atmosphere. The X-ray diffraction (XRD) patterns of pure and Cr³⁺ ions doped PVP polymer electrolytes were studied using a Siemens D5000 diffractometer. The prepared samples were scanned under glancing angles in the range of 5° to 80° with a step size of 0.02 using CuK α radiation. Using origin pro 8.0 commercial software package with Gaussian fitting of the observed XRD broad peaks the estimated values of 2 θ , β , d, and D. The surface morphology of the films observed by Scanning electron microscope (SEM) was done using JOEL JSM 840A electron microscope with scanning attachment.

Results and Discussion

Thermogravimetric studies

The first derivatives of Thermogravimetric (dTG) curves of pure and different concentrations (1,2,3,4 and 5 mol%) of VO²⁺ ions doped PVP films with a heat of 10°C/min in the temperature range from room temperature of 30°C to 600°C are shown in Figure 1. Figure 2 shows the TGA/dTG curve of 5 mol% of VO²⁺ doped polymer film. It is clear from the figures, that the recorded dTG curves of VO²⁺ ions doped PVP samples show multi-step decomposition mechanisms. The dTG thermogram revealed the thermal stability of the present polymer system in which it has completed the degradation process in two minor and one major weight loss phases. Analysis of dTG curves reveals three distinct steps of similar degradation was reported by Sreekanth et al., [19]. Based on the pure PVP curve, the first stage in the 54°C to 115°C range is associated with water loss.

This irst decomposition was accompanied by a slight weight loss (6-10%) due to decomposition of the hydroxyl group.

A similar observation was reported by Mazuki et al., where the first phase corresponds to a reduction in sample moisture due to the evaporation and dehydration process which contributes to the initial weight loss [20].

The initial 6-10% weight loss between 54° C to 115° C is mainly due to the evaporation of moisture adsorbed by the sample during the process of sample loading.

The second weight loss occurs in the range of 166° to 231° , with a weight loss of 4-16%, which included both the melting point and degradation temperature of PVP, is attributed to the splitting of monomers and bond scission in the polymeric backbone [21].

Beyond the second stage, the samples have a drastic weight loss in the temperature range 322° C to 430° C, which is assigned to melting temperature (Tm).

The melting temperature of the all VO^{2+} ions doped ilms exhibits increasing nature as VO^{2+} content increases in the polymer matrix [22].

Figure 1: dTG thermograms of (a) pure and (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, (e) 4 mol% and (f) 5 mol% VO^{2+} ions doped PVP polymer ilms.





Figure 2: The TGA/dTG curve of 5 mol% of VO²⁺ doped polymer film.

This is due to the formation of homogenous polymer electrolytes over the entire content and this would allow PVP-VO2+ to receive ionic charge. Further, it is evident that PVP would provide more sites for ion hopping when VO2+ is introduced into the system and leads to an increase in the decomposition temperature [23]. This results in an increase in the amorphous nature of polymer electrolyte films. This observation is supported by the XRD analysis. The melting temperatures and decomposition temperatures of pure and VO2+ ions doped polymer electrolyte films are presented in Table 1. The plateau region between 322°C-430°C indicates that samples are stable in this range.

Table 1: The decomposition steps and percentage weight loss for pure and different concentrations (1.0, 2.0, 3.0, 4.0 and 5.0 mol %) of VO^{2+} ions doped PVP polymer films.

Concent ration in mol %VO ²⁺ : PVP	Temperature (°C)			Weight loss (%)	
	Start	End	TP	Partial	Total
Pure PVP	55	109	90	8.0	83.4
	176	227	198	8.6	
	322	418	368	66.8	
1 mol%	54	101	87	8.8	81.7
	176	231	206	16.2	
	341	430	381	56.7	
2 mol%	57	112	90	8.3	80.6
	166	223	201	15.4	
	331	417	375	56.1	
3 mol%	54	107	79	10.1	76.2
	171	216	191	9.4	
	324	422	375	49.6	
4 mol%	56	108	80	8.7	74.7
	181	226	204	8.6	
	337	417	372	49.4	
5 mol%	54	115	80	6.2	69.1
	172	224	201	4.4	
I	333	420	372	58.5	

X- ray diffraction studies



Figure3: XRD Spectra of (a) pure and (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, (e) 4 mol% and (f) 5 mol% VO^{2+} ions doped PVP polymer films.

X-ray diffraction patterns of pure and various concentrations (1, 2, 3, 4 and 5 mol%) of a PVP polymer film doped with VO2+, as shown in Figure 3. In Figure 3, X-ray diffraction, the appearance of two broad peaks at 20=11.87° and 16.37° indicate the amorphous nature of the samples, and a moderately sharp peak at 2θ = 22.84° indicates a semi-crystalline nature of polymer films. It can be seen from Figure 3, that a decrease in the intensity of the peak is observed without any significant change in its position at 2θ =22.84° with an increase in the concentration of the dopant. This may be due to the strong intermolecular interaction of the polymer with VO²⁺ ions through hydrogen bonding interaction in the amorphous component, which leads to an increase in the amorphous region [24]. The increase in the amorphicity results in a reduction in the energy barrier and an increase in the segmental movement of the polymer due to VO²⁺ doping leading to a continuous increase in electrical in conductivity [19]. The interplanar spacing(d) between planes and the mean value of crystalline length (D) of the crystalline phase of the investigated samples can be estimated from Bragg's law [25-27] and Scherrer's equation respectively, where is the X-ray radiation wavelength, is the diffraction and is the full width at half maximum (FWHM) in radians unit.

 $2d \sin\theta = n\lambda$ (1)

D= $(0.94\lambda)/\beta(\cos\theta).....(2)$

Using the Gaussian fit of the observed large XRD peaks (Figure 3), the estimated values of 2θ , β ,d, and D of pure and VO²⁺ doped PVP composites are recorded in Table 2. The spacing parameter d of the pure PVP is relatively less and there is no large difference between the value of this parameter for PVP and samples doped with VO²⁺. The length D values of the crystallites of the spherulites of the samples doped with VO²⁺ are significantly lower than those of pure PVP. Further this result is strong evidence for the decrease in the degree of crystallinity due to the size disturbance of pure PVP spherulite due to its complexation with PVP and VO²⁺ ions in their composites in the amorphous structure.

Table 2: Bragg's angle (20), Full-width Half maximum (FWHM) (β), d spacing and crystallite size (D) of pure and VO²⁺ doped films.

PVP: VO ²⁺ concentrati on (mol %)	20°	β (rad)	d (nm)	D (nm)
pure	22.92	0.052	0.387	2.719
1	22.99	0.102	0.387	1.387
2	23.11	0.102	0.385	1.387
3	23.15	0.151	0.385	0.940
4	23.23	0.150	0.382	0.934
5	23.47	0.187	0.379	0.757

Morphological studies

The morphology of the pure and VO^{2+} ions doped (1, 2, 3, 4 and 5 mol %) PVP films studied by the SEM technique are shown in Figure 4 (a- f).



Figure 4: SEM images of (a) pure and (b) 1 mol%, (c) 2 mol%, (d) 3 mol%, (e) 4 mol% and (f) 5 mol% VO^{2+} ions doped PVP polymer films.

The pure PVP film appears to be the smoothest, most uniform and homogeneous surface, suggesting a good control structure [28]. This suggests that PVP molecules can disperse in the soft segment phase with little influence on the separation of microphages and the mixing of hard and soft segments as shown in Figure 4 (a). Figure [4 (b-f)] shows, the SEM images of different concentrations shows, the SEM images of (1, 2, 3, 4 and 5 mol%) of PVP polymer films doped with VO^{2+} ions. By adding VO^{2+} ions to PVP films, the surface morphology of pure PVP films changes from smoother to rougher. The increase in the degree of roughness with an increased concentration of VO^{2+} ions indicates that the crystalline material has been broken into small pieces and mixed into the polymer. These results indicate the improvement of the surface of the doped films and mean that the VO^{2+} ions firmly adhere to the PVP film. The lower degree of crystallinity and uniform morphology, which are also confirmed by XRD and conductivity studies.

Conclusions

Solid polymer electrolyte films of polyvinyl pyrrolidone (PVP) complexed with different (1-5 mol%) concentrations of VO²⁺ ions were prepared by the solution cast method. The dTG curves show three different steps of weight loss. This is due to the loss of adsorbed water, the cleavage of monomers, breaking of bonds and the decomposition of the main chain. The dTG study shows an enhancement of the thermal stability of the system with an increase in dopant concentration. In X-ray diffraction, the appearance of the two broad peaks at 2θ =11.87° and 16.37° indicates the amorphous nature of the samples and the moderately sharp peak at 20=22.84° indicates semi-crystalline nature of polymer films. Structural analysis of the obtained samples by X-ray diffraction shows a broadening of the diffraction peak upon doping, which means a lower degree of crystallinity at a higher VO²⁺ concentration. Lower crystallinity with higher dopant concentration was confirmed by SEM photomicrographs. Therefore, polymer electrolytes doped with VO²⁺ are considered as potential materials for the manufacture of solid-state batteries and other electrochemical devices

References

- Masoud EM, Hassan ME, Wahdaan SE (2016) Gel P(VdF/ HFP)/PVAc/lithium hexafluorophosphate composite electrolyte containingnano ZnO filler for lithium ion batteries application:effect of nano filler concentration on structure, thermal stability and transport properties. Polym Test 56:277– 286.
- Masoud EM, El-Bellihi AA, Bayoumy WA (2018) Polymer composite containing nano magnesium oxide filler and lithiumtriflate salt: an efficient polymer electrolyte for lithium ion batteries application. J Mol Liq 260:237–244.
- Mazuki NF, APP AM, Nagao Y (2020) Studies on ionics conduction properties of modification CMC-PVA based polymer blend electrolytes *via* impedance approach. Polym Test 81:106234.
- Shujahadeen BA, MFZ Kadir, MH Hamsan, HJ Woo, MA Brza (2019) Development of polymer blends based on PVA:POZ with low dielectric constant for microelectronic applications. Sci Rep 9:13163.
- Kumar S, Prajapati GK, Saroj AL (2019) Structural, electrical and dielectric studies of nano-composite polymer blend electrolyte films based on (70–x) PVA–x PVP–Nal–SiO₂. physica B: condens Matter. 554:158–164.

- Naveen Kumar K, Misook Kang, Bhaskar Kumar G, Ratnakaram Y.C (2016) Energy transfer based photoluminescence properties of co-doped (Er3+ + Pr3+): PEO + PVP blended polymer composites for photonic applications Optical Materials: 54:6-13.
- Angulakshmi N, Sabu Thomos KS, Nahm KS, Manuel Stephan A, Nimma Elizabeth R et al. (2011) Electrochemical and mechanical properties of nanochitin-incorporated PVDF-HFP-based polymer electrolytes for lithium batteries Ionics. 17: 407-413
- Kiran Kumar K, Ravi M, Pavani Y, Bhvani S, Sharma AK, Narasimha Rao VVR (2014) Investigations on PEO/PVP/NaBr complexed polymer blend electrolytes for electrochemical cell applications, J Membrane Sci 454: 200-211
- Shahenoor Basha SK, Sunita Sundari G, Vijay Kumar K (2016) Electrical studies of PVP based solid Polymer electrolyte For Solid state battery applications International Journal of Chem Tech Research 9:165-169.
- 10. Armand MB (1986) Polymer electrolytes, Annual Review Material Science 16:245-261.

- H D Wu, I-D Wu, F-C Chang (2001) The interaction behavior of polymer electrolytes composed of Poly (vinyl pyrrolidone) and lithium perchlorate (LiClO4), Polymer 42:555-562.
- 12. Linga Raju C, Rao JL, Reddy B, Veera Brahmam K (2007) Thermal and IR studies on copper doped polyvinyl alcohol Bulletin of Material Science, 30: 215-218.
- Madhav Kumar Y, Bhagya Sree K, Gopal NO, Ramu CH (2018) Thermal and Conductivity Studies of VO²⁺ Doped Methacrylic Acid-Ethyl Acrylate (MAA:EA) Copolymer Films. Mater Res 21:20170328.
- Kumar YM, Bhyagyasree K, Gopal NO, Ramu CH (2018) Structural and Optical Properties of VO²⁺ Doped Methacrylic Acid Ethylacrylate (MAA:EA) Copolymer Films. Mater Sci Poland 36:34–41.
- Madhava Kumar Y, Gopal NO, Ramu CH, Babu S, Lakshman Rao J, Nagabhushana H, Sharma C et al. (2017) Structural, Thermal and Optical Properties of Cu2+ Doped Methacrylic Acid-Ethyl Acrylate (MAA:EA) Copolymer Films. Bull Mater Sci 40:877–886.