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# Structural, surface morphological and dielectric studies of guanidinium salt incorporated poly (ethylene oxide)/poly (vinyl pyrrolidone) solid polymer electrolytes

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# ABSTRACT

The research article investigates the effect of incorporating the guanidinium carbonate (GuC) salt into the poly vinylpyrrolidone (PVP) and polyethylene oxide (PEO) polymer matrix. Various weight percentages of GuC enriched PVP/PEO solid polymer electrolytes (SPEs) have been prepared by the simplest solution casting process. XRD analysis revealed that the incorporation of the GuC salt led to changes in the crystalline structure of the PVP/PEO. FTIR analysis confirms the presence of guanidinium carbonate in the blended polymeric system. FESEM imaging showed the uniform and smooth surface view of the electrolytes. DSC analysis suggests that the addition of the GuC led to a decrease in the melting temperature and an increase in the crystallisation temperature. The temperature-dependent dielectric constant of the polymer blend. Among all the prepared electrolytes, 25 wt.% GuC added polymer electrolyte achieved a higher conductivity of 3.00764  $\times$  10<sup>-7</sup> S/cm. Overall, the results of the study suggest that the incorporation of the GuC salt into the PVP/PEO can lead to significant changes in the structural, thermal, and dielectric properties of the blend. These findings have potential implications for the use of PVP/PEO blends in solid state battery applications.

## 1. Introduction

Due to their potential use in numerous electrochemical devices, such as batteries, fuel cells, and sensors, polymer electrolytes have drawn a lot of attention in recent years. Polymer electrolytes are substances made of an electrolyte contained in a polymer matrix [1,2].

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Due to their potential uses in numerous industries, they have attracted a lot of attention lately. Compared to conventional liquid electrolytes, polymer electrolytes have various benefits, including increased safety, stability, and handling simplicity. Getting high ionic conductivity while employing polymer electrolytes is one of the main difficulties. To increase the ionic conductivity of polymer electrolytes, various methods have been used [3–5].

It is widely acknowledged that the polymers' highly crystalline structure limits their ionic conductivity by allowing coupling between ionic motion and segmental motion as well as local relaxation of the polymer chains. Therefore, the best way to improve the conductivity of polymers is to reduce their crystallinity. Many attempts have been undertaken over the years utilising a number of methods to increase the conductivity of SPEs, including polymer blending, adding plasticizers, or adding ceramic nanofillers [6,7]. The fundamental benefit of polymer blends is that the composition and synthesis conditions may be easily changed to regulate the physical qualities. Blend polymer electrolytes, which are composed of a combination of two or more polymers, have emerged as a promising alternative to traditional single-polymer electrolytes due to their improved properties such as higher conductivity, better mechanical stability, and enhanced thermal and electrochemical stability. The development of efficient and high-performance electrolytes is crucial for the advancement of rechargeable batteries [8–10]. Due to their distinctive qualities, such as strong ionic conductivity, superior mechanical stability, and simplicity of production, polymer electrolytes have garnered a lot of interest. Polyvinylpyrrolidone and polyethylene oxide are two polymers commonly used in battery electrolytes due to their high ionic conductivity and low toxicity [11–13].

Due to the amorphous matrix support provided by the polyvinylpyrrolidone, PEO combined with PVP demonstrates a high level of ionic mobility. PVP's side chains contain a carbonyl group, which combines with inorganic salts to produce complexes. According to reports,  $(PEO-PVP)_8$ -NaPF<sub>6</sub> solid polymer composites exhibit the best electrochemical properties and the highest ionic conductivity  $(\sim 10^{-6} \text{ Scm}^{-1})$  when compared to composites of PEO with other sodium salts, such as NaClO<sub>4</sub>, NaF, NaI, NaBr, and NaIO. However, their low ionic conductivity at room temperature and poor stability at high temperatures limit their practical application [14]. To overcome these limitations, researchers have explored the use of guanidinium salt-based polymer electrolytes. Guanidinium salts have unique properties such as high ionic conductivity, thermal stability, and low toxicity, which make them suitable for battery application.

In this research article, the development of PEO/PVP with guanidinium salt-based polymer electrolytes has been discussed. The addition of guanidinium carbonate salt as the electrolyte material can further improve the electrochemical performance of the battery. The effects of various parameters such as salt concentration, and temperature depended dielectric and conductivities of the electrolytes have been investigated. The results of this study have provide valuable insights into the development of efficient and high-performance polymer electrolytes for advanced battery applications. Further research is needed to optimize their properties and explore their suitability for specific battery applications.

# 2. Experimental details

#### 2.1. Materials

For the present work, all chemicals were of analytical grade and were used without further purification. polyethylene oxide with an average molecular weight of Mw = 1,00,000 g/mol (>99 %), and Poly(vinyl pyrrolidone) with a molecular weight of Mw = 90,000 g/mol (>99 %). Guanidinium carbonate (99 %) were purchased from Merck.



Fig. 1. Preparation of PVP/PEO/GuC Solid polymer electrolytes.

#### 2.2. Preparation

In various wt.% compositions of Guanidium carbonate (GuC) salt (x = 5, 10, 15, 20, 25) with 70 wt. % of PVP and 30 wt.% of PEO polymer electrolytes have been prepared by inexpensive solution casting. To get the clear, transparent solution, 70 wt.% of PVP was dissolved in distilled water. The preparation of different weight percentages of guanidium carbonate solution and 30 wt.% PEO was done independently. To create a homogenous solution, the prepared solutions were thoroughly combined and swirled for 24 h at room temperature. To get rid of the extra solvent in the trace, the uniform final solution was placed into a polypropylene Petri dish and allowed to dry at room temperature. After the fifth day, the uniform, flexible, and transparent films were obtained and kept in the desiccators for further characterisation. Fig. 1 provides a scheme for the preparation of PVP/PEO/GuC electrolytes.

## 2.3. Characterization details

Bruker D8 advanced powder X-ray diffraction was used to study the structure of the electrolytes. Shimadzu's IR Tracer-100 was used to perform Fourier transform infrared spectroscopy in the 4000-400 cm<sup>-1</sup> region. The dielectric properties of prepared electrolytes were evaluated by HIOKI 3532-50 LCR HI-TESTER. Thermal nature of electrolytes has been studied by NETZSCH DSC analzer. The morphological perspective of the SPEs was investigated using a Carl Zeiss Model Supra 55 Field Emission Scanning Electron Microscope (FE-SEM).

## 3. Results and discussion

## 3.1. Structural study

The X-ray diffraction analysis (XRD) can be used to investigate both the crystalline and amorphous structures of materials. Fig. 2 displays the XRD patterns of PVP/PEO and different concentrations of GuC with a PVP/PEO polymer blend electrolytes. Due to PEO's involvement, polymer blend PVP/PEO exhibits two crystalline peaks at 18° and 23° on the XRD graph [11]. These peaks are a result of the molecules on the polyether side chain of PEO polymer strongly interacting with one another [15,16]. The strength of the peak falls to increase their broadness by the addition of salt. This indicates an increase in the amorphous nature of the polymer electrolytes. There is no additional salt peaks appeared up to 25 wt.% composition. Since, salt completely dissolved in the electrolyte to make salt polymer complex. The degree of crystallinity of the electrolytes was determined by the XRD deconvolution method. XRD peaks are deconvoluted with a Gaussian function using OriginPro 8.5 software. The following equation was used to calculate the crystallinity index (CI) of the prepared electrolytes [17].



Fig. 2. X-ray diffraction patterns of PVP/PEO and PVP/PEO/x wt. % GuC.

$$CI(\%) = \frac{A_c}{A_c + A_a} \times 100$$

where  $A_c$  represents the area of the crystalline domain and  $A_a$  the area of the amorphous domain. Calculated % CI values are tabulated in Table 1. Among these PVP/PEO/25 wt.% GuC composition achieves low percentage of CI, which means that it has the highest amorphousness.

Fourier transforms infra-red spectra of PVP/PEO polymer blend and with different wt. % of GuC incorporated polymer blend electrolytes are shown in Fig. 3. Intermolecular interaction between PVP, PEO polymer blend and also interaction with GuC has been detected by this strong technique. FTIR band position (wavenumber) and its corresponding assignment were listed in Table 2. FTIR spectra for PVP/PEO blend are well match with Abdelrazek EM et al. reports [18]. –OH stretching, C–H asymmetric stretching of ethylene group, Symmetric & asymmetric of C=O, CH<sub>2</sub> scissoring, CH<sub>2</sub> asymmetric bending, CH<sub>2</sub> wagging or twisting, C–O–C stretching mode of PEO, C–O stretching with some CH<sub>2</sub> asymmetric rocking and CH<sub>2</sub> rocking in PVP and with some C–O [19–21] stretching in PEO of FTIR vibration bands are observed at 3389, 2886, 1640, 1463, 1340, 1280, 1096, 957 and 842 cm<sup>-1</sup>. The GuC have N–H···O stretching at 3361 and 3162 cm<sup>-1</sup>, NH<sub>2</sub> bending vibration at 1666 cm<sup>-1</sup>, C=O asymmetric stretching at 1573 and 1388 cm<sup>-1</sup>, NH<sub>3</sub> rocking at 1176 cm<sup>-1</sup> and NH<sub>2</sub> rocking at 613 cm<sup>-1</sup> [22]. As the wt.% of GuC in the PVP/PEO polymer blend increases, the –OH and C–H bands becomes overlapped due to the interaction of N–H···O stretching band of GuC [23]. And also two new peaks originated at 872 and 549 cm<sup>-1</sup>. These are corresponded to –C=O bending of inorganic carbonate and NH<sup>+</sup><sub>3</sub> torsion vibration band. Further CH<sub>2</sub> rocking bands become vanished. Peak modulation also observed in C=O band. The intensity of CH<sub>2</sub> twisting, CH<sub>2</sub> wagging and C–O–C stretching mode of PEO is diminished. Addition of GuC to the PVP/PEO polymer blend results in salt polymer complex as confirmed by arrival of new peaks, disappearance of peaks, decrease of peaks intensity, overlapping and peak modulation.

## 3.2. FTIR deconvolution

FTIR deconvolution for different wt.% GuC added PVP/PEO polymer blend electrolyte in between 1775 and 1475 cm<sup>-1</sup> region is depicted in Fig. 4(a–e). For this operation FTIR absorbance spectrum was deconvoluted using OriginPro 8.5 software based on Gaussian-Lorentz function [24]. Cation of GuC salt forms bonds with electro negative atoms in the polymer chains. PVP/PEO polymer blend having electron rich group/anion peak of  $C = \ddot{O}$  and it is easily coordinate with the electropositive atom of the salt. For this reason, the symmetric & asymmetric of C=O stretching vibration band were selected for FTIR deconvolution. Three deconvoluted peaks close to 1684 cm<sup>-1</sup>, 1641 cm<sup>-1</sup> and 1610 cm<sup>-1</sup> wavenumber were obtained. These suggest that GuC plays an important role to alter the structure of polymer matrix and formation of polymer-salt complexation. Similarly, arrival of two new peaks of C=O bending of inorganic carbonate and NH<sub>3</sub><sup>+</sup> torsion vibration band due to the polymer salt interaction. The overlapping of –OH stretching, C–H asymmetric stretching of ethylene group peaks becomes broadened with increases of salt ratio in the polymer blend. This is the evidence for increased amorphous nature due to disruption of the ordered arrangement of polymer chains and is agrees with the XRD results.

## 3.3. Surface morphological analysis

FE-SEM a state-of-the-art technique, was used to record the morphological image and microstructure of the materials. FE-SEM is often conducted in a high vacuum because gas molecules have a propensity to impact the electron beam and the resultant secondary and backscattered electrons used for imaging. Fig. 5(a–f) displays FE-SEM micrographs of PVP/PEO with varying weight ratios of GuC salt-based polymer electrolytes. PVP/PEO blend has smooth surface shape, as may be shown. Due to the likely molecular level interactions between PVP and PEO, there has been no phase separation, indicating the homogeneity [11]. According to Fig. 5b, the blend electrolyte films' surfaces smooth out as the concentration of complexing salt increases. This shows the rise in the amorphous of material in the blend's electrolyte matrix as a result of salt's dissociation and random dispersion. The high-magnified FE-SEM picture of PVP/PEO with 25 wt percent of GuC shown in Fig. 5 reveals that the membrane's surface contains numerous gaps and cavities (free spaces) of various sizes. The ion transport creates a new kinetic channel through polymer-salt barriers utilizing the benefit of unusual hierarchical structure with empty space [25].

Calculated CI (%) values of different v PEO polymer blend electrolytes.	vt.% GuC added PVP/
Polymer blend electrolytes	CI (%)
PVP/PEO Blend	79.01 %
PVP/PEO/5 wt% GuC	29.14 %
PVP/PEO/10 wt% GuC	28.50 %
PVP/PEO/15 wt% GuC	28.09 %
PVP/PEO/20 wt% GuC	28.04 %
PVP/PEO/25 wt% GuC	27.96 %

Table 1



Fig. 3. FTIR spectra for PVP/PEO polymer blend and different wt. % of Guanidinium carbonate.

FTIR assignment of PVP/PEO polymer blend and different wt.% of Guanidinium Carbonate added polymer blend electrolytes.

PVP/PEO	PVP/PEO/GuC	Assignment of FTIR band
Wavenumber (cm <sup>-1</sup> )	Position of Peaks	
3389	Overlap	-OH stretching
2886		C-H asymmetric stretching of methylene group in PEO
1640	modulate	Symmetric & asymmetric of C]O
1463	Peak are merged to form	CH <sub>2</sub> scissoring
	C]O symmetric stretching band at 1360 cm <sup>-1</sup>	
1420		C–H stretching
1340		CH <sub>2</sub> asymmetric bending
1318	Intensity decrease	CH <sub>2</sub> twisting
1280	Intensity decrease	CH <sub>2</sub> wagging or twisting
1096	Intensity decrease	C–O–C stretching mode of PEO
957	Disappear	C–O stretching with some $CH_2$ asym. Rocking
-	New peak at 872 $cm^{-1}$	Bending –C]O inorganic carbonate
842	Disappear	CH <sub>2</sub> rocking in PVP and with some C–O stretching in PEO
-	New peak at 549 cm <sup>-1</sup>	NH <sub>3</sub> <sup>+</sup> torsion

## 3.4. Ac impedance analysis

Impedance plot of PVP/PEO polymer blend electrolytes with 5–25 wt. % of GuC at 303 K was shown in Fig. 6. From a low frequency of 42Hz to a high frequency of 1 MHz (right to left), the real impedance decreases while the imaginary impedance increases, reaching a maximum value and then decreasing. Thus the electrolytes reveal a semi-circle. This is due to the parallel combination of resistance and capacitance [26,27]. All occurrence of single semicircle confirms the single relaxation of the material. The conductivity of the prepared electrolytes is calculated by,

# $\sigma = \mathsf{I} \; / \; R_b A \; (S/cm)$

Since, I and A are the thickness and conduct area of the polymer membrane. The semicircle extends further where it meets the x-axis is the bulk resistance ( $R_b$ ) of the electrolyte. As the presence of GuC in the polymer blend increases from 5 to 15 wt. %, the conductivity of the electrolytes decreases. Calculated conductivity values of the electrolytes are listed in Table 3. Further increasing the wt. % of GuC the conductivity of the electrolytes becomes increased. Since, 25 wt.% GuC electrolyte achieve the higher conductivity of  $3.00764 \times 10^{-7}$  S/cm due to the presence of numerous gaps and cavities. From the comparative analysis (Table 4) of the values, it is found that the conductivity increases with increased temperature as well as the concentration of salts. The conductivity value of the



Fig. 4. FTIR deconvolution of the C=O peak for various wt.% GuC added PVP/PEO polymer blend electrolyte.

PEO/PVP/25 wt.% GuC is greater than in the prepared polymer electrolytes of the present work.

#### 3.5. Dielectric studies

The dielectric behaviour of polymer electrolyte matrix is described by the complex permittivity ( $\varepsilon^*$ ).

$$\varepsilon^* = \varepsilon'(\omega) - j\varepsilon''(\omega) = \frac{-j}{\omega C_0 Z^*}$$
$$\varepsilon' = \frac{-Z^*}{\omega C_0 (Z'^2 + Z''^2)}$$
$$\varepsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)}$$

Where  $\omega$  is the angular frequency of the applied electric field,  $\varepsilon'$  is the dielectric constant (charge storage),  $\varepsilon'$  is the dielectric loss (energy loss),  $C_0$  is the vacuum capacitance, and Z\* is the complex impedance. The frequency dependence of the dielectric constant and the dielectric loss of PVP/PEO polymer blend electrolytes with various GuC weight percentages are shown in Figs. 7 and 8 at 303 K



Fig. 5. FESEM micrographs a) PVP/PEO, b) PVP/PEO/5 wt% GuC, c) PVP/PEO/10 wt% GuC, d) PVP/PEO/15 wt% GuC, e) PVP/PEO/20 wt% GuC and f) PVP/PEO/25 wt% GuC.



Fig. 6. Impedance plot of different wt. % of Guanidinium carbonate added polymer blend electrolytes.

Conductivity value of different wt.% of guanidinium carbonate-added polymer blend electrolytes.

Electrolytes	R <sub>b</sub> (ohm)	Conductivity (S/cm)
PVP/PEO/5 wt.% GuC PVP/PEO/10 wt.% GuC PVP/PEO/15 wt.% GuC	648052.2 2040996 12589595	$\begin{array}{c} 1.80513 \times 10^{-7} \\ 5.73162 \times 10^{-8} \\ 9.29196 \times 10^{-9} \end{array}$
PVP/PEO/20 wt.% GuC PVP/PEO/25 wt.% GuC	7790239 388950.1	$\begin{array}{l} \textbf{1.50165}\times \textbf{10}^{-8} \\ \textbf{3.00764}\times \textbf{10}^{-7} \end{array}$

## temperature, respectively.

At low frequency both  $\varepsilon'$  and  $\varepsilon''$  are reaches high value due to the accumulation of more charge carriers at electrode||electrolyte interface [33]. Its values decrease towards higher frequency and reach a constant value. In the high frequency region, the sufficient time is not available for ion orientation [34].  $\varepsilon'$  versus salt concentration plot at 1 MHz frequency is shown in Fig. 7 (insert figure). The  $\varepsilon'$  values rises by increment of salt concentration in the polymer blend electrolytes. Both figures expose the higher conducting electrolyte of 25 wt. % GuC added PVP/PEO polymer blend electrolyte achieve the higher value of the dielectric constant and dielectric loss because more charge accumulation occurs in high frequency region. It stabilizes when moving to the higher frequency side. Due to this the value of dielectric constant is calculated on the high frequency side.

Comparative analysis of the conductivity of the title material against other reported materials.

S. No.	Polymer electrolytes	Conductivity (S cm <sup>-1</sup> )	Ref.
1.	PVP/PEO/1.5 wt.% (NH <sub>4</sub> ) <sub>2</sub> Ce (NO <sub>3</sub> ) <sub>6</sub>	$2.88\times 10^{-5}$	[28]
2.	PEO/PVP/15 wt.% NaCl	$1.66 \times 10^{-7}$	[19]
3.	PEO/PVP/30 wt.% Mg(NO3)2	$5.8 imes10^{-4}$	[29]
4.	PEO/PVP/15 wt.% NaF	$1.19  imes 10^7$	[21]
5.	PEO/PVP/NaIO4/0.6 wt.% GO	$1.89 imes10^{-6}$	[30]
6.	PEO/PVP/20 wt.% lithium acetate	$2.56\times 10^{-6}$	[31]
7.	PEO/PVP/15 wt.% NaBr	$1.90 imes10^{-6}$	[32]
8.	PEO/PVP/25 wt.% GuC	$3 imes 10^{-7}$	Present work



**Fig. 7.** Dielectric constant (ɛ') plot versus frequency for different wt.% of Guanidinium Carbonate incorporated with PVP/PEO polymer blend electrolytes and Dielectric constant versus salt concentration plot (inside figure).



Fig. 8. Dielectric loss (ɛ") plot versus frequency for different wt. % of Guanidinium Carbonate incorporated with PVP/PEO polymer blend electrolytes.

## 3.6. Dielectric energy dissipation factor (tangent loss spectra)

Through the use of the frequency-dependent parameters of loss tangent, dielectric loss factor, and energy dissipation in dielectric, the electrical characteristics of polymers are examined. Variation in tangent loss with frequency at ambient temperature of different wt.% of GuC incorporated with PVP/PEO polymer blend electrolytes is exposed in Fig. 9. Single hump of tangent loss plot reveals that the electrolytes have a single relaxation process. The fact that these electrolytes obey non-Debye behaviour which is confirmed by the



Fig. 9. Tangent loss spectra with frequency at ambient temperature for different wt.% of GuC added PVP/PEO polymer blend electrolytes.

difference in relaxation hump height of all the electrolytes [35]. The tangent loss initially increases with frequency due to the loss caused by the Ohmic component's dominance over the capacitive element, and it then reaches its peak at a single frequency, which is the relaxation frequency. It is possible when the frequency of the applied electric field and the frequency of molecule rotation are well matched. Moving to higher frequencies cause the loss to diminish. Here, the ohmic and dominant capacitive components are frequency independent [35]. The relaxation time ( $\tau$ ) is the reciprocal of the angular frequency ( $\omega$ ) of the maximum height of the hump gives the relaxation time ( $\tau = \frac{1}{\omega}$ ) of the material.

The relaxation time is inversely proportional to the angular frequency. That is, if the hump of the tangent plot moves towards higher frequency, the relaxation time of the electrolyte will be shorter. The calculated value of relaxation time of the electrolytes was listed in Table 5. The relaxation hump position of 10, 15 and 20 wt.% GuC electrolytes is at low frequency and others at high frequency. In that respect higher conducting electrolyte of 25 wt.% GuC has low relaxation time of 5.78  $\mu$ s.

## 3.7. Differential scanning calorimetry analysis

Fig. 10 displays the differential scanning calorimetric pattern of free-standing solid films made of a blended polymer with various stoichiometric salt ratios. It is crucial that the crystalline materials have a lower melting point, which favours ion dynamics by allowing for quicker ion transit through coordinating sites in the polymer chain. Fig. 10 indicates that the mixed polymer with salt exhibits a melting temperature between 80 and 110 °C. All of the prepared GuC added blend electrolytes showed very broad endothermic peaks with well-defined peak maxima between 60 and 120–140 °C. The melting temperature of pure PEO and PVP is associated with the peak maximum. With increasing GuC salt concentration, there was a change in peak maximum temperature and a relative increase in the broadness of the endothermic peaks. Additionally, it implies that matrix disorder and the breakdown of polymer chain organisation promote ion mobility. Yet another change towards high temperatures is seen at high salt content, which may be related to the salt problem with the weak polymer. The glass transition temperature (T<sub>g</sub>) informs us about the miscibility of blended polymers and the segmental motion of polymer chains. Tg values for PEO and PVP have been previously reported to be about 69 °C [36]. In the present investigation, GuC added blend polymer electrolytes displayed decreasing values, which are shown in Table 6. The change in mobility of the crystallizable units of PEO and PVP is related to the decrease in glass transition temperature of the PEO and PVP blend matrix. The increase in amorphous fraction allows polymer chains to achieve quicker internal modes in which bond rotations allow for greater segmental motion.

electrolytes.		
Polymer blend electrolytes	Relaxation Time (Second)	
PVP/PEO/5 wt.% GuC	$5.04 imes10^{-6}$	
PVP/PEO/10 wt.% GuC	$2.10 imes 10^{-5}$	
PVP/PEO/15 wt.% GuC	$1.49 imes10^{-4}$	
PVP/PEO/20 wt.% GuC	$8.55 imes10^{-5}$	
PVP/PEO/25 wt.% GuC	$5.78\times 10^{-6}$	

 Table 5

 Relaxation time of different wt.% GuC added PVP/PEO polymer blend electrolytes.



Fig. 10. Differential scanning calorimetric patterns.

Glass transition temperature of different wt.% GuC added PVP/PEO polymer blend electrolytes.

Polymer blend electrolytes	T <sub>g</sub> (°C)
PVP/PEO/5 wt.% GuC	105
PVP/PEO/10 wt.% GuC	102
PVP/PEO/15 wt.% GuC	100
PVP/PEO/20 wt.% GuC	85
PVP/PEO/25 wt.% GuC	81

## 4. Conclusions

The conventional and simple solution casting method was used to prepare solid polymer electrolytes with varying amounts of guanidinium carbonate, 70 wt. % of PVP and 30 wt. % of PEO. The increase in amorphousness shows that the salt in the polymer matrix has dissolved entirely. With an increase in salt concentration, there is a tendency for the distinctive bands of PEO and PVP polymer matrices as confirmed by FTIR. Furthermore, the complex formation of blend polymer and salt was confirmed by the FTIR deconvolution method. Impedance study was used to determine the conductivity of solid polymer electrolytes, 25 wt.% GuC achieved a higher conductivity of  $3.00764 \times 10^{-7}$  S/cm. The loss tangent peak of a higher conducting electrolyte is located on the higher frequency side, and a low relaxation time is sufficient for this. According to DSC experiments, the glass transition temperature decreased, which improved the amorphous nature and segmental mobility of polymer chains in response to salt concentration. Based on the above observations, the prepared GuC added PVP/PEO solid state polymer electrolytes are good candidates for battery applications.

## CRediT authorship contribution statement

**R. Pradeep:** Writing – original draft. **V. Siva:** Writing – review & editing, Supervision, Conceptualization. **M. Anandha Jothi:** Data curation. **A. Murugan:** Methodology, Investigation. **A. Shameem:** Investigation. **S. Sanjana:** Validation. **E. Hemnath:** Formal analysis. **Abdullah G Al-Sehemi:** Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### References

- A. Szczęsna-Chrzan, M. Marczewski, J. Syzdek, M.K. Kochaniec, M. Smoliński, M. Marcinek, Lithium polymer electrolytes for novel batteries application: the review perspective, Appl. Phys. A 129 (2023) 37, https://doi.org/10.1007/s00339-022-06269-3.
- [2] X. Ji, Y. Zhang, M. Cao, Q. Gu, H. Wang, J. Yu, Z.H. Guo, X. Zhou, Advanced inorganic/polymer hybrid electrolytes for all-solid-state lithium batteries, J. Adv. Ceram. 11 (6) (2022) 835–861, https://doi.org/10.1007/s40145-022-0580-8.
- [3] S. Choudhury, S. Stalin, D. Vu, A. Warren, Y. Deng, P. Biswal, L.A. Archer, Solid-state polymer electrolytes for high-performance lithium metal batteries, Nat. Commun. 10 (1) (2019) 4398, https://doi.org/10.1038/s41467-019-12423-y.
- [4] Y. Zhang, W. Lu, L. Cong, J. Liu, L. Sun, A. Mauger, C.M. Julien, H. Xie, J. Liu, Cross-linking network based on Poly(ethylene oxide): solid polymer electrolyte for room temperature lithium battery, J. Power Sources 420 (2019) 63–72, https://doi.org/10.1016/j.jpowsour.2019.02.090.
- [5] B. Sun, J. Mindemark, K. Edström, D. Brandell, Polycarbonate-based solid polymer electrolytes for Li-ion batteries, Solid State Ionics 262 (2014) 738–742, https://doi.org/10.1016/j.ssi.2013.08.014.
- [6] M. Dirican, C. Yan, P. Zhu, X. Zhang, Composite solid electrolytes for all-solid-state lithium batteries, Mater. Sci. Eng. R Rep. 136 (2019) 27–46, https://doi.org/ 10.1016/j.mser.2018.10.004.
- [7] J. Feng, L. Wang, Y. Chen, P. Wang, H. Zhang, X. He, PEO based polymer-ceramic hybrid solid electrolytes: a review, Nano Convergence 8 (2021) 1–12, https:// doi.org/10.1186/s40580-020-00252-5.
- [8] N. Yazie, D. Worku, N. Gabbiye, A. Alemayehu, Z. Getahun, M. Dagnew, Development of polymer blend electrolytes for battery systems: recent progress, challenges, and future outlook, Materials for Renewable and Sustainable Energy (2023) 1–22, https://doi.org/10.1007/s40243-023-00231-w.
- [9] V. Siva, D. Vanitha, A. Murugan, A. Shameem, S. Asath Bahadur, Studies on structural and dielectric behaviour of PVA/PVP/SnO nanocomposites, Compos. Commun. 23 (2021), 100597, https://doi.org/10.1016/j.coco.2020.100597.
- [10] M. Anandha Jothi, D. Vanitha, K. Sundaramahalingam, N. Nallamuthu, Utilisation of corn starch in production of 'eco friendly' polymer electrolytes for proton battery applications, Int. J. Hydrogen Energy 47 (67) (2022) 28763–28772, https://doi.org/10.1016/j.ijhydene.2022.06.192.
- [11] W. Ramya, V. Siva, A. Murugan, A. Shameem, S. Kannan, K. Venkatachalam, A novel biodegradable polymer-based hybrid nanocomposites for flexible energy storage systems, J. Polym. Environ. 31 (4) (2023) 1610–1627, https://doi.org/10.1007/s10924-022-02695-9.
- [12] B. Jinisha, K.M. Anilkumar, M. Manoj, V.S. Pradeep, S. Jayalekshmi, Development of a novel type of solid polymer electrolyte for solid state lithium battery applications based on lithium enriched poly (ethylene oxide) (PEO)/poly (vinyl pyrrolidone) (PVP) blend polymer, Electrochim. Acta 235 (2017) 210–222, https://doi.org/10.1016/j.electacta.2017.03.118.
- [13] A. Chandra, Hot-pressed PEO-PVP blended solid polymer electrolytes: ion transport and battery application, Polym. Bull. 73 (10) (2016) 2707–2718, https://doi.org/10.1007/s00289-016-1616-4.
- [14] C. Devi, J. Gellanki, H. Pettersson, S. Kumar, High sodium ionic conductivity in PEO/PVP solid polymer electrolytes with InAs nanowire fillers, Sci. Rep. 11 (1) (2021), 20180, https://doi.org/10.1038/s41598-021-99663-5.
- [15] E.M. Abdelrazek, A.M. Abdelghany, S.I. Badr, M.A. Morsi, Structural, optical, morphological and thermal properties of PEO/PVP blend containing different concentrations of biosynthesized Au nanoparticles, J. Mater. Res. Technol. 7 (4) (2018) 419–431.
- [16] S. Shenbagavalli, M. Muthuvinayagam, S. Jayanthi, M.S. Revathy, Investigations on Al2O3 dispersed PEO/PVP based Na+ ion conducting blend polymer electrolytes, J. Mater. Sci. Mater. Electron. 32 (2021) 9998–10007, https://doi.org/10.1007/s10854-021-05658-3.

[17] R. Rotaru, M. Savin, N. Tudorachi, Ferromagnetic iron oxide-cellulose nanocomposites prepared by ultrasonication, Polym. Chem. 10 (2017) 1039.

- [18] E.M. Abdelrazek, I.S. Elashmawi, A. El-Khodary, A. Yassin, Structural, optical, thermal and electrical studies on PVA/PVP blends filled with lithium bromide, Curr. Appl. Phys. 10 (2) (2010) 607–613, https://doi.org/10.1016/j.cap.2009.08.005.
- [19] K.K. Kumar, M. Ravi, Y. Pavani, S. Bhavani, A.K. Sharma, V.V.R. Narasimha Rao, Electrical conduction mechanism in NaCl complexed PEO/PVP polymer blend electrolytes, J. Non-Cryst. Solids 358 (23) (2012) 3205–3211, https://doi.org/10.1016/j.jnoncrysol.2012.08.022.
- [20] K.K. Kumar, M. Ravi, Y. Pavani, S. Bhavani, A.K. Sharma, V.V.R. Narasimha Rao, Investigations on PEO/PVP/NaBr complexed polymer blend electrolytes for electrochemical cell applications, J. Membr. Sci. 454 (2014) 200–211, https://doi.org/10.1016/j.memsci.2013.12.022.
- [21] K.K. Kumar, M. Ravi, Y. Pavani, S. Bhavani, A.K. Sharma, V.V.R. Narasimha Rao, Investigations on the effect of complexation of NaF salt with polymer blend (PEO/PVP) electrolytes on ionic conductivity and optical energy band gaps, Phys. B Condens. Matter 406 (9) (2011) 1706–1712, https://doi.org/10.1016/j. physb.2011.02.010.
- [22] B. Deepa, P. Philominathan, Optical, mechanical and thermal behaviour of Guanidinium Carbonate single crystal, Optik 127 (3) (2016) 1507–1510, https://doi. org/10.1016/j.ijleo.2015.10.159.
- [23] A. Suvitha, P. Murugakoothan, Synthesis, growth, structural, spectroscopic andoptical studies of semiorganic NLO crystal: zinc guanidinium phosphate, Spectrochim. Acta, Part A 86 (2012) 266–270, https://doi.org/10.1016/j.saa.2011.10.034.
- [24] N. Shukla, A.K. Thakur, Role of salt concentration on conductivity optimization and structural phase separation in a solid polymer electrolyte based on PMMA-LiClO4, Ionics 15 (2009) (2009) 357–367, https://doi.org/10.1007/s11581-008-0275-3.
- [25] V. Siva, A. Murugan, A. Shameem, S. Thangarasu, S. Asath Bahadur, A facile microwave-assisted combustion synthesis of NiCoFe2O4 anchored polymer nanocomposites as an efficient electrode material for asymmetric supercapacitor application, J. Energy Storage 48 (2022), 103965, https://doi.org/10.1016/j. est.2022.103965.
- [26] A.S. Samsudin, W.M. Khairul, M.I.N. Isa, Characterization on the potential of carboxy methylcellulose for application as proton conducting biopolymer electrolytes, J. Non-Cryst. Solids 358 (8) (2012) 1104–1112, https://doi.org/10.1016/j.jnoncrysol.2012.02.004.
- [27] M. Anandha Jothi, D. Vanitha, N. Nallamuthu, A. Manikandan, S. Asath Bahadur, Investigations of lithium ion conducting polymer blend electrolytes using biodegradable cornstarch and PVP, Physica B 580 (2020) (2020), 411940, https://doi.org/10.1016/j.physb.2019.411940.
- [28] S. Shenbagavalli, M. Muthuvinayagam, M. S Revathy, P. Sasikumar, Ionic conductivity and dielectric studies on PVP/PEO/(NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> based solid polymerblend electrolytes, Bull. Mater. Sci. 45 (3) (2022) 125.
- [29] K.M. Anilkumar, B. Jinisha, M. Manoj, S. Jayalekshmi, Poly (ethylene oxide) (PEO)–Poly (vinyl pyrrolidone)(PVP) blend polymer based solid electrolyte membranes for developing solid state magnesium ion cells, Eur. Polym. J. 89 (2017) 249–262.
- [30] H.K. Koduru, F. Scarpelli, Y.G. Marinov, G.B. Hadjichristov, et al., Characterization of PEO/PVP/GO nanocomposite solid polymer electrolyte membranes: microstructural, thermo-mechanical, and conductivity properties, Ionics 24 (2018) 3459–3473.
- [31] K. Sundaramahalingam, M. Muthuvinayagam, N. Nallamuthu, AC impedance analysis of lithium ion based PEO: PVP solid polymer blend electrolytes, Polym. Sci. 61 (2019) 565–576.
- [32] R.D. Armstrong, T. Dickinson, P.M. Willis, The AC impedance of powdered and sintered solid ionic conductors, J. Electroanal. Chem. Interfacial Electrochem. 53 (3) (1974) 389–405, https://doi.org/10.1016/S0022-0728(74)80077-X.
- [33] M. Hema, S. Selvasekarapandian, D. Arunkumar, A. Sakunthala, H. Nithya, FTIR, XRD and ac impedance spectroscopic study on PVA based polymer electrolyte doped with NH4X (X= Cl, Br, I), J. Non-Cryst. Solids 355 (2) (2009) 84–90, https://doi.org/10.1016/j.jnoncrysol.2008.10.009.
- [34] K. Sundaramahalingam, N. Nallamuthu, A. Manikandan, D. Vanitha, M. Muthuvinayagam, Studies on sodium nitrate based polyethylene oxide/polyvinyl pyrrolidone polymer blend electrolytes, Phys. B Condens. Matter (2018), https://doi.org/10.1016/j.physb.2018.08.002.
- [35] W. Zhou, Y. Kou, M. Yuan, B. Li, H. Cai, Z. Li, F. Chen, X. Liu, G. Wang, Q. Chen, Z.M. Dang, Polymer composites filled with core@ double-shell structured fillers: effects of multiple shells on dielectric and thermal properties, Compos. Sci. Technol. 181 (2019), 107686, https://doi.org/10.1016/j.compscitech.2019.107686.
- [36] H.K. Koduru, L. Marino, F. Scarpelli, A.G. Petrov, Y.G. Marinov, G.B. Hadjichristov, M.T. Iliev, N. Scaramuzza, Structural and dielectric properties of NaIO4 complexed PEO/PVP blended solid polymer electrolytes, Curr. Appl. Phys. 17 (2017) 1518–1531, https://doi.org/10.1016/j.cap.2017.07.012.