Copper Ion-Conducting PVP-Based Solid Polymer Electrolyte with TiO_2 Nanofiller for Solid-State Battery Applications

Cu Ion Solid Polymer Electrolytes for Energy Storage Devices

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Abstract

The growing demand for sustainable and efficient energy storage solutions has led to the development of rechargeable battery technologies. Solid polymer electrolytes (SPEs) have been considered as a promising alternative to the conventional liquid electrolytes because of their better safety and mechanical flexibility. A series of solid polymer electrolytes based on polyvinylpyrrolidone (PVP) doped with Cu^{2+} were prepared by solution casting in the present study. The formation of complex was confirmed by FTIR and UV-Visible spectroscopy. The ionic conductivity at room temperature was highest (1.07×10^{-3} S cm^{-1}) for the 15% Cu^{2+} doped PVP electrolyte. The conductivity was further improved to 1.65 x 10^{-3} S cm^{-1} on incorporation of 0.2% TiO_2 nanofiller. Temperature dependent studies showed the optimum operating temperature to be 60 °C with maximum conductivity of 1.97×10^{-3} S cm^{-1}. The Cu^{2+}/PVP/TiO_2 composite electrolyte has the potential to be applied in the flexible, all-solid-state and temperature-variable rechargeable battery systems.

Keywords: Polyvinylpyrrolidone (PVP), Solid polymer electrolyte, UV-Visible spectroscopy, FTIR, Nanofiller, Ionic conductivity

1. Introduction

Rechargeable batteries have now become essential parts of modern energy technology and can undergo multiple charge-discharge cycles via reversible electrochemical reactions [1,2]. Lithium-ion batteries have become the leading technology in modern battery systems in both commercial and research fields. These systems have significantly improved performance characteristics compared to alternative rechargeable battery chemistries, such as higher specific energy, greater energy density, improved energy efficiency, longer cycle life and longer calendar life relative to traditional lead-acid, nickel-cadmium and nickel-molybdenum battery systems [3,4].

However, traditional lithium-ion batteries use organic liquid electrolytes, which consist mainly of lithium salts dissolved in volatile organic solvents. However, these traditional electrolyte systems are associated with safety concerns because of their flammable and volatile properties, leading to fire and

explosion hazards for battery applications, especially during thermal or mechanical abuse [5,6]. These safety concerns have prompted extensive research into development of safer electrolyte alternatives.

Recently the solid polymer electrolytes (SPEs) have been considered as the promising substitutes of conventional liquid electrolytes. SPEs have several advantages that make them suitable candidates for future battery technologies [7,8]. These materials provide enhanced safety arising from their intrinsic non-flammability and the ability to remove leakage hazards from their solid state architecture, excellent mechanical flexibility for integration into various device geometries, low weight compared to ceramic alternatives and cost-effective manufacturing through scalable production techniques. Solid polymer electrolytes are generally composed of polymer matrices with dissolved salts without the addition of any other liquid solvents and are prepared by simple and economical techniques such as solution casting, extrusion and hot moulding processes [9,10].

However, efficient SPE performances in battery applications necessitate that polymer matrices fulfill several important requirements. Polymer-cation interactions must be sufficiently labile to allow ionic hopping between sequential coordination sites, but sufficiently strong to maintain salt solubility through effective cation solvation [11]. An efficient charge separation of dissolved salts and generation of significant concentrations of mobile charge carriers require a high dielectric constant of the polymer host [12]. Ion transport in polymer electrolytes is inherently coupled to the segmental dynamics of the polymer backbone [13,14]. Flexibility of the polymer chains is essential to reduce the energy barriers for bond rotation and to allow polymer segmental motion. Furthermore, the large molecular weight of the polymer matrix leads to a considerable enhancement of the mechanical strength of the resulting SPE materials [15].

The ionic conductivity of solid polymer electrolytes can be enhanced by strategic modification with metallic ion doping where transition metal ions can provide additional coordination sites for ion transport and improve ion hopping mechanisms [6,16]. Copper ions are a very attractive choice of dopant due to their favourable ionic size, variable oxidation states and strong coordination affinity for ether and carbonyl oxygen donors present in polymer matrices. Moreover, composite polymer electrolytes that contain ceramic nanofillers such as titanium dioxide (TiO_2) have shown remarkable improvements in ionic conductivity through multiple mechanisms, including the disruption of polymer crystallinity and promotion of amorphous phase formation, the provision of additional ion coordination sites through surface hydroxyl and oxide groups, the formation of Lewis acid-base interactions at the polymer–nanofiller interface, and the creation of fast-ion conduction pathways at interfacial regions [17–19].

Therefore, this study is focused on the synthesis and systematic characterisation of polyvinylpyrrolidone (PVP) doped with copper ions (PVP/Cu^{2+}) as a solid polymer electrolyte system for possible applications in rechargeable battery. The work is a systematic study of the influence of doping with Cu^{2+} ions at different dopant concentrations on the electrochemical performance and on the mechanisms of thermal and conductivity enhancement induced by the addition of nanofillers. Moreover, this work delineates the optimal temperature window for SPE performance and thermal stability, and establishes the fundamental structure-property relationships that govern ionic conductivity in this material system. The primary objective is to develop an advanced solid polymer electrolyte formulation that offers practical ionic conductivity and proven thermal stability through a simple synthesis method and cost-effective base materials.

2. Materials and Methods

2.1 Materials

The polyvinylpyrrolidone (PVP, average molecular weight: 40 000 Da) and copper sulphate pentahydrate ($CuSO_4 \bullet 5H_2O$, analytical grade, purity ≥99%) were obtained and used as received without further purification. The nanofiller additive was titanium dioxide nanoparticles (TiO_2, anatase phase, particle size: 100 nm). All the solutions were prepared in distilled water. All materials were of analytical grade and used without further purification.

2.2 Synthesis of PVP/Cu^{2+} Gel and Solid Polymer Electrolytes

2.2.1 Preparation of Pure and Cu^{2+}-Doped PVP Electrolytes

Solid polymer electrolytes were prepared by solution casting technique which is a widely adopted method for the preparation of SPEs. The systematic steps for synthesis were carried out as follows.

Pure PVP Gel Polymer Electrolyte: A weighed amount of PVP (0.5 g) was dissolved in distilled water (1 mL) in a clean borosilicate bottle. The mixture was stirred by magnet at room temperature (25 ± 2 °C) until a homogeneous gel polymer electrolyte was obtained, which was about 2 h stirring time.

Cu^{2+}-Doped PVP Gel Polymer Electrolyte: To prepare Cu^{2+}doped polymer electrolytes with varying concentrations, $CuSO_4 \cdot 5H_2O$ was added separately to freshly prepared PVP solutions in the amounts specified in Table 2.1. Each mixture was continuously stirred for 4 hours at room temperature to ensure uniform dispersion of Cu^{2+} ions throughout the polymer matrix and complete complex formation, yielding homogeneous gel polymer electrolytes characterised by the development of progressive blue-green coloration.

Table 1

Composition and mass specifications of PVP/Cu^{2+} electrolyte samples

Sample ID	**PVP Mass (g)**	**Cu^{2+} Concentration (wt%)**	**$CuSO_4 \cdot 5H_2O$ Mass (g)**
PVP-0	0.5	0	0.000
PVP-5	0.5	5	0.025
PVP-10	0.5	10	0.050
PVP-15	0.5	15	0.075
PVP-20	0.5	20	0.100
PVP-25	0.5	25	0.125

2.2.2 Film Casting and Conversion to Solid Polymer Electrolytes

The prepared gel polymer electrolytes were carefully transferred onto clean glass plates and allowed to dry at ambient conditions (25 ± 2 °C, relative humidity 50–60%) under a dust-free

environment. The drying process typically required 48–72 hours, resulting in the formation of free-standing, flexible solid polymer electrolyte films.

2.3 Preparation of TiO_2 Nanofiller-Enhanced Composite Polymer Electrolytes

In order enhance the ionic conductivity of the optimal Cu^{2+}-doped electrolyte (15 wt% Cu^{2+} in PVP) further, composite polymer electrolytes were synthesised by incorporating TiO_2 nanoparticles at the specified weight percentages detailed in Table 2.2. The TiO_2 nanoparticles were calculated amounts corresponding to the total mass of the 15% PVP/Cu^{2+} electrolyte system.

The calculated amounts of TiO_2 nanoparticles were added separately to freshly prepared 15 wt% Cu^{2+}-doped PVP solutions. Each suspension was vigorously stirred using magnetic stirring for 6 hours at room temperature to ensure homogeneous dispersion of nanoparticles throughout the polymer matrix. The resulting nanofiller-containing gel electrolytes were then cast onto glass plates and dried following the procedure described in section 2.2.2.

Table 2.

Composition and mass specifications of TiO_2-modified 15% PVP/Cu^{2+} composite electrolytes

Sample ID	TiO_2 Concentration (wt%)	TiO_2 Mass (g)
PVP-15-TiO_2-0.05	0.05	0.00030
PVP-15-TiO_2-0.10	0.10	0.00057
PVP-15-TiO_2-0.20	0.20	0.00115
PVP-15-TiO_2-0.30	0.30	0.00172

2.4 Characterisation Techniques and Experimental Procedures

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectra of the solid polymer electrolytes were acquired using a Fourier Transform Infrared Spectrometer (Serial No. 119152) equipped with an attenuated total reflectance (ATR) accessory. Spectra were recorded in the wavenumber range of 4000–400 cm^{-1}. Background correction was performed prior to each measurement to ensure data quality.

2.4.2 UV-Visible Spectroscopy

UV-Visible absorption spectra of the solid polymer electrolytes were obtained using a UV-Visible spectrophotometer operated in the wavelength range of 190–1100 nm at room temperature (25 ± 2 °C).

2.4.3 Electrochemical Impedance Spectroscopy (EIS) for Ionic Conductivity Determination

The complex impedance measurements and the ionic conductivity determinations were carried out using an Autolab Potentiostat/Galvanostat (Metrohm, Model PGSTAT 128N) coupled with Frequency Response Analyser (FRA 32M module).

Gel Polymer Electrolyte Configuration: The gel electrolyte samples were sandwiched between two polished stainless steel (SS316) blocking electrodes with diameter of 4 mm, hence a circular cross-sectional area of 12.56 mm^2. The gel electrolyte layer was kept at 2 mm in thickness. The assembled cell was placed in a custom designed Teflon holder to ensure uniform contact of the electrodes.

Configuration of solid polymer electrolyte: The free standing SPE films were sandwiched in between two polished copper plate electrodes (diameter 5 mm each) which provided a circular contact

area of 19.63 mm^2. The film thickness was measured individually with a digital micrometer and the value was recorded for each sample, with typical values of 1-2 mm.

EIS Measurement Conditions: Complex impedance was measured in the frequency range from 0.01 Hz to 1 MHz with AC voltage amplitude of 10 mV (peak-to-peak) at open circuit potential. All measurements were carried out at room temperature (25 ± 1 °C) unless otherwise specified.

Ionic Conductivity Calculation: The ionic conductivity (σ) of the electrolytes was calculated from the bulk resistance using:

$$\sigma = \frac{L}{RA}$$

where σ is the ionic conductivity (S cm^{-1}), L is the thickness or length of the electrolyte material (cm), R is the bulk resistance obtained from impedance measurements (Ω), and A is the cross-sectional contact area of the electrolyte sample (cm^2).

2.4.4 Temperature-Dependent Ionic Conductivity Measurements

Thermal stability studies and temperature-dependent ionic conductivity measurements were conducted on the best-performing composite electrolyte sample (15 wt% Cu^{2+} + 0.2 wt% TiO_2). The sample was placed in a hot air steriliser (temperature precision: ±2 °C) and thermally equilibrated at each target temperature for a minimum of 30 minutes prior to conducting impedance measurements. Temperature-dependent conductivity was systematically evaluated at 10 °C intervals spanning the range from 30 °C to 80 °C.

3. Results And Discussion

3.1 Ionic Conductivity Analysis of Cu^{2+}-Doped PVP Gel and Solid Polymer Electrolytes

3.1.1 Effect of Cu^{2+} Ion Concentration on Ionic Conductivity

The ionic conductivity data for gel and solid polymer electrolytes doped with varying concentrations of Cu^{2+} ions are presented in Tables 3.1 and 3.2, respectively. The measured ionic conductivities for the gel polymer electrolyte ranged from 0.537 × 10^{-3} S cm^{-1} (0% Cu^{2+}) to a maximum of 9.81 × 10^{-3} S cm^{-1} (15% Cu^{2+}), representing approximately an 18 times increase in conductivity. The corresponding data for the solid polymer electrolyte (SPE) ranged from 0.057 × 10^{-3} S cm^{-1} (0% Cu^{2+}) to a maximum of 1.070 × 10^{-3} S cm^{-1} (15% Cu^{2+}), demonstrating approximately a 19 times enhancement in ionic conductivity.

Table 3

Ionic conductivity of PVP/Cu^{2+} gel polymer electrolytes at room temperature

Cu^{2+} Concentration (wt%)	**Thickness (mm)**	**Area (mm^2)**	**Resistance (Ω)**	**Conductivity (×10^{-3} S cm^{-1})**
0	2	12.56	2959	0.537
5	2	12.56	258	6.16
10	2	12.56	231	6.88

15	2	12.56	162	9.81
20	2	12.56	309	5.14
25	2	12.56	468	3.39

Table 4

Ionic conductivity of PVP/Cu^{2+} solid polymer electrolytes at room temperature

Cu^{2+} Concentration (wt%)	**Thickness (mm)**	**Area (mm^2)**	**Resistance (Ω)**	**Conductivity ($\times 10^{-3}$ S cm^{-1})**
0	2	19.63	8929	0.057
5	2	19.63	1213	0.419
10	2	19.63	920	0.553
15	2	19.63	473	1.070
20	2	19.63	636	0.800
25	2	19.63	760	0.669

The ionic conductivity profiles exhibited a characteristic bell-shaped curve, with conductivity increasing progressively from 0% to 15% Cu^{2+} concentration, followed by a marked decrease at higher dopant concentrations (20% and 25%). This behaviour is consistent with the observed performance of other transition metal doped polymer electrolytes. In particular, the maximum conductivity at 15 wt% Cu^{2+} suggests the best compromise among numerous competing physical and electrochemical mechanisms.

The first increase in conductivity with Cu^{2+} concentration can be explained by increased ion mobility due to increased availability of mobile charge carriers [20]. When Cu^{2+} ions are incorporated into PVP matrix, they form coordination complexes with carbonyl oxygen atoms of polymer, which results in the formation of additional charge carrier species, and additional ion transport pathways [21]. Besides, the increased segmental motion of the polymer chains caused by the disruption of the polymer crystallinity and increased chain flexibility by metal-ion doping [22] also contribute to the conductivity enhancement. This ion hopping mechanism is inherently coupled to the segmental dynamics of the polymer backbone with the ion mobility proportional to the polymer chain movement [23].

However, the observed decrease in conductivity beyond 15% Cu^{2+} concentration is an important observation and needs a detailed interpretation. The reduction of conductivity in higher dopant concentration (20% and 25% Cu^{2+}) can be mainly explained by some competing mechanisms. High dopant concentration causes higher interaction and collision probability between the charge carriers (ions). This decreases the ion mobility and increases the electrical resistance [24]. At high concentrations, Cu^{2+} ions can form ion aggregates or clusters that trap mobile ions and reduce the concentration of free ions available for charge conduction [21]. High dopant concentrations may cause

increased polymer crystallinity or gelation, which limits the segmental motion of polymer chains and thus decreases the diffusivity of ions in the solid state. This is in agreement with the results reported for similar systems, where manganese(II) ions (Mn^{2+}) and vanadyl ions (VO^{2+}) doped PVP showed monotonic increases in conductivity with dopant concentration up to about 5 mol%, while iron(III) ions (Fe^{3+}) doped PVP systems showed a similar maximum at around 20 wt% and a decrease in conductivity at higher dopant concentrations [21,24]. The conductivity maximum of Cu^{2+} at 15 wt% which is between Mn^{2+}/VO^{2+} and Fe^{3+} systems is indicative of the difference in ionic sizes, charge densities and the coordination chemistry of transition metal ions with the PVP polymer matrix.

3.2 Structural Characterisation via FTIR Spectroscopy

Fourier Transform Infrared spectroscopy was used to study the nature of interactions between the PVP polymer matrix and the incorporated Cu^{2+} ions. Figure 3.1 shows the FTIR spectra in the range of 4000–400 cm^{-1} for pure PVP and selected Cu^{2+}-doped PVP samples (5%, 10%, 15%, 20% and 25% Cu^{2+})

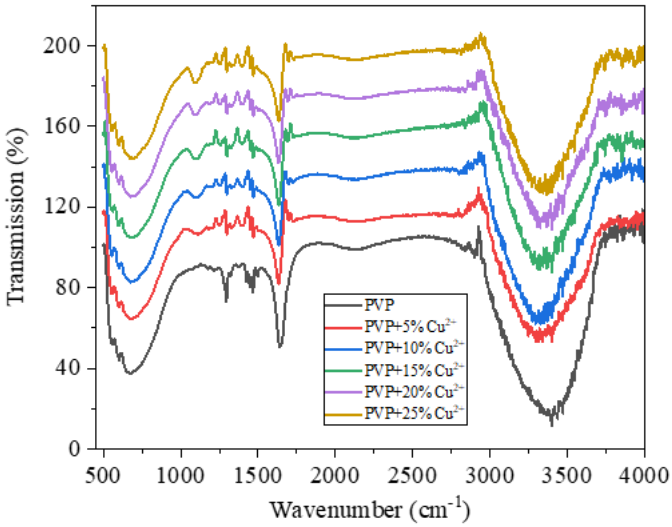

Figure 3.1: FTIR spectra obtained for solid polymer electrolyte for pure PVP and selected Cu^{2+}-doped PVP samples (5%, 10%, 15%, 20%, and 25% Cu^{2+}).

The addition of Cu^{2+} ions caused a remarkable and systematic spectroscopic feature, that is, a significant shift of the vibrational band of the carbonyl (C=O) stretching which was originally located at around 1650 cm^{-1} for pure PVP. The characteristic shift in wavenumber of this carbonyl band with increasing doping of Cu^{2+} suggested the changes in the electronic environment and bond strength of the carbonyl functional groups. The observed shift in the carbonyl stretching region can be attributed to the formation of a coordination complex between the Cu^{2+} ions and the oxygen atoms of the PVP carbonyl groups as direct spectroscopic evidence. This interaction is responsible for the enhanced ionic mobility exhibited by the doped electrolytes, where the coordination sites provide the favorable energetic conditions for an ion to hop between sequential coordination sites along the polymer chain.

The systematic nature of FTIR spectral changes is consistent with the formation of labile metal-polymer coordination complexes. The changes in bond strength reflected in the carbonyl vibrational shift suggest that Cu^{2+} ions form transient associations with oxygen donors that favor ion transport via activated hopping between sequential coordination sites [23]. This coordination mechanism is important for the room temperature ion conductivity observed in these SPEs. Similar spectroscopic signatures have been reported for comparative FTIR analyses of chemically similar systems. For instance, Fe^{3+}-doped PVP electrolytes showed similar band position shifts and intensity variations in the carbonyl region with increasing dopant concentration, with the largest shifts at the concentration of maximum conductivity (~20 wt% Fe^{3+}) [21]. The Mn^{2+}- and VO^{2+}-doped PVP systems showed progressive decrements in band intensity with increasing metal-ion concentration, indicative of progressive increases in metal-polymer interaction strength that correlate with enhanced ionic conductivity [24].

3.3 Optical Characterisation via UV-Visible Spectroscopy

UV-Visible absorption spectra of solid polymer electrolytes with different Cu^{2+} concentrations (0-25 wt %) are given in the wavelength range of 200-1100 nm. Undoped PVP (0% Cu^{2+}) shows very low absorption in the whole visible range while Cu^{2+} doped PVP has absorption bands in the visible range due to the characteristic electronic transitions and ligand-to-metal charge-transfer (LMCT) transitions, suggesting the coordination of Cu^{2+} ions with the carbonyl oxygen atoms of PVP.

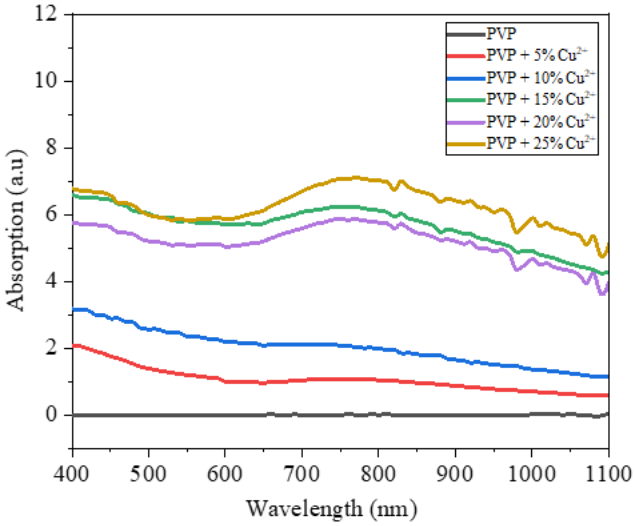

Figure 3.2: UV-Visible absorption spectra for Solid Polymer Electrolytes

The absorption intensity increases systematically with Cu^{2+} concentration, reaching maximum at 15% Cu^{2+} in accordance with maximum complex formation and the optimal conductivity observed in electrochemical measurement. The direct correlation of the spectroscopic and electrochemical maxima confirms that at this concentration of dopant the available coordination sites on the polymer chains are saturated. Despite the increase in absolute Cu^{2+} content, the absorption intensity decreases at

concentrations higher than 15% (20% and 25% Cu^{2+}), which indicates the formation of inactive Cu^{2+} aggregates and disturbance of the regular coordination geometry at excessive dopant levels.

The results of the UV-Visible spectrum provide an independent confirmation of the FTIR results and confirm that Cu^{2+} ions form stable co-ordination complexes in the PVP matrix. The progressive deepening of the characteristic blue-green colouration of gel films with increasing Cu^{2+} concentration, is in direct correlation with quantitative absorption measurements and offers visual evidence of enhanced complex formation at lower concentrations and aggregate formation at higher concentrations.

3.4 Ionic Conductivity Enhancement via Nanofiller Incorporation

To enhance the ionic conductivity of the optimum Cu^{2+} doped PVP electrolyte (15% Cu^{2+}), composite polymer electrolytes were prepared by adding titanium dioxide (TiO_2) nanoparticles at different weight percentages. The ionic conductivity data of these nanofiller enhanced composites are given in Table 5.

Table 5.

Ionic conductivity of 15% PVP/Cu^{2+} composite electrolytes enhanced by TiO_2 nanofiller

TiO_2 Concentration (wt%)	**Thickness (mm)**	**Area (mm^2)**	**Resistance (Ω)**	**Conductivity ($\times 10^{-3}$ S cm^{-1})**
0.05	1	19.63	393	1.29
0.10	1	19.63	353	1.44
0.20	1	19.63	307	1.65
0.30	1	19.63	335	1.51

TiO_2 nanofiller incorporation increased ionic conductivity from 1.070×10^{-3} S cm^{-1} (baseline, 15% Cu^{2+} without filler) to a maximum of 1.65×10^{-3} S cm^{-1} (15% Cu^{2+} + 0.2% TiO_2), representing a 1.54 times enhancement. The conductivity enhancement mechanism operates through three pathways: first, surface hydroxyl and oxide groups on TiO_2 nanoparticles create additional coordination sites for ion hopping, establishing fast-ion conduction channels at the polymer-nanofiller interface [18]; second, TiO_2 incorporation disrupts polymer crystallinity and increases the amorphous phase, enhancing polymer chain segmental mobility [17]; and third, Lewis acid–base interactions between titanium centres and PVP carbonyl oxygen atoms create an interfacial phase with enhanced conductivity [25].

The conductivity maximum at 0.2 wt% TiO_2 followed by a decrease at 0.30 wt% reflects competing detrimental effects at excessive filler loading. The 'blocking effect' limits free volume for ion diffusion and chain mobility; nanoparticle agglomeration reduces effective surface area [26]; and local chain immobilisation due to strong surface interactions traps ions and reduces overall conductivity [18]. The optimal loading of TiO_2 (0.2 wt%) in the PVP matrix is less than that reported for polyethylene oxide systems (5 wt%) [17,18]. This is due to the fact that the base conductivity of PVP is inherently lower than that of polyethylene oxide and the polymer chemistry is different. Therefore, the loading of the nanofiller for optimal enhancement is proportionally lower.

3.5 Thermal Stability and Temperature-Dependent Conductivity Studies

Thermal stability is an important parameter for evaluating the practical feasibility of solid polymer electrolytes in rechargeable battery applications operating under various ambient and device generated thermal conditions. Thus, temperature dependent ionic conductivity measurements were carried out on the best performing composite electrolyte (15 % Cu^{2+} + 0.2 % TiO_2) in the temperature range 30–80 °C with an interval of 10 °C.

The temperature dependent ionic conductivity profile was observed to be non-monotonic in nature with conductivity gradually increasing from 30 °C to 60 °C, reaching a peak value of 1.97×10^{-3} S cm^{-1} at 60 °C and then followed by a sharp and substantial drop in conductivity at temperatures above 60 °C. The conductivity at 70 °C was lowered to 0.90×10^{-3} S cm^{-1} (54% reduction from the maximum) and to 0.75×10^{-3} S cm^{-1} at 80 °C. The thermal profile clearly indicates that 60 °C is the best and thermally stable operating temperature for this SPE system in rechargeable battery applications.

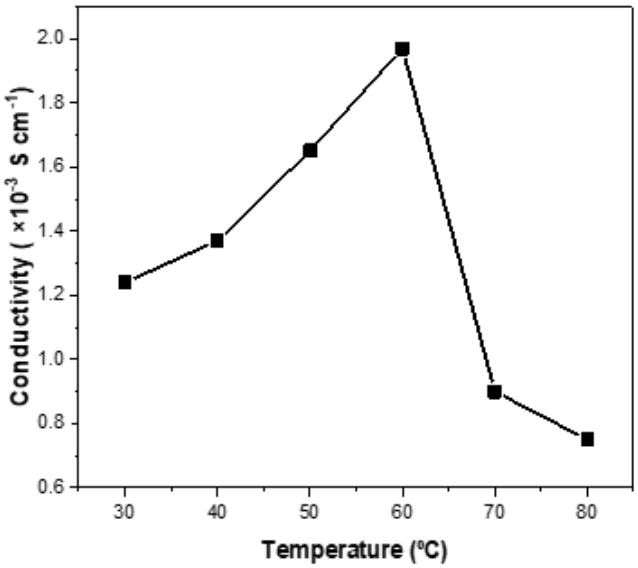

Figure 3.3: Temperature-dependent ionic conductivity of optimized SPE (15% PVP/Cu^{2+} + 0.2% TiO_2)

The physical and electrochemical phenomena responsible for this thermal behaviour should be studied in detail. The initial gradual increase in conductivity from 30 °C to 60 °C agrees with the standard thermal activation of ionic transport processes. As temperature increases, thermal energy increases the kinetic energy of charge carriers, which leads to an increase in ion mobility and promotes ion hopping between coordination sites [6]. At the same time, higher temperature leads to higher segmental mobility of the polymer backbone due to a lower distance from the glass transition, which further enhances the ion diffusion coefficients.

However, the conductivity drops abruptly above 60 °C indicating a critical thermal transition in the system. This sharp decrease can be explained by several processes happening at the same time. First, temperatures above 60 °C are near the glass transition temperature (Tg) and thermal

decomposition regimes of the polymer electrolyte system. The higher thermal energy at these temperatures allows for relaxation of polymer chains and potentially partial crystallization, resulting in reduced amorphous content and constraining the segmental motion needed for coupled ion transport [13]. Second, at temperatures near or above 60 °C, evaporation of residual solvent (water) from the composite electrolyte becomes thermodynamically favourable, reducing the dielectric constant of the medium and destabilising metal-ion coordination complexes [27]. Third, at these high temperatures, thermal decomposition of the polymer backbone and TiO_2-polymer interfacial species could begin, resulting in structural defects and breakup of the continuous ion transport channels.

The observed thermal profile is quantitatively in agreement with thermal stability studies of related metal-ion doped polymer electrolyte systems. The Mn^{2+} and VO^{2+} transition metal doped PVP electrolytes displayed much lower optimal operating temperatures (around 40-45 °C) than the Cu^{2+} system, which is attributed to the different thermal decomposition and coordination stability of the metal ions [24]. The Fe^{3+}/PVP electrolytes had a higher optimal working temperature of about 70 degrees Celsius, which is consistent with the improved thermal stability stemming from the higher charge density and stronger coordination affinity of Fe^{3+} [21]. The optimum temperature of the Cu^{2+}/PVP/TiO_2 system, 60 °C, is thermodynamically intermediate between these comparison systems, which reflects the intermediate ionic size, charge and coordination chemistry of Cu^{2+}.

The practical significance of the identification of 60 °C as the thermal stability optimum from a battery engineering point of view is very high. This temperature is easily achievable within the standard thermal management techniques under laboratory and field conditions, indicating that the Cu^{2+} /PVP/TiO_2 composite electrolyte is a promising candidate for commercial battery applications in moderate to warm environmental conditions. The conductivity at 60 °C (1.97×10^{-3} S cm^{-1}) is about 188 times larger than the pure PVP baseline and demonstrates the effect of metal-ion doping and nanofiller incorporation on the electrolyte performance in the corresponding operating temperature window.

4. Conclusions

Copper ion-doped polyvinylpyrrolidone (PVP) solid polymer electrolytes were successfully synthesized by solution casting and characterized. Coordination complex formation between Cu^{2+} ions and the PVP polymer matrix was confirmed through FTIR and UV-Visible spectroscopy.

Ionic conductivity demonstrated strong dependence on Cu^{2+} concentration, achieving maximum values at 15 wt% Cu^{2+}: gel electrolytes showed an 18 times increase and solid electrolytes showed a 19 times increase in ionic conductivity. Higher concentrations (20–25 wt%) reduced conductivity through ion clustering effects.

TiO_2 nanofiller incorporation (0.2 wt%) further enhanced conductivity through surface coordination sites, crystallinity disruption, and interfacial effects. Excessive nanofiller concentrations reduced conductivity via blocking effects and agglomeration.

Temperature-dependent studies identified 60 °C as the optimal operating temperature with maximum conductivity of 1.97×10^{-3} S cm^{-1}. Conductivity increased from 30–60 °C (Arrhenius behaviour), then declined above 60 °C due to polymer relaxation and solvent evaporation.

The Cu^{2+}/PVP/TiO_2 composite electrolyte achieves ionic conductivity competitive with polyethylene oxide-based systems whilst demonstrating superior thermal stability. Its straightforward

synthesis, cost-effective materials, and non-flammable nature position it as a viable candidate for flexible, all-solid-state, and temperature-variable rechargeable battery systems.

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