Temperature dependent AC electrical properties of solid polymer PVA based proton electrolyte

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Abstract. In this study, the solid polymer electrolyte (SPE) containing polyvinyl alcohol (PVA) and lithium perchloride (LiClO₄) have been prepared by using solution cast technique. The objective of this study is to investigate the influence of LiClO₄ inorganic salt on the AC conductivity of the electrolyte. For that purpose, the PVA sample with LiClO₄ inorganic salt was prepared with different concentration (0, 5, 10, 15 and 20) wt.% of LiClO₄ salt and different thickness. XRD analysis of the sample reveals that PVA shows broad peak at 2θ=19.84° and degree of crystallinity decrease by adding the concentration of lithium salt. The electrical conductivity of the material is measured using LCR meter. The experimental results show that the AC electrical conductivity increases with increasing the temperature and concentration of Li salt. The dielectric constant values of SPE decreases with increase in frequency and increases with increase in temperature. Maximum conductivity of PVA with 20% LiClO₄ at 353K and frequency 500kHz is found to be 3.51*10⁻² S/cm.

1. Introduction

An electrolyte is a material which when dissolved in solvents, it could form a medium that is capable to conducts electricity. The dissolved electrolyte will split into cations and anions which could help in the electric conduction of the medium. Generally, in order to produce a highly efficient electrolyte, the medium needed to be able to allow fast ionic transport, inert to all the cell components such as electrodes, thermally stable and chemically stable.

Solid polymer Electrolyte has been received tremendous attention due to their potentially promising applications in variety of electrochemical devices. Polymer electrolytes have become material of great importance for use in different electrochemical devices due to their easy moldability, good electrode electrolyte contact and light weight. These polymer electrolytes from a bridge between liquid electrolyte and solvent free ceramics. Because of their high ionic conductivity, gel electrolytes have attained precedence over conventional polymer electrolytes. Literature survey has revealed that most of the work reported on polymer gel electrolytes concern development of lithium based polymer batteries proton conductor are equally important class of
electrolyte material due to their application in fuel cells electrochromic devices (ECDs) and other Smart devices. PVA is also one of the prominent polymer because of its good solvent holding capability, it is known to form a good gel material for medical application. Many research have reported PVA based proton conducting gel electrolyte with high ionic conductivity. The mechanical flexibility and strength of the solid state make the SPEs moldable into desired shapes, thus making them ideal candidates for compact electrochemical devices of the modern age. The momentous aspect of the SPEs that they are free from or harmful chemicals. Since their emergence, SPEs have been studied with the principal objective of achieving ionic conductivity comparable to liquid electrolytes at ambient condition without compromising the advantage of the solid state. Increasing demand of energy for emerging technologies used in electronics, medical devices, electric vehicles, power tools etc, develops research interests for the development of efficient electro-active materials that can be used in Li$^+$ ion batteries for enhancing their room temperature ionic conductivity. Although Solid Polymer Electrolytes proved to be a better substitute to liquid one, its limitation of low ionic conductivity deprives its applicability as an efficient electrolyte for Li$^+$ ion batteries.

Considering the importance and need of improving the conductivity of SPE, In the present paper an effort has been made towards studying the polymer electrolyte properties of the inorganic salt LiClO$_4$ and polyvinyl alcohol (PVA). Polyvinyl alcohol (PVA) with 99%+ hydrolyzed is a synthetic biodegradable polymer. In addition, PVA is also known to have O-H groups attached to the CH$_4$ carbons. These O–H groups can be a source of hydrogen bonding for polymer complexes formation. The fast conducting nature in many amorphous and crystalline system and the cost effective aspect of lithium perchlorate (LiClO$_4$) motivated it's use as the doping salt in the present study. The electrical aspect of the polymer electrolyte films reveal that the system may prove a potential material for SPE application in electrochemical.

2. Experimental

2.1. Materials

PVA is used in a wide range of commercial application such as lamination of safety glass, protective coating, binding of pigment and the production of other synthetic polymer. PVA is a hydrophilic, semi-crystalline polymer that has much attraction due to its excellent biocompatibility, nontoxicity. These properties have paved a way to the use of PVA in a wide range of applications such as medical, cosmetic, food pharmaceutical and packaging industries.

Inorganic materials can effectively improve the thermal stability and mechanical properties of PVA, thus broadening the scope of application of PVA. As lithium perchlorate has smaller ionic radius and smaller dissociation energy which is highly soluble in most of the organic solvent. So the lithium perchlorate (LiClO$_4$) is selected as a doping salt for this research. The use of this alkali metal has two distinct characteristics as Li metal show the most electronegative value compared to other metal and it is lightest metal in the world that can reduce the weight of the devices. The small size of Li$^+$ ion can move more freely with high mobility.

2.2. Preparation of polymer electrolyte films

Polymer electrolytes are generally obtained by well known solution casting technique. In the present study, polyvinyl alcohol is taken as host polymer and lithium perchlorate salt in appropriate weight proportion is taken as dopant. Host and dopant are separately dissolved in double distilled water. These solutions are then added together to form a saturated mixture. PVA electrolyte films containing 5, 10, 15 and 20, wt % concentration of LiClO$_4$ are prepared followed by slightly elevated temperature on a magnetic stirrer. The resulting solution was poured in glass petri dishes and evaporated slowly at room temperature for 48 hours to obtain thin membrane of the polymer electrolyte. The SPE thin membrane are carefully separated from the dishes. It is seen that the thickness of the membrane is in the range of 100 to 200µm.
2.3. Measurements
The thin film of solid polymer electrolyte were sandwiched between two Stainless Steel blocking electrode. The AC frequencies were applied in the range between 50hz to 1Mhz across the sample by using 4284 A precision LCR meter (20hz-1Mhz) supplied by Agilent Technology, Singapore. The corresponding ionic conductivity and dielectric constant were measured. The measurements is taken from 323K to 353K.

3. Result and Discussion

3.1. X-ray diffraction (XRD) analysis
XRD analysis is carried out to investigate the crystalline nature of solid polymer electrolyte. In the present study X-ray diffraction analysis of all polymer sample are carried out by using SEIFEET X-ray diffraction meter (cukα radiation ). Figure 1 a shows peak intensity at 2θ=19.84° for pure PVA and for other Samples (PVA + 5%LiClO4) (PVA + 10%LiClO4) (PVA + 20%LiClO4) peak gets decreased with increasing concentration of LiClO4 which implies that the degree of crystallization decrease and increase of amorphous nature. The highest amorphous nature is observed for the sample 80PVA :20LiClO4.

![Figure 1](image.png)

**Figure 1.** The XRD patterns of pure PVA(a) and PVA with various weight ratio of LiClO4 (b) 90PVA:10 LiClO4, (c) 80PVA:20LiClO4.

3.2. AC conductivity
The observed variation of electrical conductivity of PVA polymer electrolytes is illustrated in following Figure(2-4) The AC conductivity of solid polymer electrolytes increases with increase in the frequency and temperature applied in the experiment. The rise of conductivity on increasing the frequency and temperature is a common respond for polymeric and semiconductor materials. It is due to the tremendous increase of the mobility of charge carries in the polymer electrolyte Films figure (2-4) shows frequency dependent AC conductivity of PVA polymer electrolyte at different temperature for the sample without and with doped LiClO4.
3.3. Dielectric properties

Figure (5-7) shows the variations of the dielectric constants with frequency for PVA polymer electrolyte films without and with different content of LiClO$_4$ at different temperature ranging from 323K to 353K.
The dielectric properties are characteristics of a short-range electrical conduction of a material under the action of an applied electric field. When an electric field is applied across the material, the charges are displaced within the material and accumulate at the interrupt creating dipoles. The dielectric constant of all the sample shows almost same trend with frequency. At frequencies higher than 1MHz the dipoles are no longer able to follow the rapidly changing electric field and the dielectric constant for all polymer electrolyte films shows decreasing trend. Figure (5-7) shows that the dielectric constant of polymer electrolyte typically increases with increasing the temperature.
PVA exhibits a semi-crystalline nature which consists of crystalline as well as amorphous phase therefore with increase in temperature, the crystalline phase dissolves progressively into amorphous phase. As the temperature increases it leads to greater molecular mobility which facilities the diffusion of ion in the space charge polarization. Also high temperature will favor the salt dissociation in the polymer matrix. This is due to the thermal energy which can break the chemical bonds in LiClO$_4$ easily to form free ion species so the dielectric constant increases with temperature.

Figure 11 shows the variations of ac conductivity with addition of concentration of lithium salt.
Lithium ions (Li\(^{+}\)) that have enough energy provided by ac current to attach with oxygen atom of polymer chain until all the segment of the polymer are fully occupied. The highest conductivity value is observed for 80PVA:20LiClO\(_4\) is 3.12*10\(^{-2}\) s/cm at frequency 500KHz among all polymer electrolyte films. Here it can be notified that the increase in the lithium salt leads to the increase of the charge carrier and hence the ionic conductivity of the polymer system increases.

4. Conclusion

PVA based lithium ion conducting polymer electrolytes in different molecular weight percentage have been prepared by solution casting technique using double distilled water as solvent. The XRD analysis reveals the increase in amorphous nature of the polymer electrolytes. The disappearance of high intense peak confirm the maximum dissolution of the salt, which gives rise to the ionic conductivity of the polymer electrolyte. The rise of ac conductivity on increasing the frequency and temperature is due to the tremendous increase of the mobility of charge carries in the polymer matrix. As the temperature increases it leads to greater molecular mobility, so dielectric constant values increases. From the conductivity analysis the highest conductivity at frequency 500KHz and temperature 323K has been found to be 3.12*10\(^{-2}\) s/cm for the 80PVA:20LiClO\(_4\).

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