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Transport Studies of Xanthan Gum based Gel Electrolytes containing Ammonium Chloride Salt

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Abstract
This paper reports the synthesis and transport studies of xanthan gum based gel electrolyte containing NH_4Cl salt. Change of ionic conductivity of liquid and gel electrolytes have been studied with different salt concentrations, xanthan gum contents and with the increase of temperature ranging from 10–70°C. The maximum ionic conductivity of gel electrolyte observed is 86 mS/cm at R.T. Room temperature change in conductivity has been observed with the passage of time for gel electrolyte containing NH_4Cl. pH measurements has been carried out to study the acidic/basic behaviour of gel electrolyte.

Keywords
Ionic Conductivity, Gel Electrolyte, pH, Time Span

I. Introduction

Gel is a substance that contains a solid matrix swelled by continuous dispersion of liquid phase. Liquid helps for swelling the matrix and the matrix prevents the liquid from flowing away. Due to this property gel state behave as a semi-solid and it shows liquid like behaviour at high temperature and behave as a rubbery solid at low temperature. Mainly gel electrolytes have high ionic conductivity; make good electrode-electrolyte contacts; good mechanical as well as adhesive properties etc. compared to that of solid electrolytes. Two processes are generally used to obtain gels, one is chemical cross-linking and the other is physical cross-linking. In chemical cross-linking process, numbers of junctions are formed due to the chemical reactions with the polymer chain which possess the covalent bonding. The numbers of junctions formed in this process do not change with change of temperature, stress and other external factors. Others are the physical cross-linking; in which no reaction takes place i.e. solvent, salt and polymer just dissolve with each other and make hybrid mixture.

A large number of gel electrolytes systems have been studied since 1973 and high ionic conductivity has been reported mainly with different lithium salts like lithium tetrafluoroborate ($LiBF_4$), lithium hexafluoro phosphate ($LiPF_6$), lithium trifluoromethane sulfonimide {$LiN(CF_3SO_2)_2$}, lithium perchlorate ($LiClO_4$), lithium trifluoromethane sulfonate ($LiCF_3SO_3$) etc. [1-4]. Hence these gel electrolytes find their applications in high energy density lithium batteries, electrochromic displays, sensors, supercapacitors etc.. In recent years, electronic device technology is developing at a greater pace and there is reduction in the sizes of electrochemical devices also. From three decades a lot of interest has been developed on lithium based gel electrolyte due to small radii of lithium ions; principally act as ionic conductor and also due to their wide applications in different solid state ionic devices. These materials are receiving much attention due to some of their unique properties like high value of ionic conductivity, ease of preparation, wide range of composition and hence wider control of properties, good elastomers and adhesive properties suitable for electrode, good thermal/electrochemical stability etc. [5-8, 19-27].

Alongwith this; number of polymer gel electrolytes containing strong acids like sulphuric acid, phosphoric acid, hydrochloric acid etc. has been studied due to their higher dissociation constant of these acids. So, these acids are fully dissociated in electrolyte and provide large number of H^+ ions for conduction medium. In spite of these, strong acids degrade the polymer used and as a result they are not used for practical applications. Weak acids may prove to be better alternate which provide high ionic conductivity and do not degrade the gel electrolyte as well. Number of weak acids i.e. oxalic acid, malonic acid, succinic acid, benzoic acid, o-, m-, p- nitrobenzoic acid, o-, m-, p- hydroxybenzoic acid etc. have been used in gel electrolytes, which provide H^+ ions upon dissociation due to their higher dissociation constant [9,11,12,15].

Also another category of proton conducting gel electrolytes i.e. natural gums, which are found from the woody elements of plants or in seed coatings e.g. xanthan gum, rosin gum, gum arabica, karya gum, gum tragacanth etc. are polysaccharides of natural origin and capable of causing a large increase in a solution's viscosity, even at small concentrations alongwith self ion conduction in gel electrolyte. In the food industry they are used as thickening agents, gelling agents, emulsifying agents, and stabilizers. In other industries, they are also used as adhesives, binding agents, crystan inhibitors, clarifying agents, encapsulating agents, flocculating agents, swelling agents, foam stabilizers, etc. [10,13,14, 16-18].

In the present research work, electrical conductivity and pH measurements has been made for different xanthan gum based gel electrolytes with varying salt concentration, gum content and temperature.

II. Experimental Details

It involves two steps:-

1. Liquid electrolyte was prepared by dissolving different concentration of salt in solvent at room temperature.
2. Gel electrolyte was prepared by gradually adding gum to the liquid electrolyte. The mixture so obtained was continuously stirred for half an hour at room temperature in order to avoid any inhomogeneity and was kept for 24 hours before investigation.

Conductivity is the direct measurement of the extent of the fast ion transport in electrolyte. The direct measurement of electrical conductivity is given by $\sigma = C(t/A)$ $S.cm^{-1}$

where C is the conductance which is reciprocal of resistance, t is the distance between the electrodes and A is the area of cross-section of the electrode. Conductivity meter (WTW 3210) has been used; which is based upon four probe method and inbuilt temperature sensor; to measure the electrical conductivity of both liquid and gel electrolyte.

pH is a measure of the acidity or basicity of an aqueous solution/ gel electrolyte; with a pH less than 7 is said to be acidic and a pH greater than 7 represent basic or alkaline. Pure water has a pH very close to 7. pH measurements of xanthan gum based gel electrolyte has been done with pH meter (Model: Systronics 361).

III. Results and Discussion

Conductivity variation of liquid electrolyte has been studied with different concentration of NH_4Cl salt having distilled water used as a solvent and the results are shown in fig. 1.

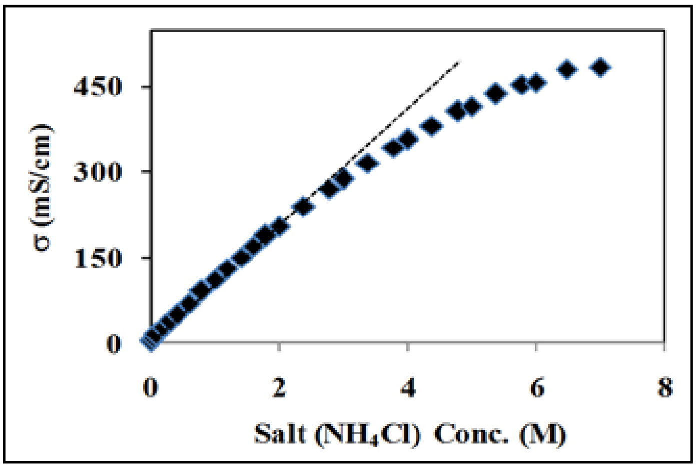

Fig. 1: Conductivity variation of liquid electrolyte with different conc. of NH_4Cl salt at R.T.

From fig. 1, it has been observed that the conductivity of solvent (~ μS/cm) increase by three orders of magnitude with addition of even small amounts of salt and reaches a saturation value at higher salt concentration range. Therefore the conductivity of liquid electrolyte increases linearly upto 3.0 molar NH_4Cl salt. This may be due to the dissociation of salt (NH_4Cl) into ions (NH_4^+, Cl^-, H^+, OH^-, H_3O^+ etc.), which tends to increase the number of charge carriers and hence conductivity value. After that; there is not much increase of conductivity and shows a deviation from linear behavior, which may be due to the formation of ion aggregates as well as increases the viscosity of liquid electrolyte.

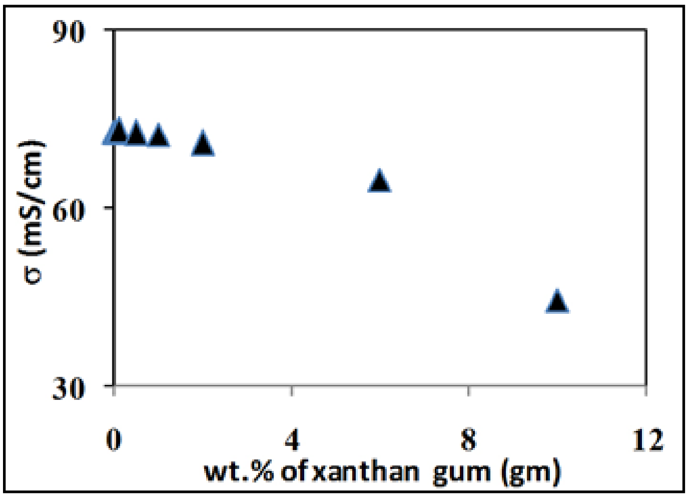

Fig. 2: Room temperature change in conductivity of gel electrolyte containing NH_4Cl (0.625M) salt with different content of xanthan gum.

From fig. 2, it has been observed that the conductivity of gel electrolyte decreases with the addition of the xanthan gum, and is may be due to the increase in viscosity of gel electrolyte. As the viscosity increases; the movement of charge carriers in gel electrolyte decreases and hence conductivity decreases; according to the relations: $\mu = q/6\pi\eta r$, where μ be the mobility of the ions, η be the viscosity and r be the radius of the ion and $\sigma = nq\mu$, where σ represents the ionic conductivity, n is the number of charge carriers and μ be the mobility of ions.

Effect of temperature on the conductivity behavior of gel electrolyte with and without salt has been studied and the results are shown in fig. 3.

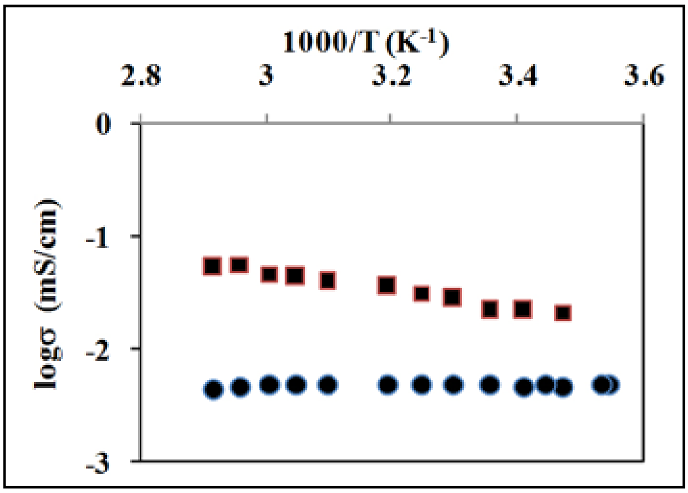

Fig . 3: Log σ vs. 1000/T for gel electrolyte with salt {distilled water +0.625M NH_4Cl +5wt% xanthan gum} (■) and gel electrolyte without salt {distilled water + 5wt.% xanthan gum} (•).

From fig. 3, it has been observed that the conductivity of xanthan gum based gel electrolyte with and without salt increases linearly with increase of temperature (range: 10-70°C). But however, this increase in conductivity with increase of temperature is in factor-wise only, which make these gel electrolytes suitable for device applications particularly for fuel cell. It has also been observed that the conductivity of gel electrolyte with salt is higher than that of gel electrolyte without salt at all temperature regions, which may be explained to be due to more number of charge carriers {due to dissociation of salt (NH_4Cl) into ions (i.e. NH_4^+ and Cl^-)} present in gel electrolyte compared to gel electrolyte without salt.

Ionic conductivity of xanthan gum based gel electrolyte containing 0.625M NH_4Cl has been studied at different time span and the results are shown in fig. 4.

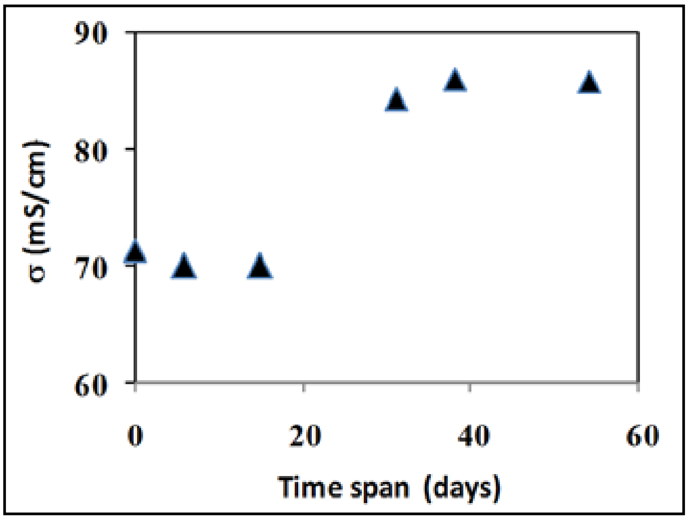

Fig. 4: Conductivity variation of 5wt.% xanthan gum based gel electrolyte containing 0.625M NH_4Cl with the passage of time

From fig. 4, it has been observed that the conductivity of gel electrolyte increases continuously with the passage of time (upto one month). This can be explained on the basis of the interactions, continuous movements of ions as well as contraction and expansion of xanthan gum in gel electrolyte with the passage of time [Chandra et al 2000]; hence leads to increase the mobility of neighboring ions and hence conductivity value [15]. After one month; conductivity of gel electrolyte gets saturated and the maximum conductivity i.e. 86 mS/cm has been observed.

pH measurements of gel electrolyte containing NH_4Cl salt has been studied at different time spans and the observed values are shown in fig. 5.

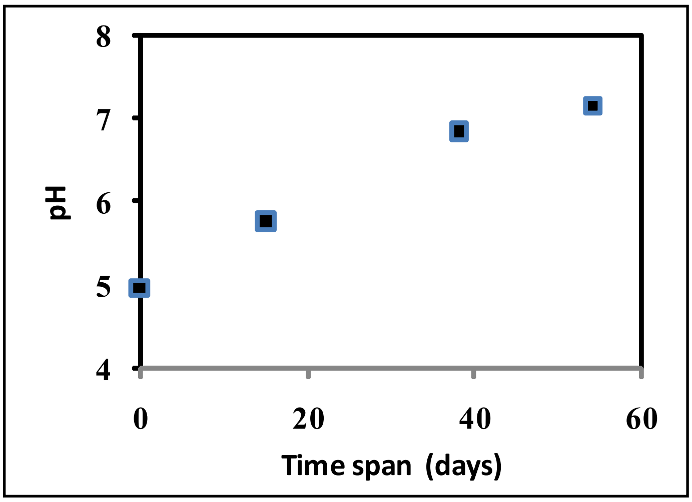

Fig. 5: Room temperature pH variation of 5wt.% xanthan gum based gel electrolyte containing 0.625M NH_4Cl with the passage of time

From fig. 5, it has been observed that pH of xanthan gum based gel electrolyte containing NH_4Cl salt increases with the passage of time and shows it's acidic to neutral behaviour, which may be explained to be due to the stabilization of gel electrolyte in terms of restrict the movement and interactions of charge carriers (i.e. H^+, Cl^-, NH_4^+, OH^-, H_3O^+ etc.) and/with long chain polysacharide with the passage of time at room temperature.

pH values of distilled water, xanthan gum based gel electrolyte without salt and xanthan gum based gel electrolyte containing 0.625M NH_4Cl has been found to be 6.9, 5.98 and 4.98 respectively at room temperature.

IV. Conclusion

Conductivity of gel electrolyte containing 0.6251M NH_4Cl salt decreases with an increase in content of xanthan gum and maximum conductivity observed is 73.1 mS/cm at 0.1 wt% of xanthan gum. With increase of temperature; ionic conductivity of liquid and gel electrolyte shows similar behavior and σ (gel electrolyte with salt) > σ (gel electrolyte without salt) at all temperature studied regions. No major change in conductivity of gel electrolyte in the studied temperature range (10-70°C) has been observed; which makes these gel electrolytes suitable for fuel cell application particularly. After 30 days, gel electrolyte gets stabilized and the maximum ionic conductivity observed is 86 mS/cm. Acidic nature (pH = 4.98) of gel electrolyte was confirmed from its pH measurements (without the passage of time).

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