Effect of the reduction of silver ions to silver nanoparticles on the dielectric properties of chitosan-silver triflate electrolyte

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Abstract— Films of solid polymer electrolyte based on chitosan and silver triflate (AgCF3SO3) have been prepared by casting technique. As a confirmation, the UV-vis results show the temperature dependence of silver nanoparticles. The dielectric constant increases with increasing salt concentration. The dielectric constant and dielectric loss curves show the higher values in the low frequency region and they are almost constant at higher frequencies. The dielectric constant and dielectric loss values are decreased above 358 K, as a result of transformation from silver ion to silver nanoparticles. The loss tangent peaks are broad and their heights decrease above 358 K. The broadness of loss tangent peaks indicates the distribution of relaxation time.

Keywords-component; silver polymer electrolyte; UV-vis analysis; dielectric constant; dielectric loss; loss tangent.

I. INTRODUCTION

Recently ionically conductive solid polymers have received considerable attention in view of their technological importance in a wide variety of energy storage/conversion devices such as batteries, supercapacitors and fuel cells [1]. The mixing of polar polymers with inorganic salts is known as polymer electrolyte. Polymer electrolytes are formed when metal salts are dissolved in a polymer matrix and consequently dissociated into metal cations and corresponding counter anions. The dissolution of metal salt in a polymer matrix occurs due to the coordinative interaction between metal ions and polymer ligands [2].

The electric properties of polymers can be describe through the using of the frequency and temperature dependence of the dielectric constant (real part of complex permittivity, $\varepsilon' \rangle$ and dielectric loss (imaginary part of complex permittivity, $\varepsilon''$) [3].

Chitosan, a natural macromolecule with unique biocompatibility and adsorption property, is widely used in medical, agricultural and biological fields [4]. Chitosan is derived from chitin by deacetylation in the presence of alkali [5]. A monomer of chitosan consists of hydroxyl and amine functional groups which have lone pair electrons that are suitable for the preparation of solid polymer electrolytes [6].

Polymers such as poly (2-ethyl-2-oxazoline) (POZ), poly (ethylene oxide) (PEO) and poly (vinyl pyrrolidone) (PVP) containing polar groups in their chains have been used as a polymer solvent to dissolve the silver salts with low lattice energy such as AgBF4, AgClO4, AgCF3SO3 and AgSbF6 for facilitated olefin transport membranes [7]. The oxygen and nitrogen atoms of polar polymers play an essential role in facilitated olefin transport. However, they are also reduced silver ions and creating silver metal nanoparticles [8]. This is because silver ions are easily reduced by the lone pair electrons of the nitrogen and oxygen atoms [9].

Dielectric analysis is one of the methods to characterize materials and provides the information as well as understanding about the motion of entities having an electric charge or an electric dipole moment, which is about dipole reorientation, rotations of the main and segmental chains and conductivity mechanisms [10]. In general, dielectric properties in polymers are due to electronic, ionic, molecular and interfacial polarization [11].

To the best of our knowledge, there are no reports in the literature about dielectric properties of polymer electrolyte based on chitosan-silver triflate polymer electrolyte. Each of the nitrogen and oxygen atoms of the functional groups in chitosan has lone pair electrons where complexation can occur. The main goal of the present paper is to study the reduction effect of silver ion (Ag+) to silver nanoparticle (Ag0) on the dielectric properties of chitosan-silver triflate polymer electrolyte over a wide range of frequencies from 50 Hz to 1 MHz and over a temperature range from 303 K to 413 K.

II. EXPERIMENTAL TECHNIQUE

A. Sample Preparation

Films of chitosan based polymer electrolyte were prepared, by solution cast technique. Chitosan from crab shells (≥75% deacetylated, Sigma Aldrich) and silver triflate
with a molecular weight 256.94 (supplied by Fluka, ≥98 purity) have been used as the raw materials in this study. 1 g of chitosan was dissolved in 100 ml of 1% acetic acid solution. The mixture was stirred continuously with magnetic stirrer for several hours at room temperature until the chitosan powder has completely dissolved in acetic acid solution. To these set of solutions 2 wt. % to 10 wt. % silver triflate were added separately and the mixtures were stirred continuously until homogeneous solutions were obtained. The solutions were then cast into different clean and dry plastic Petri dish and left to dry at room temperature in order to allow complete evaporation of solvent for obtaining solvent-free films of the polymer host and polymer salt complexes respectively. The films were kept in desiccators with silica gel desiccant for further drying. This procedure yields mechanically stable and solvent-free films. The composition of the prepared samples were designated as follows, SPE for 0 wt. % of AgCF3SO3 i.e. pure chitosan acetate (CA), SPE1 for 98 wt.% CA+2 wt.% AgCF3SO3, SPE2 for 96 wt.% CA+4 wt.% AgCF3SO3, SPE3 for 94 wt.% CA+6 wt.% AgCF3SO3, SPE4 for 92 wt.% CA+8 wt.% AgCF3SO3 and SPE5 for 90 wt.% CA+10 wt.% AgCF3SO3. The impedance of the films was measured using the HIOKI 3522-01 LCR Hi-tester that was interfaced to a computer in the frequency range from 50 Hz to 1000 kHz. The software controlling the measurement calculates the real and imaginary impedances, too.

B. Complex Impedance Spectroscopy

The complex impedance spectroscopy is used to characterize the electrical properties of the materials. The SPE films were cut into small discs of 2 cm diameter and sandwiched between two stainless steel electrodes under spring pressure. The complex impedance parameters (that is \( Z' \) and \( Z'' \) where \( Z' \) and \( Z'' \) represent the real and imaginary parts of impedance respectively) were used to obtain the dielectric parameters such as dielectric constant (\( \varepsilon' \)), dielectric loss (\( \varepsilon'' \)) and loss tangent (\( \tan \delta \)). The dielectric parameters were calculated using the following relations;

\[
\varepsilon' = \frac{Z'}{oC_0(Z'^2 + Z''^2)}
\]

\[
\varepsilon'' = \frac{Z''}{oC_0(Z'^2 + Z''^2)}
\]

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]

Here \( C_0 \) is vacuum capacitance of the cell and is equal to \( \varepsilon_0 A/d \), where \( \varepsilon_0 \) is permittivity of free space, \( A \) and \( d \) are the area and the thickness of the sample respectively and \( o = 2\pi f \), were \( f \) is frequency.

C. UV-vis measurement

The UV-vis spectra of the polymer electrolyte film which contains silver nanoparticles have been recorded using Jasco V-570 UV-Vis-NIR spectrophotometer in the absorbance mode and in the wave length range 200 nm - 1800 nm.

III. RESULTS AND DISCUSSIONS

A. UV-vis Analysis

To investigate the formation of Ag nanoparticles from Ag ions in the chitosan-silver triflate system, UV vis spectroscopy was used as a common characterizing method. UV vis absorption spectra are known to be quite sensitive to the formation of silver nanoparticles [12, 13]. Figure 1 compares the absorption spectra for SPE5, before and after electrochemical impedance spectroscopy (EIS) treatment.

Before EIS treatment we measured the UV-vis spectra for the sample and we obtained a broad absorption peak whose maximum occurs at around 432 nm which is attributed to the Plasmon excitation of silver nanoparticles. It is generally accepted that the absorption peak whose maximum occurs at around 420 nm to 520 nm is related to the formation of silver metal nanoparticles and its height gives information on the concentration of silver metal particles [14-17]. After EIS treatment a sharp peak whose maximum 420 nm was obtained. The height of the peak also increases from 0.69 to 2.316, with increasing temperature implying that an increase amount of Ag nanoparticles due to the reduction of silver ions to silver nanoparticles occurs more rapidly at a high temperature [18]. Reference [12] also reported the increase of silver nanoparticles with increasing temperature for PVP/AgBF4. The UV-vis results strongly indicate the formation of silver metal nanoparticles and it is temperature dependent. To our knowledge UV-vis characterization of chitosan-AgCF3SO3 system was not reported in the literature. The formation of silver nanoparticles in the present system is also indicated by the change in the colour of the membranes to dark brown. This phenomenon is also observed by [19], for PVP -silver salt electrolyte.

B. Dielectric properties

1) Composition dependence of dielectric constant

Figure 2 shows the variation of dielectric constant as a function of salt concentration at 303 K. From the figure it's clear that, \( \varepsilon' \) increases with increasing salt concentration initially and decrease from 0.06 wt.% to 0.08 wt.% which can be attributed to ion association, finally \( \varepsilon' \) increases rapidly at 10 wt.% percentage. This is due to the increase of stored charge ions in the sample which are responsible for the dielectric polarization and electrical conduction mechanism.

2) Frequency and temperature dependence of \( \varepsilon' \) and \( \varepsilon'' \).
Figure 3a and b shows the frequency dependence of dielectric constant and dielectric loss respectively, at different temperatures for SPE5. From these figures, it is seen that both dielectric constant and dielectric loss decreases by increasing frequency while they are increases by increasing temperature until 358 K. At all temperatures, a high values of $\varepsilon'$ and $\varepsilon''$ were observed in the low frequency and high temperatures, but these are relatively constant at high frequencies. The high value of $\varepsilon'$ can be ascribed to the accumulation of charge species at the electrode-electrolyte interface [12]. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decreases, leading to the decrease in the value of $\varepsilon'$ [13]. The large value of $\varepsilon''$ is also due to the motion of free charge carrier within the material. As a result of it, power law dispersion in $\varepsilon''$ is observed and it does not reveal any peak in the measured frequency range. This suggests that ionic motion and polymer segmental motion are strongly coupled [14]. It can be observed that both dielectric constant and dielectric loss are decreases above 358 K, which can be attributed to the reduction of silver ions to silver nanoparticles at these higher temperatures. The reduction effect of silver ions to silver nanoparticles on dielectric properties could be more manifested in the case of studying of dielectric constant and dielectric loss as a function of temperature at a fixed frequency.

The temperature dependence of dielectric constant and dielectric loss are shown in Figure 4a and b respectively at different frequencies for SPE5. It is clear that both dielectric constant and dielectric loss are increase with increasing of temperature until 358 K for small frequency values, which can be explained by the increase in the mobility of polar groups and charge carrier motions within the sample and decrease in density which facilitates the orientation of mobile groups. The constant value of dielectric constant and dielectric loss at higher frequencies as a function of temperature can be ascribed to the high periodic reversal of the electric field at higher frequencies. It is clearly observed that both dielectric constant and dielectric loss are decreased above 358 K. This is due to the reduction of a large amount of silver ions to silver nanoparticles at these elevated temperatures. These silver nanoparticles are able to increase the resistance within the sample and hinder the ionic motions. The complex impendence plots for SPE5 sample at 358 K and 368 K which are shown in Figure 5, are strongly support the above interpretation for the decrease of dielectric constant and dielectric loss. The appearance of second semicircle can be attributed to silver nanoparticles that act as grain boundaries in the present system. As can be seen from Figure 5 at 368 K the bulk resistance increases (more than 0.2 k.Ohm) with respect to 358 K (less than 0.02 k.Ohm) which is due to the formation of a large amount of silver nanoparticles. This indicates that with increasing temperature more silver ions converted to silver metal nanoparticles especially after 358 K. Thus, transformation from silver ions to silver nanoparticles (Ag+) reduce the number of silver ions that contribute to polarization as well as conduction mechanisms and consequently decrease both the dielectric constant and dielectric loss. To our knowledge, this is the first report which discusses the effect of reduction of silver ions to silver nanoparticles on the dielectric properties of polymer electrolyte based on chitosan-AgCF3SO3. The results are strongly supported by UV-vis and impedance analysis.

3) Frequency and temperature dependence of $\tan\delta$

Figure 6 represents the loss tangent variation with frequency at different temperatures for SPE5. It is clear from the figure that the loss tangent maximum shifts to higher frequency as the temperature increases. In polymer electrolytes with appreciable electrical conductivity, dielectric relaxation peaks due to permanent or induced dipoles may be masked by the relaxation from polarization of mobile charged species present in the material [23]. The loss tangent shape can be interpreted on the basis of Koops phenomenological model. According to Koops model [24] the negative slope of the low frequency dispersion curve suggested conduction dominated loss at low frequency through a parallel RC circuit on assuming the system to be homogeneous. Subsequently, loss tangent increases with further rise in frequency, and shows a maximum at particular frequencies for different temperature because the active component (ohmic) of the current increases more rapidly than its reactive component (capacitive). At higher frequencies loss tangent decreases with increasing of frequency because the active component of the current is practically independent of frequency and the reactive component increases in proportion to the frequency. The broadness of the loss tangent peaks indicates that more than one relaxation process is present that is non-Debye type relaxation. The increase in height of loss tangent with temperature could be attributed to the decrease in resistivity of the sample [25]. The decrease of loss tangent height at 368 K, due to the large amount reduction of silver ions to silver nanoparticles which increase the resistivity of the sample. The increase and decrease of loss tangent height with temperature indicate a strong coupling between the polymer segmental relaxation and the ion transport in the sample.

The temperature dependence of loss tangent at different frequencies is shown in figure 7. It can be observed that the loss peaks are shifted to higher temperature with increasing of frequency. The loss peaks can not be recognized as $\beta$ or $\alpha$-relaxation peaks, because these peaks are occurred in chitosan at about -21°C and 205°C respectively [26, 27]. Rather, they can be recognized as a structural reorganization of packing of chitosan molecules due to the increase of residual water mobility, volume expansion and following change of hydrogen bond strength [26].

IV. CONCLUSIONS

The UV-vis spectra’s shows that the silver nanoparticles are increased with increasing temperature. The increase of dielectric constant with increasing salt concentration due to the increase of charge carrier concentration which are responsible for polarization. The higher values of dielectric constant and dielectric loss at lower frequencies can be ascribed to electrode polarization. The reductions of silver ions to silver nanoparticles in a large amount at higher
temperatures are responsible for the decrease of dielectric constant and dielectric loss. The appearance of second semicircle can be attributed to grain boundaries in the form of silver nanoparticles. The height of the loss tangent peak decrease at higher temperatures which can be attributed to increase of resistivity of the sample as a result of the large formation of silver nanoparticles. The loss tangent peaks at different frequencies shifted to higher temperatures.

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Figure 1 UV-vis spectra of chitosan-AgCF$_3$SO$_3$ before and after EIS for SPE$_5$.

Figure 2 Salt concentration dependence of dielectric constant at 303 K.

Figure 3 Frequency dependence of (a) dielectric constant and (b) dielectric loss at different temperatures for SPE$_5$.

Figure 4 Temperature dependence of (a) dielectric constant and (b) dielectric loss at different frequencies for SPE$_5$. 

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Figure 5 Complex impedance plots of SPE$_5$ at different temperatures.

Figure 6 Frequency dependence of loss tangent at different frequencies for SPE$_5$.

Figure 7 Temperature dependence of loss tangent at different temperatures for SPE$_5$. 

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