EFFECT OF HNO$_3$ TREATED TiO$_2$ ON STRUCTURAL AND ELECTRICAL PROPERTIES OF HEXANOYL CHITOSAN/POLYSTYRENE-LICF$_3$SO$_3$-TiO$_2$ COMPOSITE POLYMER ELECTROLYTES

N. H. A. Rosli$^{1,*}$, S. A. M. Noor$^1$, K. A. Ahmad$^2$ and T. Winie$^3$

$^1$Centre for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia, 57000 Kuala Lumpur, Malaysia
$^2$Department of Electrical and Electronic Engineering, Faculty of Engineering, Universiti Pertahanan Nasional Malaysia, 57000 Kuala Lumpur, Malaysia
$^3$Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

Published online: 10 September 2017

ABSTRACT

In searching for solutions to reduce battery weight for military applications, films of composite polymer electrolytes comprised of hexanoyl chitosan/polystyrene containing lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) and titanium oxide were prepared using solution casting technique. Two types of TiO$_2$ filler were used, which are untreated TiO$_2$ and HNO$_3$-treated TiO$_2$. The effect of untreated and HNO$_3$-treated TiO$_2$ on the structural and electrical behavior of the prepared electrolyte systems has been investigated by using X-ray diffraction and impedance spectroscopy, respectively. The ac conductivity was calculated using $\sigma(\omega) = \sigma_{dc} + A\omega^s$ formula in the temperature range from 283 K to 353 K. The conduction mechanism of the H-chitosan/PS-LiCF$_3$SO$_3$-TiO$_2$ and H-chitosan/PS-LiCF$_3$SO$_3$-HNO$_3$-treated TiO$_2$ can be interpreted based on the correlated barrier hoping model at 4 and 6 wt.% of TiO$_2$ respectively.

Keywords: hexanoyl chitosan; polystyrene; composite polymer electrolytes.

Author Correspondence, e-mail: n.hazwani@upnm.edu.my
doi: http://dx.doi.org/10.4314/jfas.v9i3s.12
1. INTRODUCTION

While able to benefit from technology, the army is facing a number of challenges in their operations today and in the future. One of the major challenges is in the power sources arena. Today’s soldier carries a wide array of electronic devices such as computers, communications equipment, weapon system and all requiring portable power. The army is aware of the situation and has identified problem areas of battery weight, space and power source carried by the soldier [1]. One area identified to further study is the electrolyte for battery system using polymer electrolyte. Polymer electrolyte offers reduction in size, weight and thermal management properties in line with the requirement of future military systems. With better process efficiency, the batteries can be designed to be lighter in weight hence reducing the operational physical load of soldiers which may contributes to longer endurance and reduce fatigue during operations.

Polymer electrolytes are of immense interest due to their applicability in energy conversion and storage devices. They present significant advantages over liquid electrolytes such as safer design, simpler stacking and hermetic sealing processes, superior in density, flame-resistance and shape suitability in the requirements of the application [2-3]. In order to achieve high performance, a battery electrolyte must possess high ionic conductivity, be stable at both the high potential of the battery cathode and the low potential of the battery anode. Various approaches to enhance the ionic conductivity of polymer electrolytes have been suggested in the literature such as by addition of plasticizer, filler and blending polymer [4-5]. The recent technique developed for solid polymer electrolyte is the dispersion of nano-size inorganic ceramic filler particles such as Al₂O₃, SiO₂, TiO₂, SnO₂, ZnO and ZrO into the polymer electrolytes system called composite polymer electrolytes (CPE). It has been shown that the addition of fillers to semicrystalline PEO-alkali metal salt complexes leads to the decrease in the crystallinity of the electrolyte and enhancement in ionic conductivity [6]. Also, the uses of fillers improve mechanical stability of the polymer electrolytes. Changes in the ionic conductivity of CPEs result from the Lewis acid-base interactions between the fillers and the polymer electrolytes components.

From ac conductivity, further information on ionic conduction model can be determined to get
more insight on ion conduction mechanism. Various models reported such as small polaron tunneling model (SPT) overlapping large polaron tunneling model (OLPT), correlated barrier hopping model (CBH) and quantum mechanical tunneling model (QMT) have been reported to discuss the ac conduction mechanism in amorphous materials such as semiconductors and glasses [7]. However, there are limited researches available regarding the use of such models to explain the ionic conduction mechanism in polymeric materials.

In order to obtain a balance for the compatibility of filler and polymer electrolytes, several investigations have been carried out such as synthesis of new polymer matrix, preparation of polymer single-ion conductor and doping with filler. Thus, in this research we prepared blended based polymer of hexanoyl chitosan and polystyrene doped with LiCF$_3$SO$_3$. Two types of TiO$_2$ filler were used, which are untreated TiO$_2$ and HNO$_3$-treated TiO$_2$. The effect of untreated and HNO$_3$-treated TiO$_2$ will be investigated on their ionic conductivity, crystalline fraction, dielectric constant and ionic conduction model.

2. RESULTS AND DISCUSSION

A structural study of solid polymer electrolyte was investigated by XRD. XRD analysis was performed to determine the degree of crystallinity and to observe the glassy nature of the H-chitosan/PS polymer electrolyte.

The degree of crystallinity in the prepared samples were estimated from the ratio of integrated intensity of the peak at $2\theta \approx 6.86^\circ$to the total integrated of the spectrum, using the Equation (1)

$$X_c = \frac{I_c}{I_T}$$

where $X_c$ is the degree of crystallinity, $I_c$ is the $2\theta \approx 6.86^\circ$peak intensity and $I_T$ is the total integrated intensity.

Fig. 1 shows the variation in the degree of crystallinity as a function of untreated and treated TiO$_2$ concentration. The crystallinity degree was estimated from the peak at $2\theta \approx 6.86^\circ$ using the same method as discussed previously [9]. It can be observed that for both the untreated and treated TiO$_2$-added electrolyte system, the degree of crystallinity decreases with addition of TiO$_2$ up to 6 wt.% which is from 19.62% to 13.52 and 14.43% respectively. The reduction
of crystallinity will produce more amorphous phase in the system. The amorphous phase makes the electrolyte more flexible, resulting in increase of the segmental motion of the polymer [10]. At 8%, the crystallinity of H-chitosan/PS increases drastically to 22.34%. This indicates that 6 wt.% of TiO₂ is the optimum amount and beyond this weight percentage, the presence of TiO₂ leads to recrystallization of H-chitosan/PS. This observation will be supported with ionic conductivity as discussed below.

**Fig.1.** The variation in crystalline fraction for composite electrolyte system as a function of (a) untreated TiO₂ and (b) HNO₃-treated TiO₂ concentration

The variation of room temperature conductivity as a function of untreated and treated TiO₂ concentration is depicted in Fig. 2. The ionic conductivity of H-chitosan/PS electrolytes without TiO₂ filler was $7.21 \times 10^{-5}$ S cm⁻¹. With addition of 2 wt.% TiO₂, the ionic conductivity of both the untreated and treated TiO₂ systems decreases to around $7.00 \times 10^{-6}$ and $5.86 \times 10^{-6}$ S cm⁻¹. Small amount of filler was not able to overcome the rate of ion association of LiCF₃SO₃. The conductivity increases with further increase in filler content, reaches a maximum and thereafter decreases with increasing filler content beyond the optimum concentration. The maximum conductivity achieved was $2.27 \times 10^{-4}$ S cm⁻¹ at 4 wt.% for untreated TiO₂ and $1.47 \times 10^{-4}$ S cm⁻¹ at 6 wt.% for HNO₃-treated TiO₂. We found that untreated TiO₂ able to improve the conductivity up to twice while treated TiO₂ only half compared to without filler. The conductivity enhancement is due to presence of oxygen sites as conduction pathways from TiO₂, hence help to increase in the number of mobile Li⁺ cation. However, HNO₃-treated TiO₂ systems produce lower ionic conductivity compared to untreated TiO₂ systems because treated TiO₂ have more acidic sites that help to increase the
degree of ion association. Treated TiO$_2$ decreased the conductivity by decreasing the anionic contribution due to the HNO$_3$-treated TiO$_2$ grain surface consists of solely OH group and it shown that anion of salt has larger affinity towards filler surface acid site than cation as reported in our previous work [11]. At 10 wt.% TiO$_2$, the ionic conductivity decreases significantly even below the unfilled electrolytes. This behavior is due to the recrystallization of polymer host as observed in XRD analysis. The conductivity variations observed also could be attributed to the variation in the number of free ions in the samples. This is reflected in the dielectric constant, $\varepsilon_r$ versus frequency curves as illustrated in Fig. 4.

![Fig. 2. Ionic conductivity of H-chitosan/PS-LiCF$_3$SO$_3$ polymer electrolytes as a function of TiO$_2$ concentration at room temperature (a) untreated TiO$_2$ and (b) HNO$_3$-treated TiO$_2$.](image)

Fig. 2. Ionic conductivity of H-chitosan/PS-LiCF$_3$SO$_3$ polymer electrolytes as a function of TiO$_2$ concentration at room temperature (a) untreated TiO$_2$ and (b) HNO$_3$-treated TiO$_2$. 

Fig. 3 represents the plot of ionic conductivity ($\log \sigma$) versus the inverse absolute temperature for untreated and HNO$_3$-treated TiO$_2$ electrolyte system respectively. The measurement was carried out from 283 K to 383 K. Within the temperature range investigated, the variations of $\log \sigma$ with $1/T$ are linear with $R^2 = 0.953$ and 0.985 for untreated TiO$_2$ and HNO$_3$-treated TiO$_2$. This indicates that the conductivities of the studied electrolyte systems are thermally activated which indicating that this system obeyed the Arrhenius rule [12]. Therefore, as temperature was increased, the number of free lithium ions was also increased. Hence, it increases the conductivity of the electrolytes [13]. The graph shows that conductivity 4 wt.% untreated TiO$_2$ is higher than 6 wt.% HNO$_3$-treated TiO$_2$. Activation energy, $E_a$ for ionic conduction were obtained from the slope of the plots in Fig. 3 and $E_a$ for 4 wt.% untreated TiO$_2$ and 6 wt.% HNO$_3$-treated TiO$_2$ was 0.048 and 0.096 eV. $E_a$ is the energy required for an ion to begin
migration from one donor site to another. This ion migration results in conduction. It can be observed that high conducting sample exhibits low value of $E_a$. This indicates that ions in high conducting sample require lower energy to begin migration.

![Fig.3](image-url) Temperature dependence of conductivity for H-chitosan/PS-LiCF$_3$SO$_3$ with a) 4 wt.% untreated TiO$_2$ and b) 6 wt.% HNO$_3$-treated TiO$_2$

The dielectric constant represents the stored charge in a material. Since charge is carried by ions, therefore it can be deduced that the increase in dielectric constant reflects the increase in the number of ions [14]. Fig. 4 shown frequency dependence of dielectric constant, $\varepsilon_r$ for H-chitosan/PS-LiCF$_3$SO$_3$ with untreated TiO$_2$ and HNO$_3$-treated TiO$_2$. The untreated TiO$_2$ system has higher dielectric constant value than HNO$_3$-treated TiO$_2$ system. This suggests that the untreated TiO$_2$ system has higher number of free ions compared with HNO$_3$-treated TiO$_2$ system and leading to higher conductivity. The calculated number of mole of H$^+$ for untreated and HNO$_3$-treated TiO$_2$ are $6.11 \times 10^{-5}$ and $7.40 \times 10^{-4}$ mol/g respectively. The acidic H$^+$ site acts as anion trapper [15]. The treated TiO$_2$ possesses more H$^+$ anion trapper on its surfaces compared to untreated TiO$_2$. The reduce number of free anions in the system contribute to the decrease in the total conductivity. This explains why the conductivity achieved for the HNO$_3$-treated TiO$_2$-added system is lower than the untreated TiO$_2$-added system.
Fig. 4. Frequency dependence of dielectric constant, $\varepsilon_r$ for H-chitosan/PS-LiCF$_3$SO$_3$ with a) untreated TiO$_2$ and b) HNO$_3$-treated TiO$_2$

The ac conductivity can be obtained from the dielectric constant, $\varepsilon_r$ and loss tangent, $\tan \delta$ according to the Equation (2)

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta$$

where $\varepsilon_0 = 8.85 \times 10^{-14}$ F cm$^{-1}$. In general, the phenomena of the conductivity-frequency dispersion are analyzed using the Jonscher’s universal power law as stated in Equation (3)

$$\sigma(\omega) = \sigma_{dc} + A\omega^s$$

where the dc conductivity, $\sigma_{dc}$ is the frequency-independent component, $A$ is a parameter dependent on temperature and $s$ is the power law exponent with values in the range $0 < s < 1.0$. $\sigma(\omega)$ is generally believed to reflect the mechanism of charge transport among charge carriers. The Jonscher universality is not limited to analyze the AC conductivity in glass but has been extended to study the ac conductivity of polymer electrolytes [16]. In order to understand the conduction mechanism, different models have been proposed to explain the
AC conductivity [17]. These models are quantum mechanical tunneling (QMT), the correlated barrier hopping (CBH) and overlapping large polaron tunneling (OLPT) [18-19]. In the QMT model, the $s$ is independent of temperature. In the CBH model, $s$ decreases with increasing temperature. While, for the OLPT model, $s$ decreases to a minimum value and increases again as temperature increases. Fig. 5 and 6 depict the plot of log [$\sigma(\omega) - \sigma_{dc}$] versus log $\omega$ at various temperatures for untreated TiO$_2$ and HNO$_3$-treated TiO$_2$. Values of exponent $s$ can be evaluated from the slope of each plots.

![Figure 5](image_url)

**Fig. 5.** Plot of log [$\sigma(\omega) - \sigma_{dc}$] versus log $\omega$ for a) 4 wt.% and b) 6 wt.% HNO$_3$-treated TiO$_2$ at different temperatures.

Fig. 6 shows the variation of exponent $s$ with temperature for both treated and untreated sample containing 4 and 6 wt.% TiO$_2$. It can be observed that the power law exponent $s$ for 4 wt.% and 6 wt.% untreated TiO$_2$ and HNO$_3$-treated TiO$_2$ decreases continuously with increasing temperature. Thus, the conduction mechanism for both electrolytes the systems can be interpreted as the correlated barrier hopping (CBH) model which means that the ions hop over a barrier between two complexation sites. According to [20], conduction mechanism for
electrolytes chitosan doped silver triflate (AgCF$_3$SO$_3$) also follows the CBH model below 358 K.

![Graph](image)

Fig. 6. Variation of exponent s with temperature for a) untreated TiO$_2$ and b) HNO$_3$-treated TiO$_2$

3. EXPERIMENTAL

H-chitosan prepared by acyl modification technique and used tetrahydrofuran (THF) as the media. Details of H-chitosan preparation were described in this paper [8]. LiCF$_3$SO$_3$ from Acros Organics were dried at 100°C for 24 hours prior to use. TiO$_2$ powder with particle size of 30-40 nm obtained from Nanostructured and Amorphous Material Inc. were used as the inorganic filler. TiO$_2$ was acid-treated by stirring in diluted HNO$_3$ solution (0.83 v/v %) for 8 hours at 80°C, rinsed with de-ionized water until the filtrates were neutralized and then dried for 12 hours at 100°C.

Films of H-chitosan/PS blend were prepared by solution casting technique. The two polymers
were first dissolved separately in an appropriate amount of THF. Then, the required amounts of LiCF$_3$SO$_3$ and TiO$_2$ were added. The resulting mixture was then stirred at room temperature until complete dissolution and homogenous. The solution obtained were cast in glass petri dishes and allowed to completely evaporate slowly at room temperature to form films. The films were kept in a desiccator for continuous drying.

In order to investigate the structure of polymer electrolyte films, XRD scans was taken using X-Pert PRO XRD which employs Cu-Kα X-radiation of wavelength $\lambda = 1.5418$ Å between a 2θ angle of 5° to 80°. The impedance measurement of the films was carried out using HIOKI 3532-50 LCR Hi Tester in the frequency range of 100 Hz to 1 MHz and in the range of temperature from 283 to 333 K. The prepared electrolyte film was sandwiched between two stainless steel electrodes with diameter 2.5 cm under spring pressure. The ionic conductivity, $\sigma$ of the sample was calculated using Equation (1).

$$\sigma = \frac{t}{R_b A}$$  (4)

where $t$ is the sample thickness, $A$ is the effective contact area and $R_b$ is the bulk resistance which can be obtained from the complex impedance plot.

4. CONCLUSION

The effect of treated and untreated TiO$_2$ on the structural and electrical properties of CPE H-chitosan/PS-LiCF$_3$SO$_3$. XRD results revealed the crystallinity of the H-chitosan/PS decreased as both types of TiO$_2$ added in the CPE up to maximum amount, which are 4 % for treated TiO$_2$ and 6 wt.% of treated TiO$_2$. Beyond this composition of TiO$_2$, the crystallinity of H-chitosan/PS increased significantly. The variation in conductivity followed the trend of crystallinity fraction, which optimum ionic conductivity can be observed at 4 wt. % for treated TiO$_2$ and 6 wt.% of treated TiO$_2$ systems. The difference in conductivity with varying TiO$_2$ content also be understood on the basis of free ion concentration as reflected in the variation in dielectric constant. The ac conductivity for H-chitosan/PS-LiCF$_3$SO$_3$-TiO$_2$ and H-chitosan/PS-LiCF$_3$SO$_3$-HNO$_3$-treated TiO$_2$ electrolyte systems follows the Jonscher’s universal power law. From this law, we concluded that the conduction mechanism for these CPE systems can be interpreted based on the CBH model.
5. ACKNOWLEDGEMENTS
The authors wish to thank the Centre for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia and University Teknologi MARA for supporting this work.

6. REFERENCES


**How to cite this article:**
Rosli NHA, Noor SAM, Ahmad KA, Winie T. Effect of hno\textsubscript{3} treated tio\textsubscript{2} on structural and electrical properties of hexanoyl chitosan/polystyrene-lif\textsubscript{3}so\textsubscript{3}-tio\textsubscript{2} composite polymer electrolytes. J. Fundam. Appl. Sci., 2017, 9(3S), 141-153.