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Ion-transport study in nanocomposite solid polymer electrolytes based on chitosan: Electrical and dielectric analysis

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ABSTRACT: In this study, (1.1111-x)(0.9CS-0.1NaTf)— $x\text{Al}_2\text{O}_3(0.02 \le x \le 0.1)$ [where CS is chitosan, NaTf is sodium triflate (NaCF₃SO₃), and Al₂O₃ is aluminum oxide] nanocomposite solid polymer electrolyte (SPE) films based on CS were prepared by a solution casting technique. X-ray diffraction and scanning electron microscopy analysis revealed that the alumina nanoparticles had a great effect on the structural and morphological behavior of the CS–NaTf (90:10) polymer electrolyte. An investigation of the electrical and dielectric parameters of the nanocomposite SPE films was conducted. Electrical impedance spectroscopy was carried out for this purpose. The relationships between the electrical and dielectric parameters were used to interpret and understand the ion-conduction mechanism. We observed that the direct-current conductivity (σ_{dc}) and dielectric constant followed the same trend with salt concentration. σ_{dc} versus temperature showed the Arrhenius and Vogel-Fulcher-Tammann (VTF) regions. The drops of σ_{dc} at high temperatures were observed for all of the samples. The ion relaxation dynamics were studied from Argand plots. For the first time, we confirmed the existence of a strong experimental relationship between the high-frequency semicircle of the impedance plots and the high-frequency dispersion regions of the alternating-current conductivity (σ_{ac}). The dispersion regions of σ_{ac} were used to study the ion-conduction mechanism. The behavior of the frequency exponent as a function of the temperature was used to interpret σ_{dc} versus the temperature. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2015, 132, 41774.

KEYWORDS: biomaterials; biopolymers and renewable polymers; dielectric properties

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INTRODUCTION

Dry solid polymer electrolytes (SPEs) have been attracting interest as a safer choice than liquid electrolytes. Pioneering work in the field of SPEs was carried out by Wright et al. cited by Singh & Bhat² who reported a direct-current conductivity (σ_{dc}) on the order of 10⁻⁵ S/cm at 330 K in highly crystalline poly ethylene oxide-Sodium thiocyanate (PEO-NaSCN) complexes. SPEs are formed by the dissolution of salts in a polymer matrix. They have received considerable attention as solid electrolyte materials for advanced applications, such as high-energy density batteries, sensors, and fuel cells.³ The main advantages of SPEs are their good mechanical properties, ease of fabrication into thin films of desirable sizes, and an ability to form good electrode/electrolyte contacts.4 A recent challenge has been to find a low-cost membrane with a high ionic conductivity (σ) and good dimensional and mechanical stabilities. Although SPEs have many advantages, such as mechanical flexibility and corrosion resistance, they also have some disadvantages, such as a low ionic σ and high crystallinity. Ionic conduction in SPEs is known to take place in the amorphous fraction of the polymer matrix, but the polymers used as hosts in polymer electrolytes are often semicrystalline.⁵ Thus, to overcome the disadvantages and improve σ of SPEs, the method that is mostly applied is the addition of plasticizer to improve the ambient ionic σ . Plasticizers can increase the amorphous content of polymer electrolytes and dissociate the ion aggregates present in polymer electrolytes and, thereby, improve the electrical σ of SPE.⁶ It is important to note that the σ and mechanical stability of plasticized polymer electrolytes are properties that have a reciprocal effect on each other; that is, the ionic σ in plasticized polymer electrolytes increases at the expense of reduced mechanical strength and vice versa.⁷ In addition to a high σ and wide electrochemical stability window, polymer electrolytes must exhibit a high thermal and mechanical performance. These performances can be obtained by the dispersal of nanosize fillers in polymer electrolytes. Since the original work of Weston and

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