Conductivity and transport studies of plasticized chitosan-based proton conducting biopolymer electrolytes

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Abstract
This paper focuses on the conductivity and transport properties of chitosan-based solid biopolymer electrolytes containing ammonium thiocyanate (NH₄SCN). The sample containing 40 wt% NH₄SCN exhibited the highest conductivity value of $(1.81 \pm 0.50) \times 10^{-4}$ S cm⁻¹ at room temperature. Conductivity has increased to $(1.51 \pm 0.12) \times 10^{-3}$ S cm⁻¹ with the addition of 25 wt% glycerol. The temperature dependence of conductivity for both salted and plasticized systems obeyed the Arrhenius rule. The activation energy ($E_a$) was calculated for both systems and it is found that the sample with 40 wt% NH₄SCN in the salted system obtained an $E_a$ value of 0.148 eV and that for the sample containing 25 wt% glycerol in the plasticized system is 0.139 eV. From the Fourier transform infrared studies, carboxamide and amine bands shifted to lower wavenumbers, indicating that chitosan has interacted with NH₄SCN salt. Changes in the C–O stretching vibration band intensity are observed at 1067 cm⁻¹ with the addition of glycerol. The Rice and Roth model was used to explain the transport properties of the salted and plasticized systems.

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1. Introduction
Green materials have attracted worldwide attention for their potential to reduce the impact of hazardous products [1]. Natural biopolymers are good candidates as electrolyte hosts for long-term use due to their biodegradable properties. Natural biopolymers have a minimal impact on the environment, are relatively low cost, are high in solubility and are able to form a mechanically stable film [2, 3]. One of the promising natural biopolymers is chitosan. Chitosan is derived from chitin [4]. Chitosan has been used as a food packaging material [5], dietary fiber [6] and potential medicine against hypertension [7]. Chitosan-based polymer electrolytes have been reported to have potential application in electrochemical devices such as proton batteries, lithium batteries and electrochemical double-layer capacitors [8–10]. To serve as a good electrolyte, conductivity is the main property that needs to be given attention. Plasticization is an approach to enhance the conductivity of the electrolyte [11, 12]. The conductivity of the order of $10^{-7}$ S cm⁻¹ of chitosan–lithium acetate (LiOAc) electrolyte has increased to $5.5 \times 10^{-6}$ S cm⁻¹ when plasticized with palmitic acid [13, 14]. The addition of ethylene carbonate (EC) to chitosan–ammonium iodide (NH₄I) has increased the conductivity from $3.7 \times 10^{-7}$ to $7.6 \times 10^{-6}$ S cm⁻¹ [15]. In the present study, chitosan was doped with NH₄SCN and plasticized with glycerol.

2. Experiment
For the preparation of the salted system, different concentrations of NH₄SCN (SYSTERM) were added to the solution containing 1 g of chitosan (viscosity: 800–2000 cP, 1 wt% in 1% acetic acid (25°C), Sigma–Aldrich) in 100 ml of 1% acetic acid (SYSTERM). All solutions were stirred until complete dissolution. For plasticized system preparation, different amounts of glycerol (SYSTERM)