Carrageenan-Ionic Liquid Composite: Development of Polysaccharide-Based Solid Electrolyte System

D. H. Camacho,* S. J. M. Tambio, and M. I. A. Oliveros

Department of Chemistry, College of Science, De La Salle University, 2401 Taft Avenue, Manila, Philippines Telephone/Fax: (+632)-5360230; E-mail: drexel.camacho@dlsu.edu.ph

Solid electrolyte system compared to a liquid electrolyte is desirable for some electrochemical applications. Natural polymers like polysaccharides were explored as polymer matrix in the development of solid electrolyte system. Among the polysaccharides screened, κ -carrageenan showed promising results. Cyclic voltammetry of the I₃-/I⁻ redox couple in κ -carrageenan gel showed improved performance compared to aqueous medium. Composite films of κ -carrageenan with KI and I₂ as triiodide sources and polymer electrolytes based on κ -carrageenan and ionic liquid, 1,3-dimethyl imidazolium iodide (DMII) with I₂ were prepared and characterized. The composite characterizations indicate that lower conductivity using Van der Pauw technique was observed with KI/I₂ system owing to its porous surface. The κ -carrageenan/DMII/I₂ system on the other hand showed a smooth surface and significantly higher conductivity making it a promising solid electrolyte system.

Keywords: Solid electrolyte, Carrageenan, ionic liquid

1. INTRODUCTION

Electrolyte systems play critical role in electrochemical devices. The transport of electrolytes or ions which facilitates the electrical circuitry in the device is efficient and convenient if the electrolytes are dissolved in molecular liquids. However in most electrochemical devices, like the Gratzel-type Dye Sensitized Solar Cell (DSSC), (O'Regan & Grätzel. 1991) fabrication and stability problems occur due to the volatile nature of the electrolyte liquid medium which may cause leakage, high pressure build-up, and corrosion affecting its form, fit, and function (Li, Qin, Deng, Luo, & Meng, 2009). To date, the liquid I_3 / Γ electrolyte system using acetonitrile as the electrolyte medium is still the best electrolyte system for DSSC. Energy conversion efficiency of ca. 11% and 8% longterm stability at 80 °C of DSSC with this volatile electrolyte system have been achieved (Chiba et al., 2006).

An active research area emerged to address the limitations of the liquid-based electrolyte systems particularly for DSSC applications. Various electrolyte systems like viscous liquid (Cerneaux, Zakeeruddin, Gratzel, Cheng, & Spiccia, 2008), gel form (Kubo et al., 2003; Murai, Mikoshiba, Sumino, & Hayase, 2002), ionic liquid (Lee, Chen, Lee, & Ho, 2009), eutectic melts (Bai et al., 2008) or polymer

slowly at room temperature. The degradation, explored cracks, disintegration, and brittleness of the film for over a span of three days was observed and taken as a measure of its stability. The electrolyte incorporation was done by soaking the film in a solution of KI (99.95%; Sigma Aldrich) and I₂ (99.99%; Sigma Aldrich) in anhydrous acetonitrile (99.8%).

> The electrochemical measurements of the triiodide redox couple were determined in polysaccharide gel media using cyclic voltammetry (CV). The gel redox systems were prepared from the mixture of polysaccharide (1-2 wt% w/v; dry weight basis), deionized water, potassium iodide, and iodine $(\Gamma/I_2 \text{ optimized})$ ratio: 4:1) stirred at room temperature and subjected to microwave heating for 40 seconds to form the gel. Cyclic voltammetry was using three electrode measured system working (reference electrode: Ag/AgCl; electrode: glassy carbon, and counter electrode: Pt) connected to a potentiostat (Powerlab/ 4SB). The electrodes were immersed in the polysaccharide gel redox systems. The CV profile of the electrolytes in polysaccharide gel is compared with the electrolytes in deionized water medium.

> The ionic liquid, 1,3-dimethylimidazolium iodide (DMII) is prepared from the reaction 1-methylimidazole between (99%; Sigma and iodomethane (99%; Sigma Aldrich) Aldrich) in HPLC grade THF as shown in the (Abdul-Sada equation et al.. 1986):



Composite films were prepared using the best polysaccharide among those screened incorporating the KI/I₂ by soaking the molded polysaccharide gel in acetonitrile solution of KI and I₂ then allowing the film to dry. Composite film of polysaccharide with DMII/I2 was done by adding DMII and I₂ in polysaccharide gel preparation and drying the film at room temperature. Characterization of the resulting film composites were done using Fourier-Transform Infrared (FT-IR) Spectrophotometer

composites (Akhtara, Cheralathan, Chun, & Yang, 2008) been have electrochemical applications. A polymer-based solid electrolyte system is an attractive alternative system where the electrolyte itself is the polymer material or the ions can be incorporated into a solid polymer matrix. A solid electrolyte is a material in which the electrolytic or ionic conductivity predominates over the inherent electronic activity of the matrix material.

The study aims to develop and characterize a solid electrolyte system using various polysaccharide films as the polymer matrix containing the electrolytes.

2. METHODOLOGY

The following polysaccharides: potato cornstarch, agar, agarose, chitin. starch. chitosan and the different carrageenan forms (lambda, iota, kappa and kappa-2; highest refined grade provided by Shemberg Corporation) were screened for gel formation, film formability, stability and electrolyte incorporation. The screening for gel formation was done using 1-2 wt% w/v of the polysaccharides (dry weight basis) mixed with deionized water, stirred at room temperature and subjected to microwave irradiation (40 sec). Film formability was done after microwave treatment by pouring the hot gels into a glass mold (7.5 cm x 2.5 cm x 1.5 mm) and drying (Nicolet 6700 FTIR) in thin films mounted between NaCl plates. Elemental analyses were done using Energy Dispersion X-Ray (EDX) Spectroscopy and the surface morphology of the film composites were analyzed using the JEOL JSM 5310 Scanning Electron Microscope (SEM). The electrical resistivity profile was obtained via a conventional 4-point probe Van der Pauw technique utilizing dried, unpressed composite film connected by silver wires and secured with silver conductive paint under ambient temperature.

3. RESULTS AND DISCUSSION

The electrolyte activity of the triiodide system in DSSC is based on the following redox reaction:

$$I_3 + 2e^- \neq 3I$$

where the triiodide (I_3) redox couple is formed in solution from iodide ions (Γ) and I_2 via the Grotthuss type mechanism as shown (Kubo et al., 2001):

$$2I^{-} + I_{2} \rightarrow [I^{-} \cdots I_{2} \cdots I^{-}] \rightarrow I_{3}^{-} + I^{-}$$

Conductivity optimization of the mole ratios of KI and I_2 shows that the ideal ratio is 4:1 (Γ/I_2). This ratio was used in the fabrication of the films for the solid electrolyte system.

The development of a solid electrolyte system is dependent on the choice of the polymer matrix. While most studies reported always explore synthetic polymers, this study investigates the cheap and readily available natural polymers, particularly polysaccharides, as matrix for solid electrolyte system. Thus various polysaccharides were screened in an attempt to find a good solid electrolyte medium. The formation of the solid electrolyte matrix depends on the following factors: (1) solubility of the polysaccharide in the preparation media, (2) its ability to form gel or film, (3) its stability under fabrication conditions. (4)its performance. electrochemical and (5)electrolyte incorporation capability. Screening results among the polysaccharides tested indicate that the κ -carrageenan is the ideal polysaccharide for composite film formation (Ueno, Endo, Kaburagi, & Kaneko, 2004). Carrageenan is a class of polysaccharides extracted from red seaweeds. Particularly, ĸcarrageenan is composed of alternating units of α -(1,3)-d-galactose-4-sulfate and β -(1-4)-3,6anhydro-d-galactose. Due to the presence of the sulfates. polymer ester the chains of carrageenans bear a negative charge and sensitive to jonic interactions with cations.

The cyclic voltammetry (CV) of the $I_3/I^$ redox couple is commonly measured in liquid solution. Its performance in a gel system however is relatively unknown (Ueno & Kaneko, 2004). To mimic the proposed solid electrolyte system, the redox behavior of the I_3^- / Γ couple in κ -carrageenan aqueous gel medium was investigated without any analytes added. The CV profile of the I_3^-/I^- redox couple in the κ -carrageenan gel medium shows a quasi reversible (Figure 1A) system. As compared to the aqueous control medium (red line), significant improvement in the reduction current and potential peaks are observed in ĸcarrageenan gel medium suggesting an efficient reduction process. In doubling the ionic concentration of the electrolytes, noticeable change was observed in *k*-carrageenan gel medium (Figure 1B) where it showed a more reversible profile with peak current ratio $(I_{\text{low}}/I_{\text{high}})$ close to unity and the peak potential separation (ΔE) is considerably good for a 2 electron system. Thus the carrageenan gel system, which consists of excess water molecules within the three dimensional network of k-carrageenan chains, does not impede the redox process and the transport of electrolytes making it highly attractive for DSSC application (Ueno et al., 2004; Nemoto Sakata, Hoshi, Ueno, & Kaneko, 2007).



Figure 1. Cyclic Voltammogram of I₃/Γ (A: mole ratio of KI/ I₂ is 4:1; B: mole ratio of KI/ I₂ is 8:2) in aqueous solution (red line) and in 2 wt% of κ-carrageenan gels (black line) measured in the range from -2000mV to 2000mV (vs. Ag/AgCl). Working electrode is glassy carbon and counter electrode is Pt. Scan rate, 50 mV/s.

The formation of a film composite incorporating the electrolytes into the κ carrageenan chains was achieved by soaking the molded gel in an acetonitrile solution of KI and I₂ (4:1). The resulting κ -carrageenan/KI/I₂ composite film is flexible plastic in form, heavy brown in color, and stable. The uniform brown coloration indicates that the triiodide from the solution has penetrated through the polymer networks acting like a plasticizer as it replaces the water molecules from the polymer matrix.

The elemental analysis of the κ carrageenan/KI/I₂ film composite using EDX spectroscopy shows the presence of the element sulfur, which is a distinct feature of this highly sulfated polysaccharide (Imeson, 2000). In the IR spectrum of pure κ -carrageenan film, the characteristic sulfate ester group was observed as strong absorption band at 1233 cm⁻¹ (Chiovitti et al., 1996; Knutsen et al., 1995). The presence of iodine in EDX spectrum confirms the incorporation of the redox couple into the film. The interaction of the electrolytes with the carrageenan chain is indicated by the observed red shift of the sulfate ester IR absorption band (1260 cm⁻¹) of the film composite.

SEM analysis of the films (Figure 2) showed the dramatic changes in the surface morphology as compared to the film made from pure κ -carrageenan.



Figure 2. SEM Images of the κ-carrageenan Control Film (A) and the κ-carrageenan/KI/I₂ composite (B)

The SEM images of the pure κ -carrageenan film shows a smooth surface (Figure 2A). The incorporation of the electrolytes in the κ carrageenan film resulted to a porous surface (Figure 2B). KI crystal deposition is not evident in the film composite indicative of $I_3/I^$ formation and that the K⁺ must have undergone electrostatic interaction with the negative sulfate ester groups of the carrageenan chain. For applications ideal to DSSC, a porous solid electrolyte film is advantageous because it maximizes the contact between the TiO_2 nanoparticles and the ruthenium dyes. A porous surface allows greater interpenetrability of the interacting species resulting to a forward electric generation process.

The electrical resistivity profile and conductivity of the film composite as measured using the four-point probe Van der Pauw technique exhibits lower conductivity (3.149 S/cm) compared to the pure κ -carrageenan control film (87.6 S/cm). This is attributed to the observed porous nature of the composite film which provides discontinuity in the material lattice where "holes", gaps, and craters on the surface as well as within the polymer matrix are evident affecting the transport of ions. It can be noted that the measurement of conductivity based on the Van der Pauw technique is dependent on the homogeneity of the material, thus the control carrageenan film, which has a smooth surface, allows less resistance in the flow of electrons from the applied voltage showing higher conductivity measurement.

To further improve the performance of the carrageenan film, incorporation of ionic liquid was done and it served a two-fold purpose: ionic liquid can act as a gelling agent or plasticizer and it can be a source of the conducting ions. Ionic liquids are non-volatile molten salts with high ionic conductivity and negligible vapor pressure making it ideal for electrochemical devices. In this study, 1,3dimethylimidazolium iodide (DMII) was used as the ionic liquid. DMII crystals are known to exhibit fast ion conduction [Every, Bishop, MacFarlane, Oradd, & Forsyth, 2001] and as electrolytes in poly(ethylene oxide) (PEO) composite, it showed promising results as polymer electrolytes (Singh, Kim, & Rhee, 2009). It is with this light that the incorporation of ionic liquids in carrageenan film is explored as a potential solid electrolyte system.

Synthesis of the ionic liquid 1,3dimethylimidazolium iodide (DMII) follows the procedure described by Abdul-Sada et al. (1986) using iodomethane as iodide source. The viscous ionic liquid solidifies upon storing at room temperature, due to the large iodide anion. The κ -carrageenan film/DMII/I₂ composite was prepared as described above. The FTIR spectra of the composite as compared to pure κ carrageenan indicate absorption peaks attributed to DMII incorporation. The peaks at ca 3147 and 3100 cm⁻¹ are attributed to the H-C=C

stretching of the imidazolium ring while the peak at 1507 cm⁻¹ corresponds to C=C stretching vibrations of the imidazolium aromatic ring. The FTIR indicates that the imidazolium iodide has been incorporated in the к-carrageenan polymer matrix via the electrostatic interaction between the positively charged imidazolium ion and the negatively charged sulfate ester groups in carrageenan. Addition of iodine (I_2) allows the formation of triiodide redox couple to give a кcarrageenan/DMII/I₂ film composite.



Figure 3. SEM image of the κ-carrageenan film incorporated with ionic liquid (DMII) and I₂. A) Surface morphology of the composite, B) cross section view.

The SEM image of *k*-carrageenan film incorporated with ionic liquid and I₂ shows a smooth surface with formation of isolated aggregate structures (Figure 3A). Formation of layers is evident in the cross section image of the film (Figure 3B). As compared to the κ carrageenan/KI/I₂ system, the film composite with DMII/I₂ differs in surface morphology and layer formation. This can be attributed to the type and orientation of the cations interacting with the κ -carrageenan. Potassium cations, distribute randomly in the polymer matrix where it interacts electrostatically with the negatively charged sulfate ester groups in carrageenan. This results polymer to orientations that give rise to bumps, lumps, and even holes producing a porous surface. Imidazolium cations on the other hand orient themselves in straight chains in the hole transport [Every et al., 2001] and since it is bigger than potassium ion, their interaction with the sulfate groups of the carrageenan will result in a linear orientation, smooth surface, and formation of layers.

The conductivity of the film composite containing DMII and I2 showed notable increase to 142 S/cm conductivity. The observed increase in conductivity, as opposed to the pure κ -carrageenan and the KI-I₂ system, may be attributed to the smooth surface and formation of well-defined layers in the composite. The conductivity response of kcarrageenan/DMII/I₂ composite over the intrinsic conductivity of the k-carrageenan matrix indicates a facile ion transport operating within the composite. To the best of our knowledge, this is the first report of ionically conductive film based on carrageenan-ionic liquid system. Further studies are underway to understand the mechanistic details of the ion transport in the film composite for DSSC application.

4. CONCLUSION

The natural polymer, κ -carrageenan, is a promising polymer matrix for the development of solid electrolyte system. Due to its polyanionic chain, it can host electrolytes and facilitate ion transport. Composite films of κ -carrageenan containing the KI/I₂ and DMII/I₂ were prepared and characterized. While the porous κ -carrageenan/KI/I₂ film composite showed high resistance in Van der Pauw conductivity, the κ -carrageenan/DMII/I₂ film, which has a smooth morphology, exhibited less resistance making it as a potential ionically conductive, solid electrolyte system for DSSC applications.

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