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Solid gellan gum polymer electrolyte for energy application

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ABSTRACT

In this paper a carbohydrate polymer (Phytagel/gellan gum) based solid gel electrolyte synthesis and its application in dye sensitized solar cell is reported. Potassium iodide has been added in Gelrite/Phytagel biopolymer matrix to develop solid gel electrolyte. Complex impedance spectroscopy shows liquid like ionic conductivity, with maximum conductivity 2.5×10^{-2} S cm^{-1} at 60:40 composition. Infrared spectroscopy (IR) confirms the formation of complex nature while x-ray diffraction (XRD) affirms the composite nature and suppression in crystallinity by salt doping. Polarized microscopy (POM) shows enhancement in amorphousity of gel matrix by salt doping which is a known favourable condition for ionic conductivity enhancement in gel electrolyte system and supported by our XRD data. A dye sensitized solar cell (DSSC) has been fabricated using maximum conductivity which shows with $J_{sc} = 3.2 \times 10^{-3}$ mA/cm^2, $V_{oc} = 0.57$, FF = 0.90, η = 1.47 at 1 sun condition.
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Introduction

Biodegradable plastics and polymers, from renewable resources have attracted an increasing amount of attention over the last three decades. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources [1,2]. In the past years, a wide range of biopolymers has been investigated as matrices to incorporate inorganic nanoparticles [3,4] and dispersoid salt [5–7]. Polysaccharides based biopolymer electrolyte (BPE) are commonly used in developing (like dye sensitized solar cells, super capacitor, actuators, batteries and fuel cells etc.) good efficient electrochemical devices. Due to the vast range of applicability of BPE, we have been working towards dye sensitized solar cell (DSSC) application using BPE [8,9]. As it is well known, solid polymer electrolytes (SPEs) have several advantages over the liquid counterpart such as desirable shape mouldability, free from leakage, mechanical strength and flexibility of design, thereby permitting miniaturization [10–13]. Unfortunately, SPEs have the inherent problem of low ionic conductivity at ambient temperature that acts as a barrier to their utility when compared with the existing conventional liquid/hybrid electrolytes. The ionic conductivity of the SPEs is strongly affected by various factors such

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as (i) crystallinity of the material, (ii) Cation and anion motions and (iii) the ion-pair formation (anion complexcation interaction) [14,15]. For electrochemical devices the efficient electrolyte needed liquid like conductivity (10^{-2} to 10^{-3} S/cm) which is easily obtained in these GPE [16]. Gel electrolytes are proposed as a novel alternative to liquid electrolytes in DSSC application [17]. Till to date, the maximum stable DSSC reported by the Prof. Gratzel group contains liquid electrolyte which has many disadvantages like corrosion, evaporation, volatility etc. GPE has already proved its suitability in DSSC. In DSSC application, it provides high electrolytic matrix as well as wetting of the working electrode [18].

In this paper, we have developed a new BPE system which offers liquid like ionic conductivity. Gel biopolymer electrolyte containing phytagel biopolymer doped with potassium iodide. Phytagel produced from a bacterial substrate composed of one rhamnose, one glucuronic acid, and carbohydrate (hydrate of carbon, i.e. glucose) two glucose units. It produces a high-strength gel; Polysaccharides serve as the primary structural support for the algae cell walls. Phytagel should be added slowly to the medium at room temperature with rapid stirring to eliminate any lumps before heating. If it is added to warm or hot medium, it will lump and not gel properly after heating. They become semi-solid at temperature is 27–32 °C. It is environmental friend and low-cost materials and does not require elaborate apparatus to manufacture [19].

Experimental details

Chemicals used in the present study were purified prior to use in the laboratory. Phytagel with average molecular weight (MW = 1000 kg/mol), potassium iodide (KI), iodine (I_2) were obtained from Sigma Aldrich, USA. While other chemicals like Dye, TiO_2 paste were obtained from the Solaronix, Switzerland while double distilled water (D2) was used as solvent.

Sol gel method is used for preparation of gel polymer electrolyte (GPE), fixed amount of Phytagel powder (0.175 g) was dissolved in D2 water (20 ml) in a beaker and continuous stirring. This ratio was used as a stock solution for the overall experiment (written here as B1). Stoichiometry ratio's of potassium iodide (KI) was then dissolved in D2 water (~5 ml) in another beaker (written here as B2). Phytagel is added slowly to the dispersoids at room temperature with rapid stirring to eliminate any lumps before heating, if it is added to warm or hot medium. Adding B2 (drop by drop) in B1 formed clear transparent GPE. These GPE's were characterized using various techniques.

Generally two electrodes, the anode and the cathode are prepared for the fabrication dye sensitized solar cell (DSSC) [20]. The anode is coated with a layer of mesoporous wide band gap semiconductor (TiO_2) and the other, the cathode, is coated with a thin layer of platinum glass with a Transparent Conductive Oxide (TCO) coating on one side. The space between the two electrodes is filled with a GPE solid electrolyte with maximum conductivity that ensures charge transportation through a redox couple [21].

Results and discussion

Impedance spectroscopy

Impedance Spectroscopy is an effective characterization technique for understanding electrochemical systems. It is a very sensitive technique for interfacial change, and is commonly used to investigate the kinetics of growth and other properties of solid biopolymer films formed at room temperature. The ionic conductivity measurement of the Phytagel-KI based biopolymer electrolyte films were carried out using CH instrument workstation (model CHI604D, USA) over the frequency range 100 Hz to 1 MHz. To measure ionic conductivity we have sandwiched free standing biopolymer electrolyte films between steel electrodes and the electrical conductivity was evaluated using formula

$$\sigma = \frac{1}{R_b}\left(\frac{l}{A}\right) \tag{1}$$

where, σ is ionic conductivity, l is thickness of sample, A is the area of given sample. R_b is the bulk resistance where the complex plane plot (also called the Bode plot or Cole–Cole plot) and the Nyquist plot intercepts with the real axis, where impedance with a real part (plotted on the X-axis = Z′) and an imaginary part (plotted on the Y-axis that is negative = −Z″). Each point on the complex plane plot represents the impedance at a certain frequency.

Nyquist plots of the biopolymer with different KI concentrations were considered for the calculation of R_b valve. The valve of R_b is provided by intersection of the imaginary axis with the real axis. The value of R_b decreases proportionally with the addition of KI achieving minima at certain point then it start decreasing.

$$\sigma = n.\, q.\, \mu \tag{2}$$

The calculated values of ionic conductivity are plotted in Fig. 1 for biopolymer based electrolyte. It was found that adding KI in phytagel matrix enhances the ionic conductivity at room temperature with fixed humidity which gives information of the interaction between salt and the biopolymer matrix. The increase in the ionic conductivity with increasing KI concentration can be further affirmed related to the

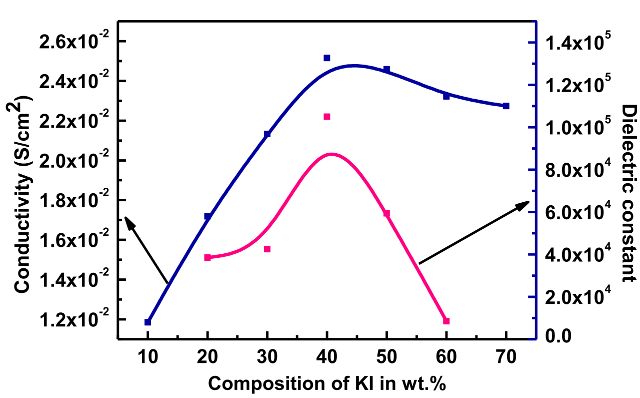

Fig. 1 – Conductivity vs composition (wt.% of KI) plot of Phytagel doped with KI system.

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