



# Tubular array, dielectric, conductivity and electrochemical properties of biodegradable gel polymer electrolyte



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## ABSTRACT

A supercapacitor based on a biodegradable gel polymer electrolyte (GPE) has been fabricated using guar gum (GG) as the polymer matrix, LiClO<sub>4</sub> as the doping salt and glycerol as the plasticizer. The scanning electron microscopy (SEM) images of the gel polymer showed an unusual tubular array type surface morphology. FTIR, DSC and TGA results of the GPE indicated good interaction between the components used. Highest ionic conductivity and lowest activation energy values were  $2.2 \times 10^{-3} \text{ S cm}^{-1}$  and 0.18 eV, respectively. Dielectric studies revealed ionic behavior and good capacitance with varying frequency of the GPE system. The fabricated supercapacitor showed a maximum specific capacitance value of  $186 \text{ F g}^{-1}$  using cyclic voltammetry. Variation of temperature from 273 K to 293 K did not significantly influence the capacitance values obtained from AC impedance studies. Galvanostatic charge–discharge study of supercapacitor indicated that the device has good stability, high energy density and power density.

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## 1. Introduction

Supercapacitor (SC) is considered as one of the most promising electrochemical energy devices which stores electrical energy through double-layer charging, faradaic processes or a combination of both [1]. To provide separator free thin-form, flexibility and reduce the risk of leakage from conventional liquid electrolyte containing supercapacitors, solid polymer electrolytes have been extensively studied by many researchers [2,3]. Major attention has been paid these days to fabricate all solid-state capacitors using solid polymer and gel polymer electrolytes because of their high ionic conductivity and advantageous mechanical properties. But solid polymer electrolyte exhibits lower ionic conductivity than gel polymer electrolytes (GPE) due to the lack of proper electrode–electrolyte contact throughout the volume of the active electrode material [4]. This distinctive advantage of better ionic conductivity is due to the fact that GPEs possess both the cohesive property of solids and the diffusive property of liquids [2]. Although the GPEs comprise of better mechanical strength for suitable applications, the phase separation that can occur between solid and liquid components within the polymer matrix still remains unsolved. GPEs employing poly(vinyl alcohol) (PVA), poly(vinyl

chloride), poly(ethylene oxide) (PEO), poly(vinylidene carbonate) and poly(vinylidene fluoride) (PVdF), etc., have been extensively studied [5,6] for improving the properties and reducing the cost to gain the attention of industries for future investments. Nonetheless, polymers that are synthesized from non-renewable sources are facing problems of exhaustion and urgent need for efficient, clean, and sustainable sources of energy [7]. Further, there is a greater emphasis now for the use of eco-friendly materials popularly known as green materials everywhere. Green chemistry deals with the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Utilization of non-toxic chemicals, environmentally benign solvents and renewable materials are the key issues in the materials science field when green chemistry methods are considered [8,9]. Hence, biodegradable polymers from renewable sources play a major role in contributing to green chemistry.

Guar gum (GG) is a hydrophilic, non-ionic polysaccharide extracted from the endospermic seed of the plant, *Cyamopsis tetragonolobus*. GG belongs to the large family of Galactomannans. The attractive features, such as low price, biodegradability and being derived from a renewable resource make GG one of the promising and potential materials for use as biopolymer [10]. GG hydrates in cold water to form a highly viscous solution in which the single polysaccharide chains interact with each other in a complex way [11]. GG is mainly used as an excellent stabilizer and binding agent in ice-cream, especially in the presence of a protein-stabilizing agent, beverages, suspensions, textiles, explosives, papers, and

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petroleum and when to improve the quality of frozen foods [12]. The unique property of sustaining the gel-like character even at low temperature has attracted our attention to use GG as a gel polymer electrolyte in supercapacitor. Further, in general fluorinated thermoplastic binders such as polytetrafluoroethylene or polyvinylidene fluoride are used in supercapacitors. These chemicals have a disadvantage of being expensive or requiring toxic solvents. Recently, Böckenfeld et al. [13] have showed that natural cellulose can be successfully used as a binder in supercapacitors. Hence, we thought it worthwhile to use GG which is economic as well as eco-friendly as a binder in our supercapacitor fabrication process.

It is known that GPEs are multicomponent systems wherein the interactions between the plasticizer and polymer, as well as plasticizer and salt, influence their properties. Our preliminary studies using non-aqueous plasticizers such as propylene carbonate, ethylene carbonate and diethyl carbonate showed non-compatibility with GG, as phase separation occurred and aggregated membranes were formed. Glycerol has been chosen as a plasticizer in this work because of its useful properties such as practical non-volatility at normal use temperatures and little change of the relative vapor pressure of glycerol solutions up to 70 °C changes in temperatures [14]. Further, hydroxyl groups of glycerol can also facilitate the dissociation of the doped salt and maintain an ion conducting viscous channel between the polymer matrices.

Lithium-polymer energy devices are known to have slightly higher energy densities and reduced weight compared to lithium ion energy devices. Therefore, particularly LiClO<sub>4</sub> has been chosen as doping salt for its smaller size and highly electropositive characteristics even at low temperatures. LiClO<sub>4</sub> also has an advantage of less hygroscopic character and no formation of HF compared to other lithium salts like LiBF<sub>4</sub>, LiPF<sub>6</sub> and LiAsF<sub>6</sub> [15]. Further, it may also be noted here that highly fluorinated compounds pose serious environmental concerns including that of biodegradation. Using lithium nitrate aqueous electrolyte Zhang et al. [16] demonstrated reversible cycling of LiMn<sub>2</sub>O<sub>4</sub> and VO<sub>2</sub> and Wessells et al. [17] investigated the electrochemical stability of LiClO<sub>4</sub> in water which was found to be ~1.6V. This shows that lithium salts has good electrochemical stability for use in supercapacitors. In general, aqueous salt solutions have very high ionic conductivities and should therefore be capable of very high power operation.

The prominent electrode materials for commercial supercapacitors are activated carbons (ACs). They exhibit desirable features such as high capacitance values because of their large microporosity, large specific surface area, superior stability, very prolonged cycle life, ease of handling and abundant availability [18]. Although many researchers have obtained biodegradable ionic conducting membranes by chemical or physical modification of natural polymers or their derivatives, such as hydroxyethyl cellulose (HEC) [19], starch [20], chitosan [21–23], natural rubber [24,25] and gelatin [26,27], studies on supercapacitors based on biodegradable GPEs are still scant [28,29].

In view of the aforesaid aspects, we report here the fabrication of a supercapacitor, employing a novel GPE system based on biodegradable renewable resources and by a greener method. Interestingly, the gel polymer formed in this study exhibited an unusual tubular array like morphology. The materials used were guar gum as gel polymer and binder, glycerol as plasticizer, lithium perchlorate (LiClO<sub>4</sub>) as doping salt and activated carbon derived from areca fibers as electrode material. Supercapacitor performance was evaluated employing AC impedance spectroscopy, cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) technique. The stability of capacitance of the supercapacitor in the temperature range of 273–293 K has also been examined using AC impedance studies.

## 2. Experimental

### 2.1. Material preparation

Guar gum (GG) (medium molecular weight) and glycerol were purchased from Merck. Lithium perchlorate (Aldrich) was dried at 393 K and kept under vacuum for 48 h before use. Stock solution was prepared by dissolving 2 g of GG in 100 ml of distilled water. The GPEs were prepared by mixing appropriate amount of salt and plasticizer, which were subsequently employed for preparing samples containing 10 ml of pure GG, others labeled as S1–S4 containing 90 wt% of GG stock solution, 10 wt% of glycerol (optimized as it showed better plasticizer retention property at this concentration) and varying LiClO<sub>4</sub> as 0.075 wt%, 0.10 wt%, 0.25 wt% and 0.50 wt%, respectively. The so prepared four solutions were placed in clean 10 ml beakers separately and allowed to bring about gelation initially at room temperature and were then kept in a water bath at 333 K for 48 h to form GPEs before subjecting to other studies.

### 2.2. Characterization

Fourier transform infrared spectroscopic (FTIR) measurements of the un-doped and LiClO<sub>4</sub> doped GG samples were carried out at room temperature using Nicolet Avatar 5700 FTIR spectrometer. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements of the un-doped and LiClO<sub>4</sub> doped GG samples were done on DSC-60 and DTA-60 Model instruments from Shimadzu, respectively. Measurements were performed over a temperature range of 303–473 K at a heating rate of 10 °C min<sup>-1</sup> under the nitrogen atmosphere at flow rate of 50 ml min<sup>-1</sup> and readings were taken from the first heating run.

The solid GPE sample was cut into small cubes and freeze dried in a deep freezer. Later, freeze dried samples were kept in nitrogen atmosphere and then subjected to high vacuum. The micro images were taken using a scanning electron microscope (SEM), ZEISS EVO 18 special edition.

For electrochemical studies, samples having thickness of ~2 mm were cut into 1 cm × 1 cm square dimension and placed between two square copper electrodes (length 1 cm) fitted with copper wires. The whole set up was held tightly with a plastic clamp. The bulk ionic conductivities ( $\sigma$ ) and dielectric properties of the blends were determined from the Electrochemical Impedance Spectra (EIS) in the frequency range of 1 MHz to 100 MHz using a small amplitude AC signal of 10 mV. Experiments were carried out in the temperature range of 303–333 K using PID controlled oven from SES instruments Pvt. Ltd. From these AC impedance data dielectric studies were carried out. The formulae and relationships between complex impedance, dielectric permittivity and dielectric modulus can be found elsewhere [30].

### 2.3. Fabrication of symmetrical supercapacitor cell

Electrode material for supercapacitor fabrication was prepared using activated carbon (AC) derived from areca fibers which have surface area of 250 m<sup>2</sup> g<sup>-1</sup>. AC was coated on two stainless steel electrodes using GG as binder (GG/AC in 0.2:1 weight ratio). The supercapacitor cell was constructed using GPE sandwiched between two prepared AC coated electrodes. The unit cell was sealed in a plastic coated aluminum pouch keeping the two wires outside. Electrochemical characterization was carried out by CV, EIS, and GCD studies. For lower temperature studies (273–293 K), the sealed unit cell was placed in water circulated low temperature bath keeping the wires above water and clamped tightly and allowed it to wait for a few minutes to attain the applied temperature (temperature error of ±1 °C), then AC impedance readings

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