Biopolymer Electrolyte Based on Gellan Gum With Magnesium Chloride for Magnesium Battery

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Abstract

Eco-Friendly, non-toxic and biodegradable natural biopolymer electrolyte, Gellan Gum with Magnesium Chloride has been prepared by solution casting technique. The prepared biopolymer electrolyte has been characterized by XRD, FTIR, DSC and AC impedance analysis techniques. XRD study is used to analyze amorphous nature/crystalline nature of the polymer electrolyte. Complex formation between Gellan Gum and magnesium chloride salt has been studied by FTIR technique. The glass transition temperature (T_g) of the polymer electrolytes are obtained by DSC measurement. The highest ionic conductivity $2.91 \times 10^{-2} \text{ Scm}^{-1}$ has been obtained for electrolyte of 1.0 g Gellan Gum with 0.5 M.wt% MgCl_2 from AC impedance analysis at room temperature. Transference number 0.97 has been obtained by Wagner's polarization method for high conducting sample. The Mg^{2+} cationic transport number 0.35 has been found by Evan's method for high conducting sample. Magnesium ion conducting battery has been constructed using the high conducting polymer electrolyte. Its open circuit voltage 2.39 V and the battery discharge characteristics are studied.

Introduction

Now a day's electrochemical device plays a very main role in all fields. Accordingly the research has been concentrated on the formation of electrochemical energy storage devices (batteries, fuel cells, capacitors). An electrolyte is one of the elements of energy storage device to decide the device performance. These electrolytes are in the form of liquid or solid. The liquid electrolytes have some drawbacks such as fluid leakage, low energy, costly and bulky. These drawbacks are overcome by solid polymer electrolytes (SPEs). Solid polymer electrolytes have the advantage no leakage, compatibility with electrolytes and low cost [1]. The solid polymer electrolytes are constructed using by synthetic polymer or bio polymer. The synthetic polymer electrolytes have the disadvantages toxic, non-renewable and high cost. To replace the limitations of synthetic polymer electrolytes the bio polymer such as cellulose, starch, chitosan, pectin, agar and carrageenan are utilized in the electrochemical devices such as batteries, fuel cells, super capacitor etc., These bio polymers are biodegradable, biocompatibility, low toxic and easily available in nature[2].

Gellan gum is one of the biopolymer with high molecular weight. It is an anionic water soluble polysaccharide produced by the fermentation of *Sphingomonas elodea* [3]. Gellan gum has high melting point, biocompatibility and high gelling ability. It is more stable under heating. The gelling property of the gellan gum is depends upon the positive charged ions (cations) such as Li^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} . The structure of gellan gum is associated with four monosaccharides including one rhamnose (Rha) rings, one glucuronic acid (GlcA) and two glucoses (Glc) [4], as shown in figure (1).

Gellan gum is used in the field of food industries and bio medicals. It also has the following important properties such as nontoxic, biodegradable and high thermal stability. Halim. N. F. A et al [5] reported an ionic conductivity $3.8 \times 10^{-4} \text{ S/cm}$ at room temperature for the Gellan-based polymer with lithium iodide (LiI). Noor. I.S.M et al [6] reported a conductivity value of $5.4 \times 10^{-4} \text{ S/cm}$ LiCF_3SO_3 dopped on gellan gum. Noor. IM [7] reported the gellan gum based polymer with LiTf has the conductivity at $5.38 \times 10^{-4} \text{ S/cm}$. The lithium ion batteries have the limitations such as safety problem and expensive. To replace the limitations, the researchers concentrate on Na^+ and Mg^{2+} ion batteries. For anode fabrication magnesium is the perfect metal, it has nearly double the volumetric capacity. magnesium ion battery has following advantages to compare lithium metal, (i)

negative reduction potential,(ii) during charging no dendrite formation (iii) safety in oxygen and humid atmosphere (iv) comparable ionic radii of Li^+ and Mg^{2+} in same magnitude (Patrick.A et al 1986) which makes the easy replacement of Li^+ ion by Mg^{2+} ions (v) high melting point (649°C) (vi) low cost (vii) easily available in nature[8]. Pandey et al [9] has found that the polymer electrolyte, PVdF-HFP with MgO has a conductivity at $8 \times 10^{-3} \text{ S/cm}$. Ramasamy et al [10] reported a conductivity $8.47 \times 10^{-4} \text{ S/cm}$ on PVA with magnesium perchlorate. Kumar et al [11] reported that PEO based polymer electrolyte doped with magnesium trifluoromethanesulfonate has a conductivity of $2.18 \times 10^{-3} \text{ S/cm}$, Adlin Helen et al [12] reported that chitosan biopolymer electrolyte incorporated with MgCl_2 has the conductivity $1.255 \times 10^{-4} \text{ S/cm}$. “No research is done in construction of Magnesium ion battery using Gellan Gum with magnesium chloride”. The chemical structure of gellan gum has more number of OH groups to which cations of salt could be attached to increase more charge carriers. Magnesium ion conducting bio polymer of 1g of gellan gum with different concentrations from 0.4 M.wt% to 0.55 M.wt% of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ have been prepared by the solution casting technique and characterized by XRD, FTIR, DSC, and AC impedance technique.

Experimental Technique

Biopolymer electrolytes of pure gellan gum and gellan gum with different compositions of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ salt (0.4 M.wt%, 0.45 M.wt%, 0.5 M.wt% and 0.55 M.wt %) have been prepared by solution casting technique using gellan gum (molecular mass of 500 kDa. from Duchefa Company, Netherland Gelrite Cat. No: G1101) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (molecular weight of 203.31 g/mol from SRL Pvt. Ltd, India). Double-distilled water is used as a solvent. 1.0 g of Gellan Gum(GG) is dissolved in 60 mL of double distilled water under magnetic stirring at 90°C . Next the different amount of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ salt (0.4 M.wt%, 0.45 M.wt%, 0.5 M.wt%, and 0.55 M.wt%) were added and stirred for half an hour. The homogeneous solution is cast in a petri dish and dried in an oven at 70°C to get a free standing film.

Characterization techniques

XRD analysis

XRD is a non destructive technique to analyze the crystalline or amorphous nature of the biopolymer membrane Rigaku Ultimate IV Japan diffractometer with $\text{Cu-K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation in the scattering angle range of 5° to 80° at room temperature is used.

FTIR analysis

BRUCKER spectrometer is used to measure the FTIR spectrum. FTIR spectra were recorded between 400 cm^{-1} to 4000 cm^{-1} with the resolution of 1 cm^{-1} in transmittance mode at room temperature.

DSC analysis

The thermal stability of the polymer electrolyte membrane was studied through DSC analysis using DSC Q20 V24.11Build 124 instrument with the heating rate of 20°C to 200°C under nitrogen atmosphere.

AC impedance analysis

The impedance of the polymer electrolyte has been made with the HIOKI 3532 LCR meter in the frequency range of 42 Hz to 5 MHz with the stainless steel as electrodes at room temperature.

Transference number measurement

Wagner's polarization method

The transference number of the maximum conductivity polymer was measured by Wagner's polarization method. The polymer was placed between the two stainless steel electrodes. A fixed voltage 1.5 was applied between the electrodes the current was measured as a function of time. From the initial and final current the ionic transference number were calculated at room temperature.

Evan's polarization method

The cationic transport number of the maximum conducting electrolyte was measured by Evan's polarization method. The polymer electrolyte was placed between the two magnesium metal plates. In this technique a fixed voltage 1.5 is applied for the cell Mg/PE/Mg, the initial and final current was noted. Then the cell is subjected to ac impedance measurement the cell impedance before and after polarization was noted.

Battery construction

Preparation of anode

Magnesium rod was purchased and circular specimen of diameter 12 mm and thickness 1 mm were sectioned out from it. The specimen is cleaned with acetone and dried for further use.

Preparation of cathode

The MnO_2 and graphite were taken in 3:1 ratio, additionally very small amount of polymer electrolyte was added and grained well. The grained powder was pressed into thin pellet using hydraulic press.

The polymer electrolyte of high conductivity was kept in between the anode and cathode pellet in order to construct a magnesium ion battery.

Results And Discussions

X-ray diffraction analysis

X-ray diffraction pattern for pure Gellan Gum is shown in the figure (2). The pure Gellan Gum sample has two broad high intense peaks at $2\theta = 6^\circ$ and 20° . This value agrees with the earlier reports [6].

The figure (3) shows the X-ray diffraction pattern of 1.0 g GG with 0.4 M.wt% MgCl_2 , 1.0 g GG with 0.45 M.wt% MgCl_2 , 1.0 g GG with 0.5 M.wt% MgCl_2 , 1.0 g GG with 0.55 M.wt% MgCl_2 . From the figure (3) it is observed that for 0.4 M.wt%, 0.45 M.wt% and 0.5 M.wt% of MgCl_2 salt concentration the intensity of a peaks decreases drastically and the broadness of the peaks also increase. This agrees well with Hodge et al [13] criterion, that gives the relationship between the intensity of peak and the degree of crystallinity. The increase in amorphous

nature of the polymer electrolyte has been illustrated by the increase in broadness of the peak and decrease in intensity of peaks. On further increases of MgCl_2 salt concentration to 0.55 M.wt% the polymer electrolytes crystallinity is increases. Amorphous phase has low energy barrier, then the ions easy move through the polymer matrix [14]. The biopolymer electrolyte 1.0 g GG with 0.5 M.wt% of MgCl_2 has a low intensity much broader peak which conforms that has more amorphous nature.

In XRD plot absence of peaks due to the MgCl_2 conveys the complete dissolution of MgCl_2 with the polymer matrix. From the deconvoluted XRD pattern the percentage of crystallinity (%C) has been calculated using the formula

$$\text{Percentage of crystallinity (\%C)} = \frac{\text{area under crystalline region}}{\text{total area of the peak (both crystalline and amorphous region)}}$$

The deconvoluted XRD pattern is shown in the figure (4). For all polymer electrolytes the percentage of crystallinity has been calculated and listed in the table1. From the table it has been observed that as increase the MgCl_2 salt concentration the percentage of crystallinity is degrades. The polymer electrolyte of 1.0 g GG with 0.5 M.wt% of MgCl_2 has low percentage of crystallinity.

Table.1 Percentage of crystallinity (%C) for all composition electrolytes

composition of electrolytes	percentage of crystallinity (%C)
Pure Gellan Gum	46
1.0g GG with 0.4wt% of MgCl_2	42
1.0g GG with 0.45wt% of MgCl_2	13
1.0g GG with 0.5wt% of MgCl_2	10
1.0g GG with 0.55wt% of MgCl_2	12

Fourier Transform Infrared spectroscopy analysis

FTIR spectrum has been used to analyze the complex formation between Gellan Gum and MgCl_2 salt. Figures (5) shows the FTIR spectra of the pure Gellan Gum and the Gellan Gum with different concentration of MgCl_2 . Pure Gellan Gum electrolyte has very large vibrational band at 3362 cm^{-1} corresponding to O–H stretching vibration from hydroxyl group of polyaccharide molecules [15]. This peak has been shifted to 3333 cm^{-1} , 3286 cm^{-1} , 3333 cm^{-1} and 3333 cm^{-1} for the electrolytes of 1.0 g GG with 0.4 M.wt% MgCl_2 , 1.0 g GG with 0.45 M.wt% MgCl_2 , 1.0 g GG with 0.5 M.wt% MgCl_2 , 1.0 g GG with 0.55 M.wt% MgCl_2 respectively, due to the interaction of Gellan Gum polymer with the MgCl_2 salt.

In pure Gellan Gum electrolyte the peak located at 2923 cm^{-1} corresponds to $\text{CH}_3\text{-CH}_2$ vibration [5] and it has been shifted to 2922 cm^{-1} , 2917 cm^{-1} , 2940 cm^{-1} and 2928 cm^{-1} for 1.0 g GG with 0.4 M.wt% MgCl_2 , 1.0 g GG

with 0.45 M.wt% MgCl_2 , 1.0 g GG with 0.5 M.wt% MgCl_2 , 1.0 g GG with 0.55 M.wt% MgCl_2 . The vibrational peak observed at 1642 cm^{-1} assigned to glycosidic bond (C = C stretching) of pure Gellan Gum [6] has been shifted to 1633 cm^{-1} , 1644 cm^{-1} , 1639 cm^{-1} and 1659 cm^{-1} for 1.0 g GG with 0.4 M.wt% MgCl_2 , 1.0 g GG with 0.45 M.wt% MgCl_2 , 1.0 g GG with 0.5 M.wt% MgCl_2 , 1.0 g GG with 0.55 M.wt% MgCl_2 respectively. The vibrational band at 1426 cm^{-1} assigned to the C-H bending of Gellan Gum [6] has been shifted to 1420 cm^{-1} , 1425 cm^{-1} and 1488 cm^{-1} 1.0 g GG with 0.45 M.wt% MgCl_2 , 1.0 g GG with 0.5 M.wt% MgCl_2 , 1.0 g GG with 0.55 M.wt% MgCl_2 respectively. The vibrational peak at 1153 cm^{-1} corresponds to C-C stretching vibration and has been shifted to 1159 cm^{-1} , 1147 cm^{-1} and 1153 cm^{-1} for the electrolytes of 1.0 g GG with 0.45 M.wt% MgCl_2 , 1.0 g GG with 0.5 M.wt% MgCl_2 , 1.0 g GG with 0.55 M.wt% MgCl_2 respectively. The peak observed at 1037 cm^{-1} for pure Gellan Gum corresponds to C-O stretching vibration [16] and it has shifted to 1044 cm^{-1} , 1033 cm^{-1} , 1038 cm^{-1} and 1043 cm^{-1} for the electrolytes of 1.0 g GG with 0.4 M.wt% MgCl_2 , 1.0 g GG with 0.45 M.wt% MgCl_2 , 1.0 g GG with 0.5 M.wt% MgCl_2 , 1.0 g GG with 0.55 M.wt% MgCl_2 respectively. The pure polymer electrolyte and polymer electrolyte of 1.0 g GG with 0.5 M.wt% MgCl_2 has a vibrational peak at 893 cm^{-1} and 899 cm^{-1} assigned to C-H rocking. The shift in peak positions confirms the complex formation between the polymer and salt [17]. The assignments of all vibration peaks for the polymer electrolytes are listed in the Table 2.

Table 2
FTIR assignments of all prepared polymer electrolytes

Wave number (cm^{-1})					
Pure Gellan Gum	1.0g GG with 0.4wt% MgCl_2	1.0g GG with 0.45wt% MgCl_2	1.0g GG with 0.5wt% MgCl_2	1.0g GG with 0.55wt% MgCl_2	Assignments
3362	3333	3286	3333	3333	O-H stretching
2923	2922	2917	2940	2928	
1634	1640	1634	1645	1645	CH ₃ -CH ₂ stretching
1426	-	1420	1425	1408	C = C stretching
1153	-	1159	1147	1153	
1037	1044	1033	1038	1043	C-H bending of CH ₂
893	-	899	-	-	C-C stretching
					C-O stretching
					C-H rocking

Differential Scanning Colorimetry analysis

The DSC analysis has been carried out in the temperature range of 20⁰C – 200⁰C to find glass transition temperature (T_g) of the prepared biopolymer electrolytes. The thermograms of pure Gellan Gum and Gellan Gum with different concentration of $MgCl_2$ are shown in the figure (6). The pure Gellan Gum has the glass transition temperature (T_g) at 44⁰C and for the electrolytes of Gellan Gum with different concentration of $MgCl_2$, the glass transition temperature (T_g) is shifted to the high temperatures. The observed T_g values of pure Gellan Gum and Gellan Gum with different concentration of $MgCl_2$ are listed in the table 3.

The electrolyte of 1.0 g GG with 0.4 M.wt% $MgCl_2$ has a glass transition temperature 55⁰C, 1.0 g GG with 0.45 M.wt% $MgCl_2$ has a glass transition temperature 60⁰C and 1.0 g GG with 0.5 M.wt% $MgCl_2$ has a glass transition temperature 102⁰C. This increase in T_g value may be due to the formation of transient cross links between the Mg^{2+} cations and the polymer chain [18]. On further adding salt concentration the polymer electrolyte of 1.0 g GG with 0.55 M.wt% $MgCl_2$ the glass transition temperature is decreased to 79⁰C due to the decrease in the effect of transient cross links between the polymer chain and magnesium cations [19].

Table.3 Glass transition temperature (T_g) for all composition of electrolytes

composition of electrolytes	T_g (⁰ C)
Pure Gellan Gum	44
1.0g GG with 0.4wt% of $MgCl_2$	55
1.0g GG with 0.45wt% of $MgCl_2$	60
1.0g GG with 0.5wt% of $MgCl_2$	102
1.0g GG with 0.55wt% of $MgCl_2$	79

AC Impedance analysis

The ionic conductivity of the polymer electrolytes have been calculated using AC impedance analysis. Figures (7) shows the Cole – Cole plot for pure Gellan Gum polymer electrolyte at room temperature and its equivalent circuit. Generally the Cole – Cole plot consists of two well defined regions. The semi circle at high frequency region represented a parallel combination of capacitor (due to an immobile polarized polymer chain) and a bulk resistor (due to mobile ions in the polymer matrix), non vertical spike at low frequency region represented by a constant phase element at the electrode electrolyte interface [20].

Figure (8) shows the Cole-Cole plot for the polymer electrolyte of 1 g gellan gum with different concentration (0.4, 0.45, 0.5 and 0.55 M.wt %) of $MgCl_2$ salt which has only the low frequency spikes, that indicates that only resistive component of the polymer electrolyte [21]. The bulk resistance (R_b), constant phase element (CPE) and n for all polymer electrolytes has been found out by EQ software program developed by Boukmap [22]. The

founded values are listed in the table 4. The constant phase elements impedance is calculated from the equation.

$$Z_{CPE} = \frac{1}{Q_0(j\omega)^n}$$

Here Q_0 and n are the frequency independent parameters. The value of n is lies between 0 and 1. If $n = 0$ it represents pure resistor and $n = 1$ it represents pure capacitor. The pure Gellan Gum polymer electrolyte has $R = 1646 \, \Omega$, $= 30.6 \, \mu F$ and $n = 0.499$. The polymer electrolyte of gellan gum with different concentration of $MgCl_2$ salt (0.4 M.wt%, 0.45 M.wt%, 0.5 M.wt %,0.55 M.wt%) has resistance value lies between $2.44 \, \Omega$ to $0.4691 \, \Omega$, CPE lies between $4.40 \, \mu F$ CPE to $0.3766 \, \mu F$ and n lies between 0.73 to 0.90 respectively.

The increase in concentration will increase the mobile charge carriers. Due to this the conductivity of the biopolymer electrolyte has increased. The conductivity of the electrolyte was calculated by using the formula

$$\sigma = \frac{l}{R_b A} \, Scm^{-1}$$

Here l is the thickness of the electrolyte, R_b is the bulk resistance and A is the area of the electrolyte.

Table.4 ESI parameters for all polymer electrolytes

Composition	R (Ω)	CPE (μF)	n
Pure Gellan Gum (GG)	1646	30.6	0.49
1.0g Gellan Gum/0.4 wt% MgCl ₂	2.44	4.40	0.77
1.0g Gellan Gum/0.45 wt% MgCl ₂	1.25	1.59	0.85
1.0g Gellan Gum/0.5 wt% MgCl ₂	0.47	25.25	0.91
1.0g Gellan Gum/0.55 wt% MgCl ₂	0.84	0.38	0.73

The ionic conductivity of the pure Gellan Gum and the different combination of gellan gum with $MgCl_2$ are calculated at room temperature and listed in the table 5. The highest conductivity of $2.91 \times 10^{-2} \, Scm^{-1}$ was obtained for 1g of gellan gum with 0.5 M.wt% of $MgCl_2$ salt, on further increase the salt concentration the conductivity decreases due to the ions aggregation.

Table.5 Ionic conductivity value for the prepared polymer electrolytes at room temperature

Polymer composition	Conductivity σ (S cm ⁻¹)
Pure Gellan Gum (GG)	4.219×10^{-6}
1.0g Gellan Gum/0.4 wt% MgCl ₂	3.516×10^{-3}
1.0g Gellan Gum/0.45 wt% MgCl ₂	7.97×10^{-3}
1.0g Gellan Gum/0.5 wt% MgCl ₂	2.91×10^{-2}
1.0g Gellan Gum/0.55 wt% MgCl ₂	1.22×10^{-2}

Variation of ionic conductivity with MgCl₂

The variation of ionic conductivity with respect to various concentrations of MgCl₂ at room temperature is shown in the figure (9). Ionic conductivity for a pure Gellan Gum polymer membrane is 4.219×10^{-6} Scm⁻¹. An adding of MgCl₂ salt with gellan gum the conductivity is also increases and it reaches the highest conductivity at 2.91×10^{-2} Scm⁻¹ for the polymer of 1.0 g gellan gum with 0.5 M.wt% of MgCl₂ due to the increase in charge carriers. On further adding of salt concentration 0.6 M.wt% of MgCl₂ leads to decrease the ionic conductivity of 1.22×10^{-2} Scm⁻¹ due to formation of ion aggregates [23].

Conductance spectra analysis

Generally the conductance spectra consist of three regions, namely low frequency region, mid frequency region and high frequency region. The low frequency dispersion region which specifies the space charge polarization at the blocking electrodes, the mid frequency plateau region which specifies the DC conductivity of the polymer electrolytes and the high frequency region which specifies the bulk relaxation process [24]. The conductance spectrum of pure gellan gum polymer electrolyte has all the three regions. The conductance spectra of the pure gellan gum biopolymer electrolyte as shown in the figure (10).

The conductance spectrum of Gellan Gum with different concentration of MgCl₂ salts has only two regions low frequency dispersion region and mid frequency plateau region. The conductance spectra of gellan gum with different concentration of MgCl₂ as shown in the figure (11). In conductance spectra extrapolating the mid frequency plateau to log σ axis the DC conductivity value is obtained [25]. There is a good agreement with the DC conductivity value obtained from the conduction spectra and Cole-Cole plot.

Transference number analysis

Wagner's polarization method

Wagner's polarization method is used to calculate the total ionic transference number of the highest conducting polymer electrolyte. The electrolyte was sandwiched between the two stainless steel electrode and a constant dc potential 1.5 V is applied across the electrodes. The current is monitored as a function of time. Current versus time graph is shown in figure (12).

At initially the peak current is obtained and rapidly decreases with time due to polarization of mobile ions at the electrode electrolyte interface. After words the current attain a constant value. The total ionic transference number of the electrolyte is calculated using the formula

$$t_{ionic} = \frac{(I_t - I_e)}{I_t}$$

Here I_t is initial total current and I_e is residual current. The transference number of 1.0 g gellan gum with 0.5 M.wt% of $MgCl_2$ is found to be 0.97. This shows that the charge transport is only due to ions rather than electrons.

Evan's polarization method

The combined ac and dc polarization technique for calculation of cation transport number has been proposed by Evan's et al. In this technique the electrochemical cell is formed by placing an electrolyte in between the two magnesium plates. The cell is polarized by applying a constant voltage $\Delta V = 1.5$ V. The initial current and final current were noted the cell Mg/PE/Mg is subjected to ac impedance measurements. The cell resistance before polarization and after polarization is noted. The cationic transport number can be calculated from the equation

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

Here I_0 is initial current, I_s is final current, R_0 is before polarization cell resistance and R_s is after polarization cell resistance. The cationic transport number for the 1.0 g GG with 0.5 M.wt% of $MgCl_2$ is 0.35. The figure (13) shows the ac impedance curve for the highest conducting sample.

Manjuladevi et al [26] reported that the transference number of Mg^{2+} ions as 0.30 for the blend polymer membrane based on poly (vinyl alcohol)-poly (acrylonitrile) with magnesium nitrate salt at room temperature. Kumar et al [27] reported the transference number of Mg^{2+} ions as 0.33 for the sample of PMMA based GPE system using 0.5 g of $Mg(CF_3SO_3)_2$ salt. Sangeetha et al [28] reported the transference number of Mg^{2+} ions as 0.26 for the sample of K-Carrageenan with $MgCl_2$. Shanmugapriya et al [29] prepared a biopolymer l-Carrageenan with magnesium perchlorate and reported the Mg^{2+} ions transference number as 0.313. Kiruthika et al [30] reported transference number for Mg^{2+} ions as 0.29 for the sample of pectin with magnesium nitrate.

Fabrication of Mg primary battery

Magnesium battery has been constructed using biopolymer electrolyte of highest ionic conducting sample. The magnesium metal in the form of pellet is taken as an anode, the cathode pellet were prepared by using MnO₂, graphite in the ratio of 3:1 and finally adding small pinch of electrolyte, these are grained well and pressed into a pellet with applying a 5-Torr pressure in the pelletizer. The biopolymer electrolyte of 1.0 g Gellan Gum with 0.5 M.wt% MgCl₂ was taken as the electrolyte for battery fabrication. The high conducting polymer was placed in between the anode and cathode pellet in the battery holder [31]. The schematic diagram of magnesium battery is shown in the figure (14)

The anode reaction is

The cathode reaction is

The overall reaction

In the Mg-MnO₂ battery the presents of hydroxide ions may be due to the moisture or hydroxyl group in the biopolymer membrane. The occluded water is the type of non-essential water that is retained due to the physical force in microscopic pores diffused irregularly throughout the gellan gum polymer [32]. An initial open circuit voltage (OCV) was observed as 2.39 V and it was recorded with respect to time. This remains the same value for 3 days. Open circuit voltage curve and its image are shown in the figure (15).

The discharge characteristics of the battery at room temperature were noted with an external load of 100 kΩ. The initial voltage is decreases from 2.39 V to 2.13 V due to the polarization at the electrode electrolyte interface. This voltage is maintained constant for 6 days. This discharge characteristics curve and its image are shown in the figure (16). The cell parameters are shown in the table 6.

Table.6 Cell parameters of Magnesium ion battery

Specification of cell parameters	Value of the cell parameters
Cell area (cm ²)	1.1304
Cell weight (g)	1.09
Cell diameter (cm)	1.2
Cell thickness (cm)	0.3291
Open circuit voltage (V)	2.39
Current drawn (μA)	27
Current density (μA cm ⁻²)	23.89

Conclusion

The magnesium conducting biopolymer electrolyte based on Gellan Gum with magnesium chloride were prepared by solution casting technique and characterized by XRD, FTIR, DSC and AC impedance analysis techniques. XRD confirmed the enhancement of amorphous nature due to addition of salt. FTIR confirmed the complex formation between the polymer matrix and salt. DSC indicated the glass transition temperature of the electrolytes. The highest ionic conductivity $2.91 \times 10^{-2} \text{ Scm}^{-1}$ has been obtained for the electrolyte 1.0 g Gellan Gum with 0.5 M.wt% of MgCl_2 . The transference number measurement specified that electrolyte of Gellan Gum with magnesium chloride as magnesium conductor. Mg^{2+} cationic transference number 0.35 has calculated for highest conducting electrolyte by Evan's method. A magnesium primary battery has constructed and their permanence is studied.

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Figures

Figure 1

Structure of gellan gum

Figure 2

XRD pattern of pure gellan gum

Figure 3

XRD pattern of (a) 1.0 g gellan gum with 0.4 M.wt% of MgCl_2 , (b) 1.0 g gellan gum with 0.45 M.wt% of MgCl_2 , (c) 1.0 g gellan gum with 0.5 M.wt% of MgCl_2 , (d) 1.0 g gellan gum with 0.55 M.wt% of MgCl_2

Figure 4

Deconvoluted XRD pattern for all electrolytes

Figure 5

FTIR spectra of (a) pure gellan gum, (b) 1.0 g gellan gum with 0.4 M.wt% of MgCl₂, (c) 1.0 g gellan gum with 0.45 m.wt% of MgCl₂, (d) 1.0 g gellan gum with 0.5 M.wt% of MgCl₂, (e) 1.0 g gellan gum with 0.55 M.wt% of MgCl₂

Figure 6

DSC thermogram of (a) pure gellan gum, (b) 1.0 g gellan gum with 0.4 M.wt% of MgCl_2 , (c) 1.0 g gellan gum with 0.45 M.wt% of MgCl_2 , (d) 1.0 g gellan gum with 0.5 M.wt% of MgCl_2 , (e) 1.0 g gellan gum with 0.55 M.wt% of MgCl_2

Figure 7

Cole-Cole plot of the pure gellan gum at room temperature and its equivalent circuit

Figure 8

The Cole-Cole plot of electrolytes a) 1.0 g gellan gum with 0.4 M.wt% of $MgCl_2$. b) 1.0 g gellan gum with 0.45 M.wt% of $MgCl_2$. c) 1.0 g gellan gum with 0.5 M.wt% of $MgCl_2$. d) 1.0 g gellan gum with 0.55 M.wt% of $MgCl_2$ at room temperature and its equivalent circuit

Figure 9

Variation of conductivity against concentrations of salt at room temperature

Figure 10

Conductance spectra of pure Gellan Gum polymer electrolyte

Figure 11

Conductance spectra of electrolytes a) 1.0 g gellan gum with 0.4 M.wt% of MgCl_2 . b) 1.0 g gellan gum with 0.45 M.wt% of MgCl_2 . c) 1.0 g gellan gum with 0.5 M.wt% of MgCl_2 . d) 1.0 g gellan gum with 0.55 M.wt% of MgCl_2 at room temperature

Figure 12

Polarizing current as a function of time in (a) Wagner's method and (b) Evan's method

Figure 13

Ac impedance plots before and after polarization

Figure 14

Schematic diagram of battery configuration

Figure 15

Open circuit voltage with respect to time and its image

Figure 16

Discharge characteristics of magnesium battery with its image