# Development And Characterization of Magnesium Ion Conducting Biopolymer Electrolyte Using Agar and Magnesium Nitrate Hexa Hydrate

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**Abstract:** The aim of the study was to develop an agar-based biopolymer electrolyte with varying concentrations of  $Mg(NO_3)_2.6H_2O$  in double-distilled water as the solvent. To better understand the impact each concentration had on the biopolymer, a range of characterisation techniques were employed - XRD, FTIR, DSC, Ac impedance analysis and transference number measurement being amongst them. XRD was used to determine whether a crystalline or amorphous polymer resulted from the process. Agar and magnesium nitrate may form complexes, according to FTIR. Through the process of differential scanning calorimetery, researchers have pinpointed the glass transition temperatures for a biopolymer electrolyte with superior conductivity. In order to study its performance, a  $Mg^{2+}$  ion primary battery was built using a biopolymer membrane with a highest ionic conducting of  $1.74 \times 10^{-4} \, \mathrm{S~cm^{-1}}$ . This electrolyte was comprised of 40% agar and 60% magnesium nitrate in water, and its ionic transference number of  $Mg^{2+}$  had been determined at 0.30 via Evan's methodology.

Keywords: Biopolymer electrolytes, Agar agar, Magnesium nitrate Hexa Hydrate, Ionic Conductivity

## 1. Introduction

A key factor in advancing science and technology is found in solid-state batteries, which are applied to a broad range of mobile devices and electric vehicles. There has been considerable research into using Li<sup>+</sup> and Li<sup>-</sup> lithium-ion batteries (LIB) due to their small ionic radii<sup>[1]</sup>. While LIBs have many advantages, they come with certain drawbacks; most noticeably a high price tag, difficulties managing lithium electrodes during production and usage, as well as potential safety hazards. Although LIBs have many advantages, the economic cost, difficulties in working with electrodes, and safety concerns are challenges that must be faced. Consequently, researchers have explored various alternatives such as Na<sup>+</sup>, Mg<sup>2+</sup>, Mg/air, and Zn<sup>2+</sup> battery technologies <sup>[2]</sup>. While all these battery types have potential for replacing LIBs, magnesium ion batteries (MIBs) may be particularly effective due to their low cost, abundant availability on Earth, superior safety, lower equivalent weight and reduced potential. Working with magnesium before and during assembly is also simpler than working with lithium metal which must not contact external air. There are a number of ways that the more common issues with limited capacity, low Mg-ion conductivity and operating voltage<sup>[3]</sup> can be addressed. Among them is the use of solid polymer electrolytes (SPEs). This has been met with great enthusiasm due to its many advantages including wide electrochemical stability, superior thermal performance and lightweight form factor. Additionally, gel polymer electrolytes, composite polymer electrolytes, and electrodes can all help to solve these problems as well. Due to the awareness of environmental contamination, research on green polymer electrolytes has been intensively conducted over the last few years. Scientists have been drawn to bio-polymers due to their special characteristics such as renewable energy capabilities, biocompatibility and degradation properties. To achieve ecologically friendly electrolytes<sup>[4]</sup>, a number of bio polymers have been employed, like cellulose derivatives, starch, pectins, dextrin, chitosan, agar aspic and carrageenan are some of them.

Research conducted by Hadi *et al.*,<sup>[5]</sup> established a reliable biopolymer electrolyte comprised of an iotacarrageenan host and Mg (NO<sub>3</sub>)<sub>2</sub> and Mg (ClO<sub>4</sub>)<sub>2</sub> incorporations. Following this, Kadir *et al.*, examined a gel

polymer electrolyte composed of potato starch and magnesium acetate. Maximum conductivity measured 6.1 x 10-4Scm<sup>-1</sup> and 2.18 x 10-3Scm<sup>-1</sup> with 0.4 weight percent Mg (ClO<sub>4</sub>)<sub>2</sub> incorporation, while the addition of 0.6 weight percent of the substance generated 2. Research performed by Abdulwahid *et al.*, revealed the electrical and electrochemical properties of a PAN/PVA/Mg (ClO<sub>4</sub>)<sub>2</sub> solid blend polymer electrolyte. At 92.5 PVA: 7.5 PAN and 0.25 (m.m%) (Mg(ClO<sub>4</sub>)<sub>2</sub>, the sample had a maximum conductivity of 2.96 x 10<sup>-4</sup> Scm<sup>-1</sup> at room temperature - far higher than that of an ionic liquid added sample with 1.12 x 10-5Scm<sup>-1</sup>, or a sample without ionic liquid at 2.96x10<sup>-4</sup> Scm<sup>-1</sup> respectively.

Agar, a biopolymer sourced from seaweed, has been discovered to have impressive mechanical strength and film-forming properties. This material has many useful industrial applications, with Mahalakshmi *et al.*, <sup>[6]</sup> chemical hydrogel (ACH) electrode providing a commercially viable option for fuel cells. Furthermore, Arockia Mary *et al.*, <sup>[7]</sup> observed that agar combined with acetic acid had an ambient temperature conductivity of 1.1 x 10<sup>-4</sup> S cm<sup>-1</sup>. Evidently, agar is an excellent choice for various industries due to its numerous advantageous characteristics. According to research conducted by Nwanya and their team, the ion conductivity values for agarbased polymer films created from acetic acid, lactic acid, KClO<sub>4</sub>, and KClO<sub>4</sub> were 6.54 x 10<sup>-8</sup> 9.12 x 10<sup>8</sup>,3.53 x 10<sup>-8</sup> and 2.24 x 10<sup>-8</sup> S cm<sup>-1</sup> respectively. Similarly, Chitra *et al.*, found that Agar with NH<sub>4</sub>SCN exhibited a conductivity of 1.03 x 10<sup>-3</sup> S cm<sup>-1</sup> while NH<sub>4</sub>Cl had a conductivity of 4 x 10<sup>-4</sup> S cm<sup>-1</sup> and NH<sub>4</sub>I had one of 1.

The current research is focused on the development of magnesium ion conducting biopolymer electrolytes that were produced through the combination of agar and Mg(NO<sub>3</sub>)<sub>2</sub>6H<sub>2</sub>O. In order gain insight into the samples, multiple techniques have been utilized such as Ac impedance analysis, XRD, FTIR and DSC. Additionally, Wagner's and Evan's polarisation techniques were leveraged to determine Mg<sup>2+</sup> transference number. Ultimately, a main magnesium battery was created based on the most conductive polymer electrolyte which is discussed within this paper.

#### 2. Materials And Methods

#### 2.1. Materials

Employing two Merck specialities of 95% purity - Agar with a molecular weight of 120,000 Da and Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O - this investigation was conducted.

## 2.2. Preparation Of The Electrolyte

To fabricate a biopolymer electrolyte, an  $80^{\circ}$ C casting method leveraging double distilled water as a solvent was used. Agar: Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was mixed for multiple hours with ratio variations of 70:30, 60:40, 50:50 and 40:60 to form a homogeneous blend. Subsequently, the solution was emptied into petri dishes and then heated in an oven at a temperature of  $60^{\circ}$  C to completely remove any traces of solvent. As a result, transparent free-standing films were crafted.

## 2.3. Electrolyte Characterization 2.3.1.X-Ray Diffraction Analysis

In order ascertain the crystalline or amorphous nature of the biopolymer electrolyte, X-ray Diffraction (XRD) patterns were recorded at room temperature with a X'pert pro diffractometer instrument utilizing the Cuk $\alpha$  radiation in the range of  $2\theta$ = $10^{\circ}-60^{\circ}$  at a rate of  $2^{\circ}$ /min.

## 2.3.2. Fourier-Transform Infrared Spectroscopy

The SHIMADZU - IR Affinity- 1 spectrometer was used to carry out an elaborate study of interactions between biopolymers and salt. The FTIR spectra were gathered with a resolution of 1 cm<sup>-1</sup> over the range of 400 cm<sup>-1</sup> - 4000 cm<sup>-1</sup> at room temperature.

## 2.3.3.DSC Analysis

The DSC Q20 V24.10 Build 122 model was employed to measure the shift of temperature when testing a biopolymer electrolyte that had been created. The TA apparatus provided accurate readings of the transition temperatures.

## 2.3.4.AC Impedance Analysis

Utilizing an HIOKI 3532 LCR meter linked to a computer, analysis of the electrical properties of biopolymer-based electrolytes via Impedance is a beneficial procedure. To determine the impedances of these electrolytes, stainless steel electrodes were placed in-between the biopolymer electrolytes.

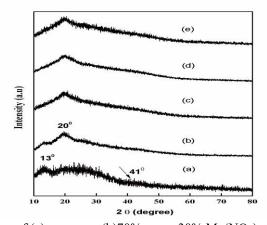
#### 2.3.5.Measurement of the Transference Number

In order evaluate the transmission coefficient of a new biopolymer electrolyte, scientists made use of dual polarization technique. A voltage source of 1.5V was installed between two stainless steel electrodes, with the biopolymer membrane sandwiched in between them. Subsequently, shifts in the polarization current were monitored over a period of time and Evans' polarisation method was employed for determining the Mg<sup>2+</sup> ion's transport number. This process entails placing the biopolymer electrolyte between magnesium electrodes (Mg/biopolymer electrolyte/Mg) and applying alternating and direct currents.

#### 3. Results And Discussion

## 3.1. X-Ray Diffraction Analysis

X-Ray Diffraction studies were performed for the biopolymer electrolytes agar with varied concentrations of Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O to assess the degree of amorphocity at room temperature. The XRD patterns are seen in figure 1. The diffraction pattern of pure agar shows a peak at  $2\theta$ =13°, a large peak between 15 and 35 of 20 values, and a shoulder at  $20=20^{\circ}$ . Tamilisai et al., [8] discovered the peak for pure agar at  $13^{\circ}, 20^{\circ}, 30^{\circ}, 41^{\circ}$ . Electrolytes identified the characteristic diffraction peak for the biopolymer. 30% Mg(NO<sub>3</sub>): 70% agar60% agar, 40% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, and 50% Mg(NO<sub>3</sub>): 40% agar 60% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O has been shown in Figure 1 depicted. 30% Mg(NO<sub>3</sub>)<sub>2.6</sub>H<sub>2</sub>O: 70% agar shoulder at 13 degrees and a strong peak at 20 degrees are seen in the 2.6H2O biopolymer membrane. When Mg(NO<sub>3</sub>)<sub>2</sub> .6H<sub>2</sub>O concentration increases, the shoulder at 130 disappears and the intensity of the peak at 200 weakens to 60% agar: 40% Mg(NO<sub>3</sub>)<sub>2</sub> .6H<sub>2</sub>O. The Buvaneshwari et al., [9] criterion was applied to analyze the data, which determined that peak intensity and crystallinity level were correlated. Moreover, the breadth of the peak also increased with increasing crystallinity. Out of all of the examined polymer membranes, a 40% agar: 60% Mg(NO<sub>3</sub>)<sub>2</sub> .6H<sub>2</sub>O solution showed the broadest peak width, suggesting it had a more amorphous form than others. Additionally, the XRD pattern demonstrates that the ratio of amorphous phase to charge carriers grows in synchrony with an increase in Mg(NO<sub>3</sub>)<sub>2</sub> .6H<sub>2</sub>O concentration, broadening the peak and lowering its relative intensity<sup>[10]</sup>. It is impossible to get a salt concentration of more than 60% in free-standing Mg(NO<sub>3</sub>)<sub>2</sub> films. Analysis of XRD data pointed to a complete dissociation of Mg(NO<sub>3</sub>)<sub>2</sub> in its polymer matrix, evident by a lack of any peak characteristics related to pure Mg(NO<sub>3</sub>)<sub>2</sub>.



 $\label{eq:fig1:Analysis} \textbf{Fig 1:} \ Analysis \ of \ XRD \ patterns \ of \ (a) \ pure \ agar \ (b)70\% \ agar : 30\% \ Mg(NO_3)_2.6H_2O \ (c) \ 60\% \ agar : 40\% \ Mg(NO_3)_2.6H_2O \ (d) \ 50\% \ agar : 50\% \ Mg(NO_3)_2.6H_2O \ (e) \ 40\% \ agar : 60\% \ agar : 60\% \ Mg(NO_3)_2.6H_2O \ (e) \ 40\% \ agar : 60\% \ Mg(NO_3)_2.6H_2O \ (e) \ 40\% \ agar : 60\% \ Mg(NO_3)_2.6H_2O \ (e) \ 40\% \ agar : 60\% \ Mg(NO_3)_2.6H_2O \ (e) \ 40\% \ agar : 60\% \ Mg(NO_3)_2.6H_2O \ (e) \ 40\% \ agar : 60\% \ Mg(NO_3)_2.6H_2O \ (e)$ 

#### 3.2. Fourier - Transform Infrared Analysis

The FTIR spectra of pure agar, agar with varying concentrations of the salt  $Mg(NO_3)_2.6H_2O$ , and agar in the frequency ranges of  $4000-1500~cm^{-1}$ ,  $1500-1200~cm^{-1}$  and  $1200~to~500~cm^{-1}$ are shown in Figures 3, 4, and 5, respectively. Table 1 displays the appropriate vibrational frequencies that were assigned<sup>[11]</sup>.

Research has found a correlation between O-H extension and an absorption band that appears in pure agar at  $3449 \text{ cm}^{-1}$  [12]. Upon investigations of biopolymer electrolytes, it was discovered that this vibration shifted to  $3471 \text{ cm}^{-1}$ ,  $3492 \text{ cm}^{-1}$  and  $3499 \text{ cm}^{-1}$ when agar was mixed with Mg (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O in certain proportions - 70% Agar :  $30\% \text{ Mg}(\text{NO}_3)_2.6\text{H}_2\text{O}$ , 60% agar :  $40\% \text{ Mg}(\text{NO}_3)_2.6\text{H}_2\text{O}$ , 50% agar :  $50\% \text{ Mg}(\text{NO}_3)_2.6\text{H}_2\text{O}$  and

40%agar : 60 % Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O. After adding different concentrations of salts to the polymer membrane, the peak originally located at 1634 cm<sup>-1</sup> in pure agar now induces an O-H bend and shifts to 1637 cm<sup>-1</sup> for all concentrations of (MgNO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O. This peak also expanded, demonstrating the presence of a chemical between the salt and the biopolymer membrane. According to FTIR measurements of pure (MgNO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O at at 1347 cm<sup>-1</sup>, the NO<sub>3</sub>- ion's asymmetric stretching is to blame<sup>[13]</sup>. As seen in our case at 1384 cm-1 for 70% Agar: 30% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O , the frequency may change when salt is introduced to the polymer matrix, while it is pushed to 1400 cm<sup>-1</sup> for the other concentrations. This shows how a compound was created between the salt and polymer membrane. The NO<sub>3</sub>- ion's symmetric stretching may be detected at 1058 cm<sup>-1[14]</sup>. When the salt is incorporated into the polymer matrix, the frequency may change, especially with 70%Agar: 30% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O. The symmetric stretching vibration of the NO<sub>3</sub>- ions results in a very little peak of 2.6H<sub>2</sub>O at 1084 cm<sup>-1</sup>. For 60% Agar: 40% Mg(NO<sub>3</sub>), use 1085 cm-1.50% Agar, 50% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O: Agar, 2.6H<sub>2</sub>O, and 60% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O. It also shows how the combination formed between the salt and the biopolymer membrane. A possible interaction between Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and the biopolymer agar is shown in Figure 2<sup>[15]</sup>.

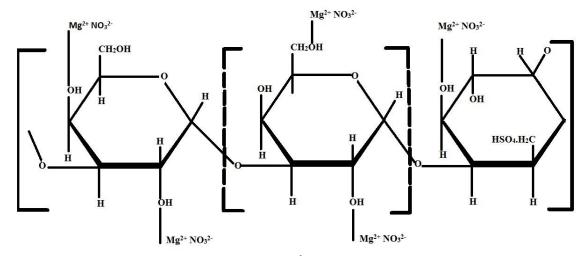
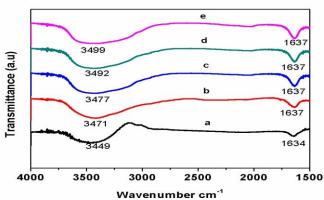


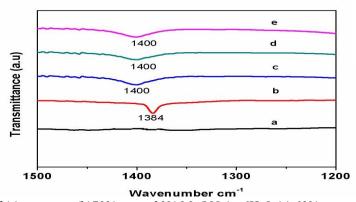
Fig 2: Possible interaction between Mg <sup>2+</sup> ions and polymer agar matrix.

Table 1: Peaks of agar's absorption with different agar-Mg(NO<sub>2</sub>)<sub>2</sub> 6H<sub>2</sub>O ratios

Wavenumber cm <sup>-1</sup>						
Pure agar	70%Agar : 30 % Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	60%Agar : 40 % Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	50%Agar : 50 % Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	40%Agar : 60 % Mg(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	Assignments	
3449	3471	3477	3492	3499	O - H Stretching	
1634	1637	1637	1637	1637	O –H bending	
-	1384	1400	1400	1400	Asymmetric stretching of NO <sub>3</sub> <sup>-</sup> ions	
-	1084	1085	1085	1085	Symmetric Stretching of NO <sub>3</sub> - ions	



 $\begin{array}{l} \textbf{Fig 3:} \ FTIR \ spectra \ of (a) \ pure \ agar \ (b)70\% \ agar : 30\% \ Mg(NO_3)_2 \ .6H_2O \ (c) \ 60\% \ agar : 40\% \ Mg(NO_3)_2 \ .6H_2O \\ (d) \ 50\% \ agar : 50\% \ Mg(NO_3)_2 \ .6H_2O \ between \ 1200 \ cm-1 \ and 500 \ cm-1 \ in \\ frequency \end{array}$ 



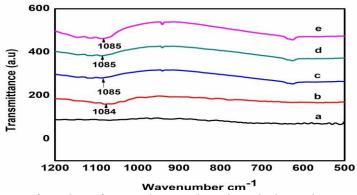


Fig 5: The FTIR spectra of a variety of agar and magnesium nitrate hydrate mixtures were studied between 1200 cm<sup>-1</sup> and 500 cm<sup>-1</sup> in frequency

## 3.3.Differential Scanning Calorimetery (DSC) Study

To identify its glass transition temperature (Tg), 40% agar: 60% Mg(NO<sub>3</sub>)<sub>2</sub>. $6H_2O$ , which had remarkable conductivity, was subjected to DSC experiments. In Fig. 6(b), we can observe results obtained from this experiment<sup>[16]</sup>. Additionally, as depicted in Fig. 6(a) where the Tg value is  $69^{\circ}$  C. For 40% agar, the result dropped to  $34.48^{\circ}$  C: Mg(NO<sub>3</sub>)<sub>2</sub>. $6H_2O$  biopolymer membrane, 60 percent. The reduction in glass transition temperature (Tg) after salt addition suggests that the rubbery state is promoted in the biopolymer electrolytes.

The more flexible nature brought on by the rubbery state promotes more Mg-ion transfer. Singh *et al.*,<sup>[17]</sup> 92.5PVA:7.5PAN:0.5 mm% MgCl<sub>2</sub> and Eswaragomathy *et al.*,<sup>[18]</sup> both reported comparable results in their studies regarding compositions of 50% PVP, 25% Mg(ClO<sub>4</sub>)<sub>2</sub>.

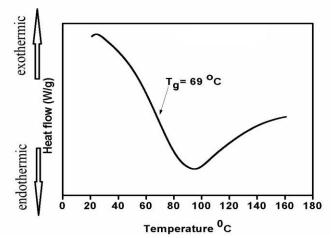


Fig 6 (a): The glass transition temperature and DSC thermogram for 40% agar: 60% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O

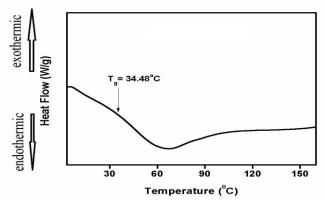


Fig 6 (b): The glass transition temperature and DSC thermogram for pure agar

## 3.4. Analysis of Impedance

Impedance spectroscopy can be used to assess ionic conductivity in biopolymer electrolytes. A number of factors determine this, including what kind of ionic carrier is present, its level of concentration and carrier mobility [19] From Figure 7, it's clear there are two distinct frequencies observed on pure agar-chol-chol lines: a high frequency semicircle followed by a low-frequency peak [20]. This is due to both bulk resistance ( $R_b$ ) and bulk capacitance ( $C_b$ ) working in parallel which produces that high semicircle while ion penetration into an electrode-electrolyte interface creates that lower peak. When  $Mg(NO_3)_2.6H_2O$  was added to agar, an observable phenomenon occurred: semicircles disappeared, indicating that components of high resistance were dominating this biopolymer matrix. For calculating total resistivity ( $R_b$ ), Boukamp's program [21] was used, and ionic conductivity ( $\sigma$ ) was established using a special formula  $\sigma = t$ /  $R_b$ ; here t and t0 represented thickness and surface area of polyelectrolyte, respectively. Table 2 presents results - in aqueous chamber biopolymer electrolyte from t0%:60% t1.74 x t10-4 S/cm .

Ionic conductivity and mobility are related according to  $\sigma=n$  e  $\mu$ , where n stands for charge carriers, e' is energy and  $\mu$ ' is mobility of charge. When added to agar, Mg (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O boosted its conductivity from 6.21 x 10<sup>-8</sup> S cm<sup>-1</sup> to 1.74 x 10<sup>-4</sup> cm<sup>-1</sup> when it was introduced at 40% concentration. This increase in charge carriers (Mg2+) consequently increases total conductivity value. As can be seen from the diagram in fig. 8, varying ratios of Mg (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O alters the diameter of the high-frequency semicircle. This is due to a distortion of polar groups within the biopolymer that affects its dipole orientation<sup>[22]</sup> Subsequently, it produces less capacitance and decreased earth resistance measurements which are proportionate to a fraction of a hemisphere.

For example, when 0.6 wt% Mg(ClO<sub>4</sub>)<sub>2</sub> and 1.0 g i-carrageenan were combined, Manjula Devi's experiment showed an electrical conductivity value of 2.18 x 10<sup>-4</sup> S cm<sup>-1</sup> with a maximum measureable being 2.96 x 10<sup>-4</sup> S cm<sup>-1</sup>. In summary, different concentrations of Mg (NO3)2.

Fig. 8 presents a diagram of different proportions of Mg (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, which indicate the effect of agar salt addition on semicircle diameter . This decrease in size can be attributed to the misalignment of polar groups within the biopolymer chain, resulting in a lower capacitance and earth resistance than what is possessed by one full hemisphere. Professor Manjula Devi's research<sup>[23]</sup> found that a 0.6 wt% solution of Mg(ClO<sub>4</sub>)<sub>2</sub> alongside 1.0 g i-carrageenan yields an electrical conductivity value of  $2.18 \times 10^{-3} \text{ S cm}^{-1}$ , with the maximum being  $2.96 \times 10^{-4} \text{ S cm}^{-1}$ .

Table 2: Ionic conductivity values of agar with MgNO <sub>3</sub> 6H <sub>2</sub> C				
Agar:MgNO <sub>3</sub> 6H <sub>2</sub> O	Ionic conductivity S cm <sup>-1</sup>			
Pure Agar	6.21 x 10 <sup>-8</sup>			
70:30	1.21 x 10 <sup>-5</sup>			
60:40	1.374 x 10 <sup>-4</sup>			
50:50	1.63 x 10 <sup>-4</sup>			
40:60	1.74 x 10 <sup>-4</sup>			

Table 2: Ionic conductivity values of agar with MgNO<sub>3</sub>6H<sub>2</sub>O

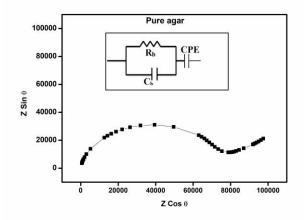
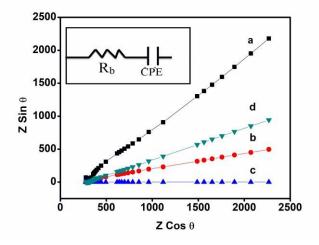


Fig 7: A pure agar Cole-Cole plot and its accompanying equivalent circuit



 $\label{eq:Fig.8:Cole} \textbf{Fig.8:} \ \ Cole \ cole \ plot \ with \ the \ corresponding \ equivalent \ circuit \ for \ (a)70\% \ agar: 30\% \ Mg(NO_3)_2.6H_2O \ (b) \ 60\% \ agar: 40\% \ Mg(NO_3)_2.6H_2O \ (c) \ 50\% \ agar: 50\% \ Mg(NO_3)_2.6H_2O \ (d) \ 40\% \ agar: 60\% \ agar: 60\% \ Mg(NO_3)_2.6H_2O \ (d) \ 40\% \ agar: 60\% \ agar: 60\% \ Mg(NO_3)_2.6H_2O \ (d) \ 40\% \ agar: 60\% \ Mg(NO_3)_2.6H_2O \ (d) \ 40\% \ agar: 60\% \ Mg(NO_3)_2.6H_2O \ (d) \ 40\% \ agar$ 

#### 3.5. Frequency - Dependent Conductivity

In fig. 9 shows the emission spectrum of pure agar at different concentrations of Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O. A long-time mode corresponding to the continuous conductivity of the resulting biopolymer electrolyte, a plateau mode independent of the averaging time, and a short diffusion time mode related to the available bias voltage at the electrode-electrolyte interface. The control spectrum consists of collective, mainly three-component relaxation processes. The conductivity spectrum of alternating current shows that the conductivity increases with increasing salinity. To ensure constant current values for all biopolymer electrodes, the graph is placed on a logarithmic axis. Therefore, conductivity values determined from Kohl-Kohl diagrams and conductivity spectra are comparable.

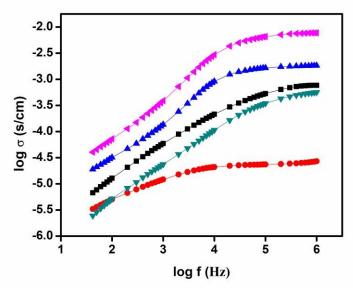


Fig 9: Waveforms of frequency-dependent conduction for (a) pure agar (b)70% agar :  $30\% \text{ Mg(NO}_3)_2$  .6H<sub>2</sub>O (c)  $60\% \text{ agar} : 40\% \text{ Mg(NO}_3)_2$ .6H<sub>2</sub>O (d)  $50\% \text{ agar} : 50\% \text{ Mg(NO}_3)_2$ .6H<sub>2</sub>O (e)  $40\% \text{ agar} : 60\% \text{ Mg(NO}_3)_2$ . 6H<sub>2</sub>O

## 3.6. Transference Number Analysis

The ion transport number is a useful measure to determine if a generated electrode is suitable for use in batteries. There are two types of bias methods used to estimate the amount of exposure. (i) Wagner's installation method ii) Evan's application procedure<sup>[24]</sup>.

#### 3.7. Wagner's Polarisation Technique:

This approach includes measuring the conductivity number, which is used to establish whether ions or electrons are responsible for a biopolymer's electrical conductivity. The number of gears is determined by the formula.

$$t_{ion} = (I_i - I_f)/I_i \tag{2}$$

The 1.5 V DC voltage was used in the experiment, and 40% agar plus 60% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O /SS made up the cellular configuration for polarity. The graph (Fig. 10) demonstrates how after being stimulated, the initial current of I<sub>i</sub> gradually decreases until its final current I<sub>f</sub> of When reaches a steady value during deep discharge due to an absence of ionic particles in the biopolymer electrolyte <sup>[25]</sup>. Beginning with equation (2), the transmission number for a biopolymer combination of 40% agar and 60% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was observed to be 0.98. This figure is almost equal to one, suggesting that ionic rather than electronic contribution account for the conduction capacity of polymer electrolyte films. In other words, the ions are primarily responsible for transporting current through this material. Modern biopolymer electrolytes have ion transport numbers which are almost identical to one,

making them applicable for solid-state electrochemical cells. Research conducted by Ponraj *et al.*, <sup>[26]</sup> discovered that PVA-NH<sub>4</sub>Br polymer electrolytes had t<sub>ion</sub> values of 0.93 to 0.96.

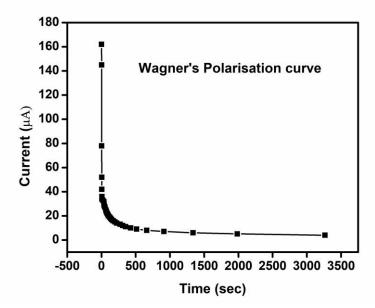


Fig 10: Wagner polarization curve for cells SS/40% agar: 60% Mg(NO<sub>3</sub>)<sub>2</sub> .6H<sub>2</sub>O /SS

## 3.8. Evans Polarisation Technique

To ascertain transport numbers (t+) of  $Mg^{2+}$  ions contained in biopolymer electrolyte, a technique referred to as Evans polarization was employed. For this purpose, AC and DC methods were utilized for culturing Mg/40% agar:  $Mg(NO_3)_2.6H_2O$  /Mg cells  $^{[27]}$  A voltage of 1.5 V DC was imposed on polarizing them and then recording first and last failure with a graph created showing its history. Moreover, AC impedance method was conducted to gauge cell resistance values before and after biasing which is shown in Fig. 12.

Subsequently, using a particular formula, it enabled us to compute amount of Mg<sup>2+</sup> ion being transported.

$$T_{+} = I_{s}(\Box V - R_{o}I_{o})/(\Box V - R_{s}I_{s})$$
(3)

Here, the starting and final current is denoted by  $I_0$  and  $I_s$ ,  $R_0$  and  $R_s$  are the resistance of the cell before and after biasing respectively and  $\Delta V$  is the applied DC voltage. For a cell cultured on 40% agar and 60% magnesium nitrate dihydrate, the carrier number was found to be 0.30. In their study of carrageenan with 0.5 g of Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O electrolyte, Ithnin *et al.*, in, the acceptance number of Mg<sup>2+</sup> ions was found to be 0.31. Asnawi *et al.*, [<sup>28]</sup> They produced a result of 0.38. The system is made up of 92.5 PVA, 7.5 PAN, and 0.5 mm% MgCl<sub>2</sub>. According to Jayalakshmi et al., [<sup>29]</sup> the PVDF-HFP magnesium triflate system with excess ionic liquid had a conductivity of 0.45 for Mg<sup>2+</sup>. The results of this study are comparable to those published.

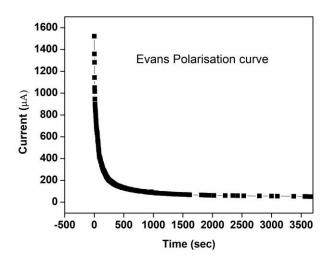


Fig 11: Evans Polarisation curve of Mg40%Agar: 60 % Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O /Mg cell

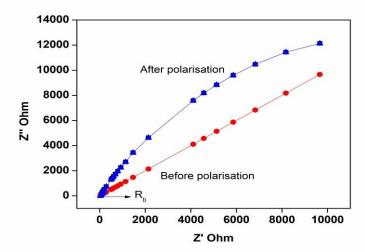


Fig 12: Cole-Cole plot of a typical symmetrical cell before and after polarization Mg/40% agar: 60% Mg(NO<sub>3</sub>)<sub>2</sub> .6H<sub>2</sub>O /Mg

## 3.9 Construction And Working of Mg Battery Cell

The effectiveness of a biopolymer electrolyte is verified through the production of a lead-magnesium battery, which uses 40% agar:60% Mg(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O as its high quality electrolyte. As the cathode, metallic magnesium is employed, and an anode formed from a 3:1 ratio of MnO<sub>2</sub> and graphite is inserted into the holder along with this biopolymer electrolyte between itself and the cathode. Figure 13 illustrates such a configuration that has an initial open circuit voltage (OCV) reading of 1.6V (Figure 14). This remains constant for 48 hours due in part due the chemical processes taking advantage associated with battery cells. At the cathode:

Mg+ 2(OH) 
$$\rightarrow$$
 Mg (OH)<sub>2</sub> + 2e At  
the cathode:  
2MnO<sub>2</sub> + H<sub>2</sub>O + 2e  $\rightarrow$  MnO<sub>2</sub> + 2OH  
Over all reaction:  
Mg + 2MnO<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  Mg(OH)<sub>2</sub> + Mn<sub>2</sub>O

The moisture/H2O present in the biopolymer membrane can be used to generate hydroxide ions found in Mg-MnO<sub>2</sub> batteries. The physical force in the small pores that are spread unevenly across the biopolymer membrane causes it to retain occluded water, a sort of non-essential water<sup>[30]</sup>.

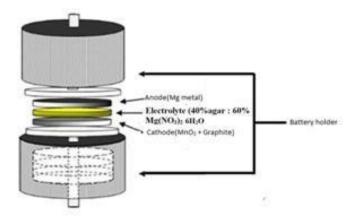


Fig 13: Schematic diagram of battery configuration.



Fig 14: Photographic image of the cell with its Open Circuit Voltage

#### 4. Conclusion

Agar-based biopolymer electrolytes  $Mg(NO_3)_2$  .6H<sub>2</sub>O were created through the casting of varying concentrations of  $Mg^{2+}$  iron and double distilled water. XRD measurements exhibited the biopolymers' amorphous nature, while FTIR proved a complex between the salt and polymer had formed. The glass transition temperature was then discovered using DSC analysis. Impedance tests yielded a maximum ionic conductivity of .74 x  $10^{-4}$  S cm<sup>-1</sup> for 40%:60%  $Mg(NO_3)_2$  .6H<sub>2</sub>O agar combination. Moreover, an exchange number study showed evidence of  $Mg^{2+}$  ions present. Mainly responsible for ionic conductivity. The main magnesium ion battery has an OCV of 1.6V at normal temperature and uses a high conductivity biopolymer electrolyte. The results show that the biopolymer electrolyte based on  $Mg(NO_3)_2$  .6H<sub>2</sub>O agar is very efficient for use in solid state devices.

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