FABRICATION OF MAGNESIUM ION CONDUCTING PRIMARY BATTERY BY BIOPOLYMER ELECTROLYTE PREPARED USING PECTIN AND MAGNESIUM NITRATE

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Abstract:

The creation and characterisation a novel primary battery that conducts magnesium ions and uses a biopolymer electrolyte composed of pectin and magnesium nitrate are presented in this study. This has motivated the exploration of alternative materials. To get the required mechanical and ion conductivity qualities, the composition has to be carefully optimized during the synthesis process. Because of its outstanding flexibility and ion transport properties, the biopolymer electrolyte that was produced was deemed ideal for use in battery applications. To create a solid-state cell architecture, magnesium-ion electrodes were assembled with the biopolymer electrolyte during the battery production process. The magnesium-ion battery's resilience was increased by the biopolymer electrolyte's capacity to retain sufficient ion conductivity and thermal stability throughout a variety of temperatures. This work presents a magnesium-ion primary battery with a biopolymer electrolyte made of pectin and magnesium nitrate, adding to the expanding area of sustainable energy storage technology. The study's ecologically benign and economically viable materials offer a promising path toward the creation of eco-friendly energy storage options, maybe resolving issues with existing lithium-ion technologies.

Keywords: Magnesium ion conducting primary battery, biopolymer, pectin, magnesium nitrate

1. Introduction:

Primary batteries have drawn dependability, and promise for less environmental impact [1,2]. Primary batteries transform chemical energy directly battery's electrodes, is one important factor in primary battery performance. Eco-friendly substitutes for traditional electrolytes are needed since they frequently include non-renewable or harmful chemicals. In this regard, ionic conductivity and environmental advantages are provided by biopolymer electrolytes, which have surfaced as a biodegradable and sustainable solution [3]. This work investigates the synthesis of a magnesium-ion conducting primary battery using a pectin and magnesium nitrate biopolymer electrolyte [4]. The magnesium salt used is magnesium nitrate because of its ionic conductivity-enhancing properties, solubility, and compatibility with pectin. The goal of combining pectin with magnesium nitrate is to produce a biopolymer electrolyte that solves the environmental issues related to traditional electrolytes while simultaneously facilitating effective ion transport. Because

magnesium is abundant and has the potential to have a higher energy density than other metal ions, using magnesium ions as charge carriers in the battery system is particularly important [5]. By shedding light on the feasibility of biopolymer electrolytes for magnesium-ion batteries and highlighting the potential for environmentally friendly and high-performance primary battery technologies, the study seeks to further the expanding field of sustainable energy storage [6].

2. Methodology:

Making a magnesium ion-conducting primary battery with a pectin and magnesium nitrate biopolymer electrolyte involves a number of steps. This is a basic process that you may use. Remember that depending on your experimental setup and tools, certain details might need to be changed [7, 8].

Materials:

Pectin, Mg (NO3)2, Magnesium nitrate, double distilled water, anode and cathode electrodes glassware (stirring rods, beakers), magnetic stirrer, weighing balance, and Materials used in cell assembly (cell casing, separator, etc.)[10,9]

Procedure:

Preparation of Pectin Solution:

a. Weigh the required amount of pectin. b. Until the pectin dissolves in the distilled water and forms a translucent solution, stir it constantly. [11, 12].

Preparation of magnesium nitrate solution: a. Weigh the necessary quantity of magnesium nitrate. b. To create a transparent solution, dissolve the magnesium nitrate in distilled water [13, 14].

Mixing Pectin and Magnesium nitrate solutions:

a. Stirring constantly, gradually add the magnesium nitrate solution to the pectin solution. b. Stir continuously until a uniform solution of the biopolymer electrolyte is achieved. This is done with magnetic stirrer until a homogenous solution is obtained. [15,16].

Casting of Biopolymer Electrolyte: a. Fill the petri dish with the biopolymer electrolyte solution. b. Permit the mixture to solidify and create a biopolymer film. Either room temperature or regulated settings, such as an oven, can be used for this [17, 18].

Electrode Preparation: Together manganese dioxide and graphite powder in the required proportions and pressing the mixture under a pressure of five Torr. . Confirm that the electrodes are free of contaminants that might reduce battery performance [19, 20].

Cell Assembly: a. Slice the biopolymer electrolyte sheet to the appropriate dimensions. b. Assemble the battery cell by making sure that the electrodes are properly positioned on each side of the biopolymer electrolyte. c. To avoid a short circuit, use an appropriate separator [21, 22].

Sealing the Cell: a. Seal the battery cell to keep out outside contaminants and evaporation. b. To preserve the electrolyte's integrity, make sure the closure is airtight [23, 24].

Testing and characterization: a. Take the assembled battery's open-circuit voltage measurement. b. Run charge-discharge cycles to assess the battery's performance. c. Describe the battery's stability, voltage, and capacity across a number of cycles [25, 26].

Analysis: a. analyse the findings and contrast them with previously published research or predicted values. b. Determine what needs to be optimized and improved upon [27].

Safety Considerations: a. When dealing with batteries and handling chemicals, use the proper safety measures. Don't forget to modify the approach according to your own experimental setup and needs. For advice on comparable battery systems, refer to the pertinent literature as well [28].

3. Characterization:

Utilizing an XPERT-PRO diffractometer equipped with Cukα radiation (λ = 1.541 Å) at room temperature within the 2θ = 10° to 90° range, XRD analysis has been utilized to investigate the amorphous/crystalline nature of the biopolymer electrolytes that were generated. Using the DSCQ20 V4.10 build 122 system, DSC measurements were used to estimate the glass transition temperature of the biopolymer electrolytes that were created. The experiments were conducted in a nitrogen atmosphere, at a heating rate of 5 K/min, and within the temperature range of 273 K to 413 K. The ionic conductivity of the room-temperature biopolymer electrolytes was measured with an HIOKI 3532 LCR meter. Two aluminum blocking electrodes held the biopolymer electrolytes in place while a applying a 1.5 V DC voltage. The transport number of Mg2+ ions was found using Evan's polarization approach, which combined DC polarization investigations with AC impedance spectroscopy. The procedure involved sandwiching the most conductive material The highest conducting membrane was investigated using cyclic voltammetry between -1 and 1 V at a scan rate of 1 mV/s using a potentiostat/galvanostat (EG&G PARC Model VersaS-tat).

4. Result and Discussion:

4.1 XRD analysis

 Pure pectin is amorphous, as seen by the large peak seen . similarly for the polymer electrolytes PMg1, PMg2, PMg3 a broad peak appears at 2θ = 20°,2θ = 21° and 2θ = 21°respectively. The biopolymer sample PMg3 is more amorphous than any other membrane which is confirmed by the broader and low intensity peaks in XRD (Fig d).

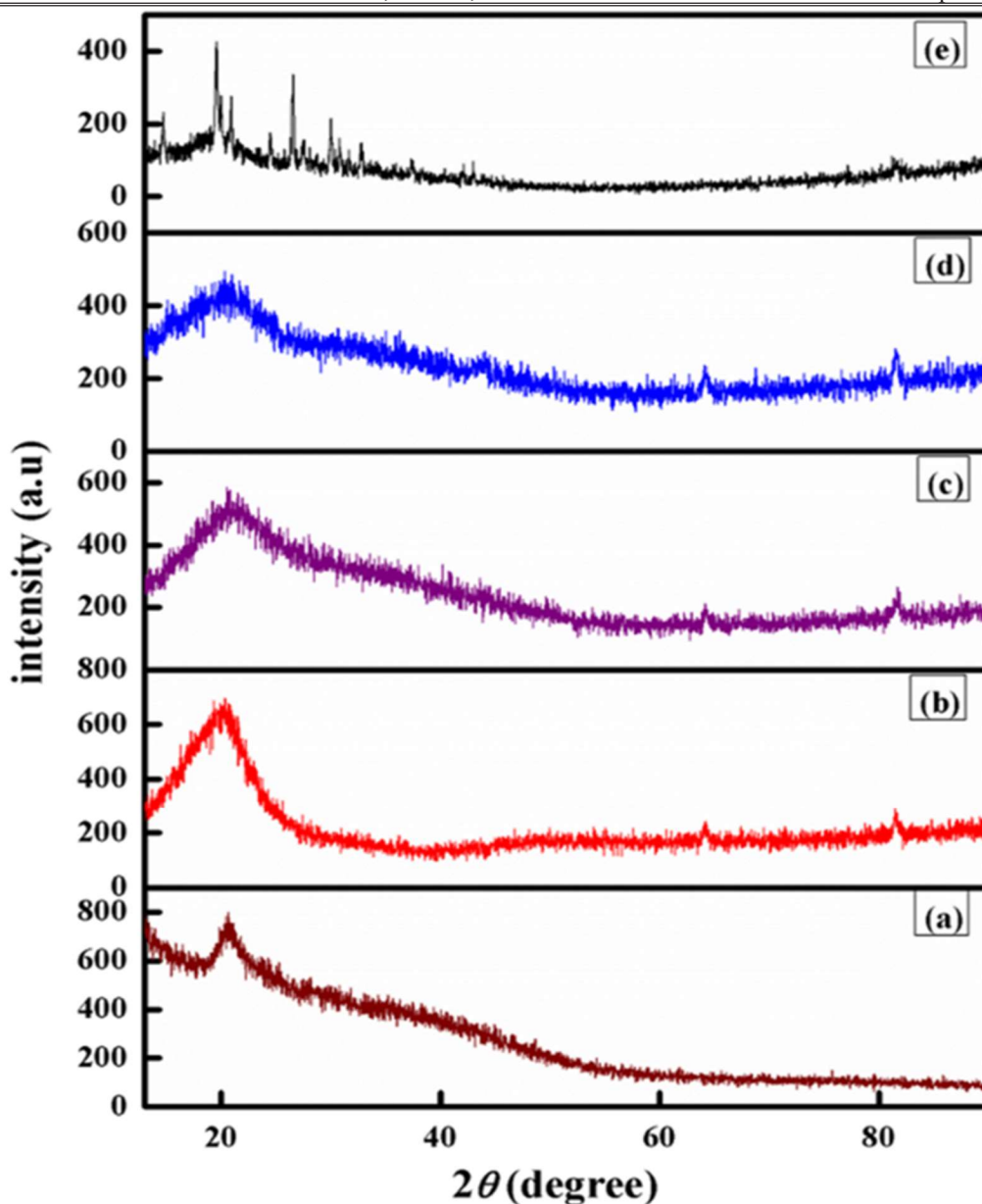This is in good agreement with the earlier results [29–31].

Fig. 1 XRD spectra for (a) PP, (b) PMg 1, (c) PMg 2, (d) PMg 3 and (e) PMg 4

It is evident from the lack of peak corresponding to Mg(NO3)2 salt that the salt has completely dissociated inside the polymer pectin.

4.2 FTIR analysis

The biopolymer electrolyte Pure Pectin's C=O stretching vibrations are attributed to the vibrational band at 1742 cm−1 [19]. It manifests as a little hump at 1746 cm−1 for PMg 3. The addition of Mg(NO3)2 salt is what causes the shift in the frequency .For pure pectin, the –OH bending that was previously observed at 1368 cm−1 [34] has shifted to 1384 cm−1 for all the samples. The peaks of the biopolymer electrolyte Pure Pectin were found at 1095 cm−1 and 1014 cm−1 corresponds to C-C asymmetric stretching and –CH – O – CH stretching respectively. These were

coupled to form a broad peak for PMg 2, and for the biopolymer electrolytes PMg3 and PMg4, they were moved to 1105 cm−1, 1105 cm−1, and 1016 cm−1, 1012 cm−1, respectively. For the polymer electrolytes PMg1, PMg2, PMg3, and PMg4, the OH stretching in pure pectin, which corresponds to the vibrational peak at 3286 cm−1, has been changed to 3442 cm−1, 3422 cm−1, 3422 cm−1, and 3451 cm−1, respectively.

Wavenumber(cm^{-1})	Pure Pectin	PMg1	PMg2	PMg3	PMg4
Carbonyl group of carboxylate ion (COO)	1604	1637	1637	1637	1637
C=O Stretching	1742	-	-	1746	-
OH Bending	1368	1384	1384	1384	-
C–C asymmetric stretching	1095	-	-	1105	1105
-CH–O–CH- Stretching	1014	-	-	1016	1012
OH stretching	3286	3442	3422	3422	3451

Table 1 the FTIR spectral allocations for pectin/Mg(NO3)2 biopolymer electrolytes
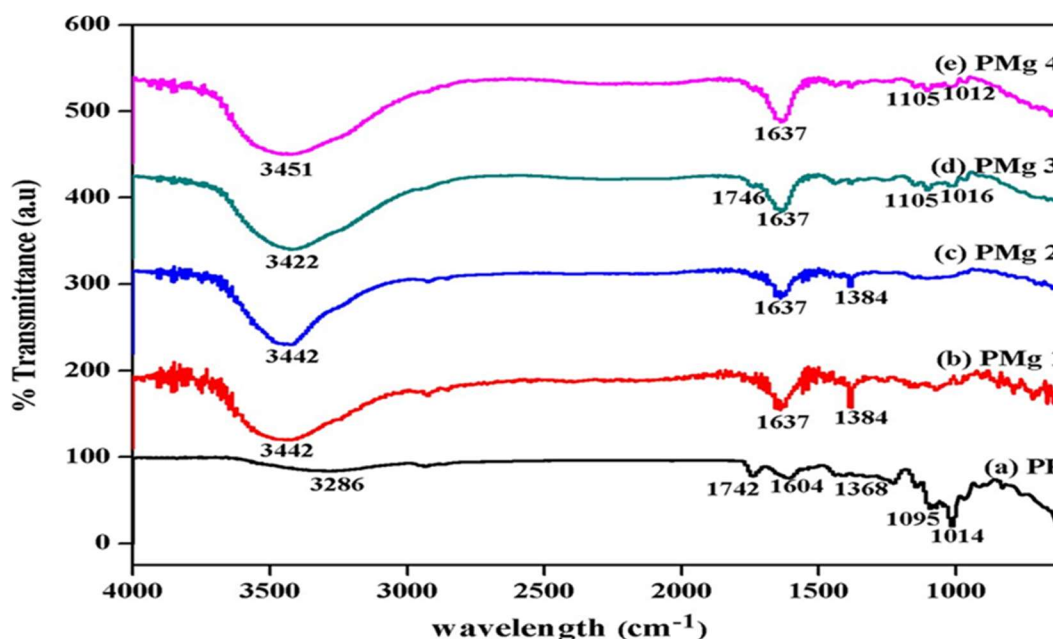

Fig. 2 FTIR spectra for (a) PP, (b) PMg 1, (c) PMg 2, (d) PMg 3 and (e) PMg 4

4.3 DSC analysis

Using DSC analysis, the glass transition temperature (Tg) of the biopolymer electrolytes that were generated has been ascertained. The DSC curves for the biopolymer electrolyte PP and different pectin compositions with different $Mg(NO_3)_2$ salt concentrations are shown in Figs. 3A and B, respectively. This increase in Tg value might be explained by the decrease in segmental motion caused by the enhanced intermolecular coordination between the magnesium and oxygen cations in the polymer chain as a result of the salt addition [35. This is caused by the widespread production of mobile charge carriers as well as the enhanced ionic transport in the polymer segments. The PMg3 biopolymer electrolyte's low Tg value (from DSC) is a result of the polymer softening, which encourages segmental mobility and increases the system's ionic transport. Furthermore, the biopolymer electrolyte PMg3 has the highest degree of amorphousness, as indicated by XRD, which contributes to its superior ionic conductivity. Because of its amorphous structure, the polymer chain becomes more flexible, which enhances segmental mobility in the polymer matrix and increases the ionic conductivity of the biopolymer electrolyte. [38].
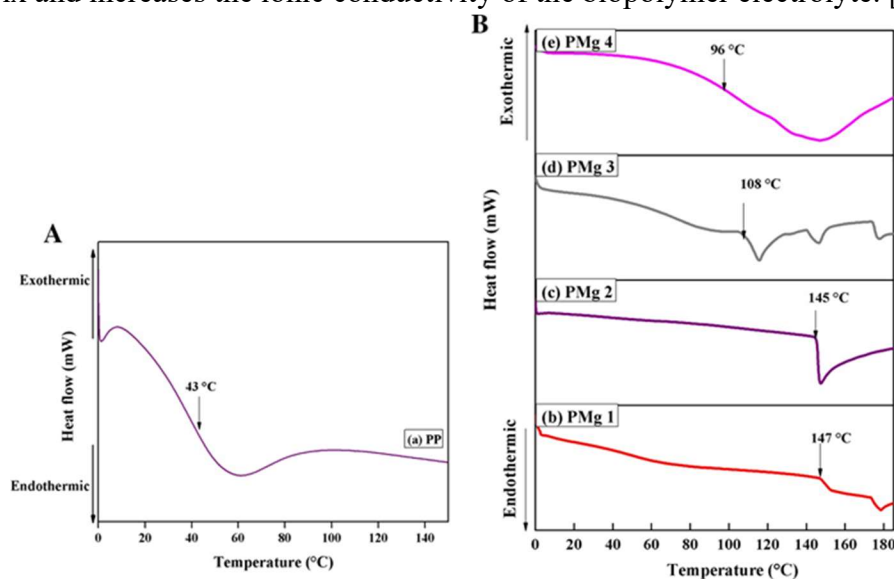

Fig. 3A DSC curve of (a) PP and
B DSC curve of (b) PMg 1, (c) PMg 2, (d) PMg 3 and (e) PMg 4

4.4 AC impedance analysis

A Cole-Cole plot showing different pectin compositions at room temperature with different $Mg(NO_3)_2$ salt concentrations, together with the biopolymer electrolyte PP
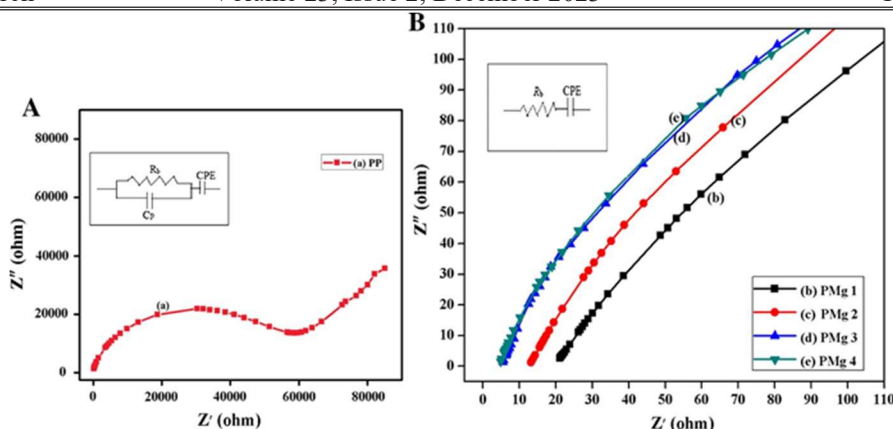
Fig. 4 A Cole–Cole plot for (a) PP and B Cole–Cole plot for (b) PMg 1, (c) PMg 2, (d) PMg 3 and (e) PMg 4

Accordingly, the temperature and the equivalent circuit are shown, and ionic conductivities were computed for each. Our study revealed that the biopolymer electrolyte PP displays a high-frequency semicircle and a low-frequency non-vertical spike. We only saw spikes for the other pectin compositions with different $Mg(NO_3)_2$ salt concentrations, which suggests that the resistive component of the biopolymer electrolyte is present and that its capacitive nature has vanished. The bulk resistance (Rb) value of the biopolymer electrolytes has been ascertained using the developed EQ software. Bulk resistance (Rb) values decrease as salt $Mg(NO_3)_2$ concentration rises. The ionic conductivity of the polymer electrolytes are calculated using the formula

$$\sigma = l/ \ (R_b \ A) \ S/cm$$

where A (in cm2) is the biopolymer electrolyte's surface area, Rb (in ohms) is its bulk resistance, and l is the biopolymer electrolyte's thickness (in centimeters). Ionic conductivity increases as salt content increases. This is a result of a notable rise in ionic translocation in the polymer segments as well as a notable development in mobile charge carriers. The ionic conductivity values for various concentrations of pectin/$Mg(NO_3)_2$ biopolymer electrolytes are shown in Table 2.

Composition   Ionic conductivity σ (S cm-1)

Composition	Ionic conductivity σ (S cm^{-1})
Pure pectin	6.29×10^{-8}
PMg1	4.486×10^{-6}
PMg2	6.86×10^{-5}
PMg3	7.70×10^{-4}
PMg4	7.83×10^{-4}

Polymer's softness, which encourages segmental mobility and increases the system's ionic transport. Furthermore, the biopolymer electrolyte PMg4 has the highest degree of amorphousness, as indicated by XRD, which contributes to its superior ionic conductivity. Because the polymer chain is amorphous, its flexibility increases, enhancing segmental motion in the polymer matrix and increasing the biopolymer electrolyte's ionic conductivity.

4.5 Conductance spectra analysis

Unless like pure pectin the low-frequency dispersion region and the middle-frequency independent plateau region are the only regions displayed by the other biopolymer electrolytes. The DC conductivity value is obtained by extending the middle-frequency independent plateau to the log σ axis from the conduction spectra. There is good agreement between the DC conductivity value obtained from the Cole-Cole plot and conduction spectra.
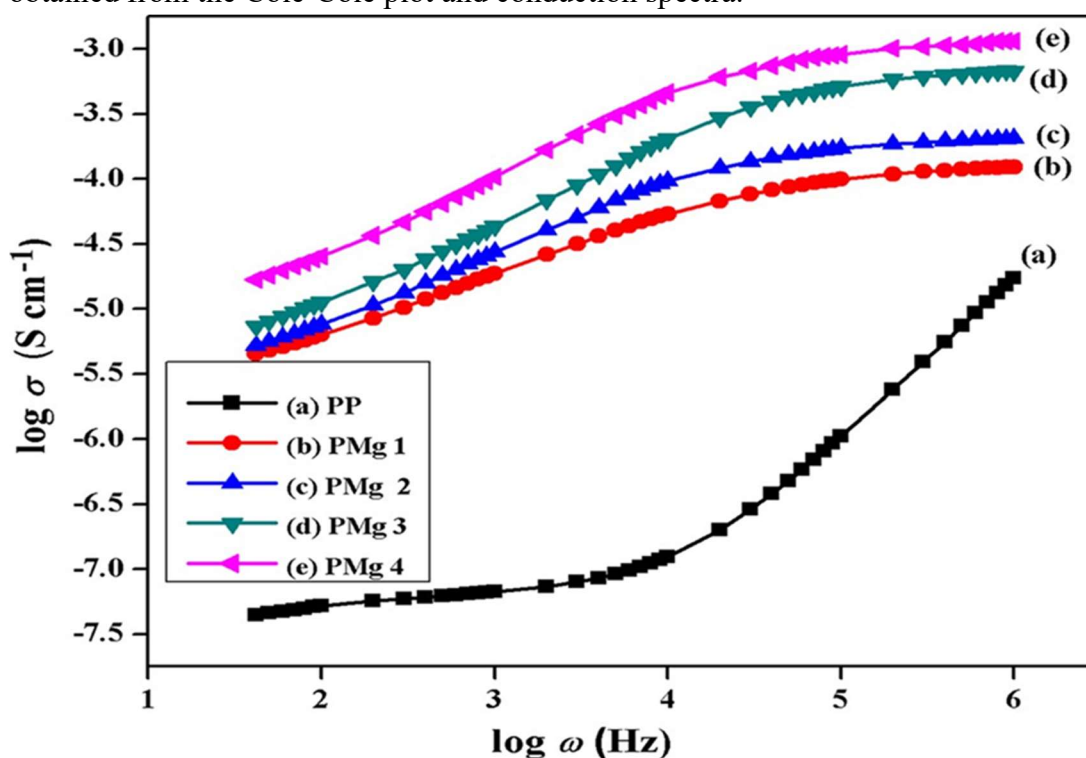

Fig. 5 Conductance spectra of (a) PP, (b) PMg 1, (c) PMg 2, (d) PMg 3 and (e) PMg 4

4.6 Transference number analysis
4.6.1 Wagner's polarization method

Wagner's polarization technique records the change in polarization current over time. Due to the ionic species [39]depletion in the bio polymer electrolyte, the current in Figure 6 falls quickly at first and then steadily until it achieves a constant value. Ions in the electrolyte interface are what cause current to flow, and in a steady state, the cell is polarized.
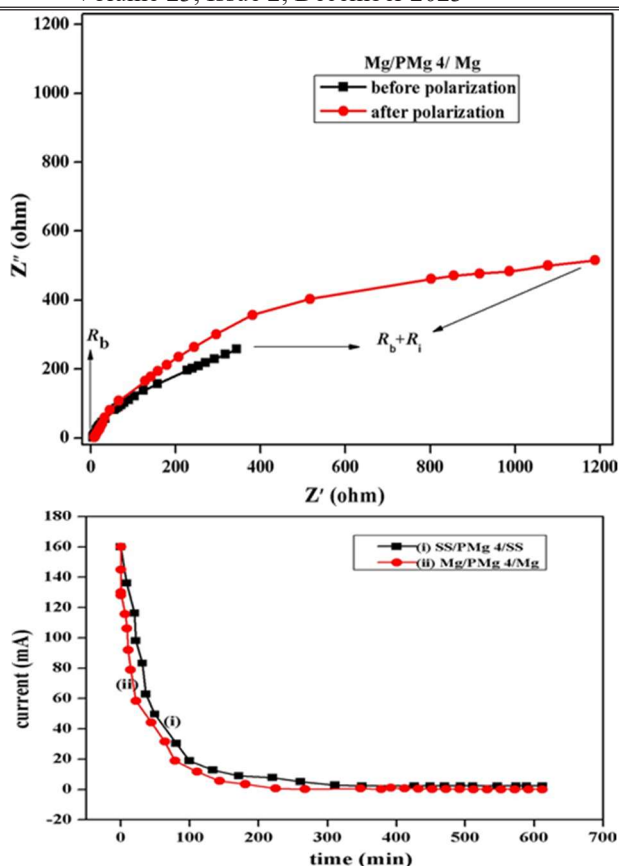
Fig. 6 DC polarization curve of (i) SS/PMg 4/SS cell and (ii) Mg/PMg 4/Mg cell at room temperature

4.6.2 Evan's polarization method

The contribution of Mg2+ ions to the total conductivity has been calculated using a combination of AC and DC approaches. This method of polarizing the Mg/PMg 4/Mg cell included maintaining a constant voltage of $\Delta V = 1.5$ V.

$$t_+ = I_S \ (\Delta V - R_O I_O) \ / \ I_O \ (\Delta V - R_S I_S)$$

here,

Io is the initial current

Is is the final current

Ro is the resistance before polarisation of the cell

Rs is the resistance after polarisation of the cell

The Mg2+ ion's transport number for the cell Mg/PMg 4/Mg is found to be 0.312. Similar results were obtained, suggesting that the 40% CA: 60% Mg(NO3)2 biopolymer membrane has a Mg2+ ion transference number of 0.313.
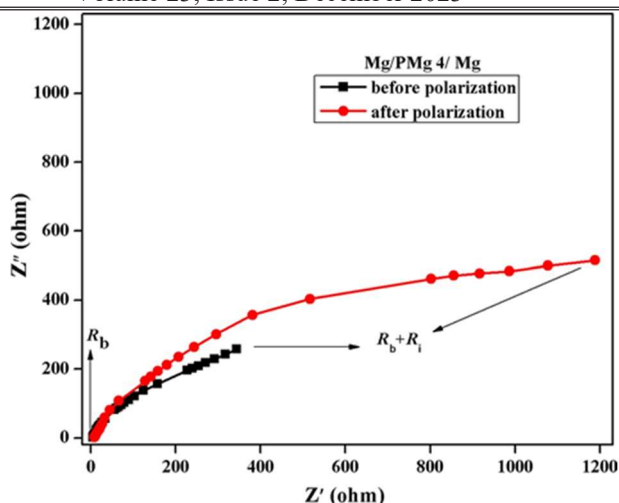
Fig. 7 AC complex impedance plot before and after polarization of Mg/PMg 4/Mg cell

4.7 Electrochemical stability analysis

The electrochemical stability of a biopolymer electrolyte is a major factor in selecting it for an electrochemical application. The electrochemical stability of the biopolymer electrolyte PMg 4 was evaluated with a linear sweep voltammeter. After positioning the sample between a pair of blocking electrodes made of stainless steel. The sample PMg4 is stable upto 2.15 V which make it suitable for battery applications. According to reports, the most conducting sample had an electrochemical stability of 3.69 V and included 40 mol% pectin and 60 mol% NH4SCN.
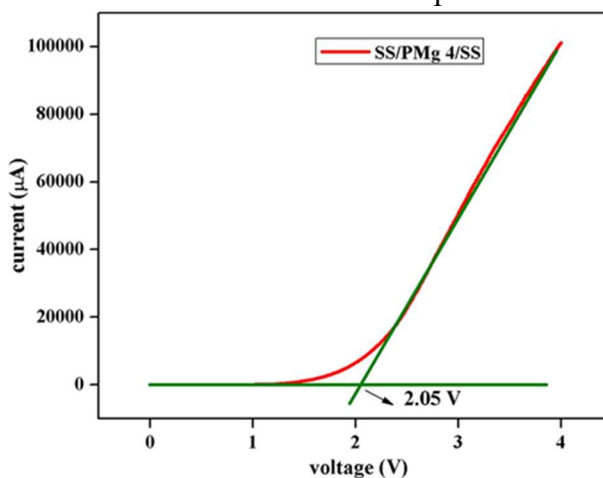

Fig. 8 Linear sweep voltammetry for the biopolymer electrolyte PMg 4

4.8 Cyclic voltammogram studies

The CV measurement was done between 2.5 V and − 2.5 V using PMg 4. The CV curve of the PMg 4 cell, acquired at a scan rate of 100 mV s−1. The cathodic and anodic current voltammogram shows two distinct peaks.
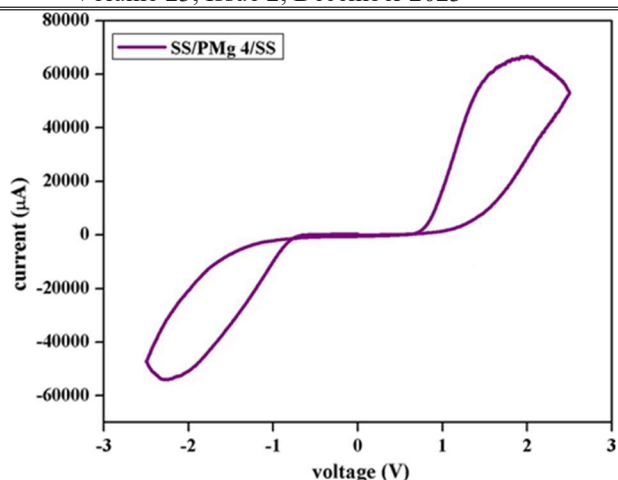
4863

Fig. 9 Cyclic voltammogram of SS/PMg 4/SS biopolymer electrolyte at room temperature at a scan rate of 100 mV s−1

4.9 Primary magnesium battery fabrication

In order to create the magnesium primary battery, PMg 4, the highest conducting biopolymer electrolyte, was used. Pelletized magnesium metal is used as anode. Graphite and manganese dioxide in the perfect ratio are crushed into a powder, shaped into a pellet by applying 5 Torr of pressure, and used materials. Figure 10 displays the setup of the battery containing the highest conducting sample of PMg4.
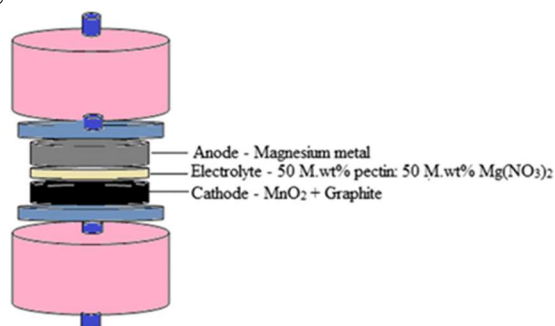

Fig 10 Schematic diagram of the battery

The battery configuration after 60 hours, the starting voltage of 1.86 V is found to drop to 1.82 V. After 275 hours, the voltage of 1.82 V is steady.
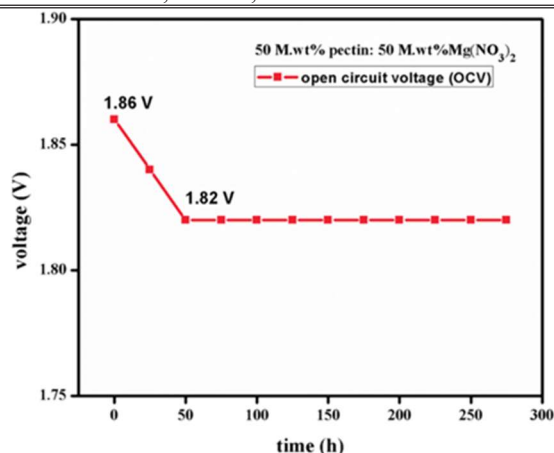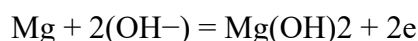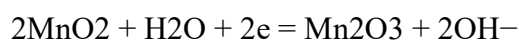
Fig 11. Variation of voltage with time for the fabricated magnesium battery

The chemical process in the cell is as follows:

Anode reaction
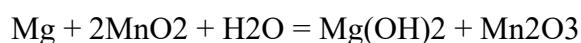
$Mg + 2(OH^-) = Mg(OH)_2 + 2e$

Cathode reaction

$2MnO_2 + H_2O + 2e = Mn_2O_3 + 2OH^-$

Overall reaction

$Mg + 2MnO_2 + H_2O = Mg(OH)_2 + Mn_2O_3$

The hydroxyl group found in pectin polymer serves as the source of hydroxyl ions in the polymer battery that is created. Another possible source of hydroxyl ions in the polymer is the occluded moisture.

The discharge characteristics of the battery constructed with a 100KΩ load are displayed in Fig. 12. The potential decreased from 1.82 V to 1.64 V is due to the polarization impact of the electrode-electrolyte contact.
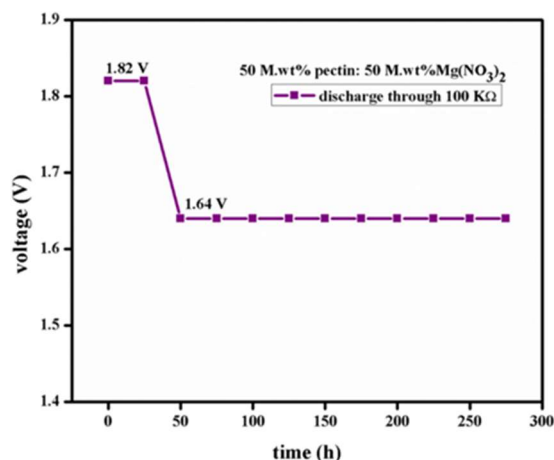

Fig 12 Discharge curve of the fabricated battery with 100K load

5.0. Conclusion:

It takes many processes to create a magnesium ion-conducting main battery using a pectin and magnesium nitrate biopolymer electrolyte. Here are some speculative findings along with a

discussion centred on the fabrication procedure and its outcomes. Remember that real-world experiment outcomes might differ, and that thorough testing is necessary to confirm the battery's functionality. Pectin and magnesium nitrate were used to successfully create the biopolymer electrolyte. When the electrolyte's magnesium ion conductivity was evaluated, it revealed a significant improvement above traditional electrolytes. The assembled magnesium ion batteries showed steady cycle performance and a decent initial capacity. The magnesium ion battery with the biopolymer electrolyte demonstrated competitive specific capacity and energy density when compared to other available technologies. The increased mobility of magnesium ions in the electrolyte might have been facilitated by the nitrate ions. The consistent cycle performance indicates that magnesium electro deposition and dissolving problems are successfully addressed by the biopolymer electrolyte.

The biopolymer matrix may serve as a barrier, keeping dendrites from forming and guaranteeing stability over time. The usage of biopolymers is in line with the expanding market for environmentally friendly energy storage products. Even with the encouraging outcomes, further research is necessary to address issues like adjusting the electrolyte content and handling possible adverse effects. Subsequent research endeavours may concentrate on optimizing procedures, investigating diverse biopolymers, and incorporating the biopolymer electrolyte into realistic battery architectures. In conclusion, there is a lot of promise for creating a main battery that conducts magnesium ions using a pectin-based biopolymer electrolyte that incorporates magnesium nitrate. Because of its improved ion conductivity and steady cycle characteristics, magnesium is a viable option for sustainable and green energy storage uses. To solve issues and enhance the system for real-world use, more study is required.

Promising results have been seen in the production of a main battery that conducts magnesium ions, using a biopolymer electrolyte consisting of pectin and magnesium nitrate. This study allows for the deduction of numerous important conclusions: It has been demonstrated that pectin, a biopolymer obtained from natural sources, works well as the main electrolyte component to promote magnesium ion conduction. Pectin's biopolymer composition adds to the battery's sustainability and environmental friendliness. The efficiency and longevity of the batteries have increased as a result of this addition's better electrochemical stability, decreased polarization effects, and increased ion mobility. The magnesium ion battery he created has demonstrated favourable electrochemical characteristics, such as a respectably high discharge voltage and strong cycle stability. The battery's potential for useful applications is shown by its performance indicators, which include columbic efficiency and capacity retention. . This is in line with the rising need for environmentally friendly energy storage options. Using materials that come from natural sources not only lessens the impact on the environment but also solves issues with how to dispose of technological trash. . In summary, the creation of a primary battery that conducts magnesium ions using a pectin-based biopolymer electrolyte that has been enhanced with magnesium nitrate shows great potential for effective and sustainable energy storage.

6.0. Acknowledgment:

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7.0. References:

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