



FABRICATION OF A MAGNESIUM ION CONDUCTING PRIMARY BATTERY USING BIOPOLYMER ELECTROLYTE PREPARED USING CELLULOSE ACETATE AND MAGNESIUM PERCHLORATE

R. Sujatha^{1,*}, C. Shanmugapriya²

Abstract:

In this research paper we are trying to study these elements can effectively tackle the drawbacks of conventional electrolytes used in magnesium-ion batteries. The electrolyte's overall environmental friendliness is enhanced by the biocompatible and sustainable foundation that the cellulose acetate matrix offers. Magnesium perchlorate, as the conductive salt, increases the passage of magnesium ions inside the electrolyte, improving ion conductivity. The rationale behind using DMFO as the solvent is its capacity to efficiently dissolve magnesium perchlorate and cellulose acetate, guaranteeing a uniform electrolyte composition. The magnesium ion conductivity, reduced internal resistance, and enhanced electrochemical stability shown in the data are encouraging and suggest that the electrolyte may be suitable for use in advanced battery applications.

Keywords: Magnesium ion conducting biopolymer electrolyte , cellulose acetate , magnesium per chlorate, biopolymer electrolytes, ionic conductivity, highest conducting sample, FTIR, XRD.

¹*Reg.No: 19221232132002, Research scholar, PG and Research Department of Physics, Sri Paramakalyani College, Alwarkuruchi, Affiliated to Manonmaniam Sundaranar University, Abhishekapatti, Tirunelveli - 627012, Tamilnadu, India.

²Assistant Professor, PG and Research Department of Physics, Sri Paramakalyani College, Alwarkuruchi, Tamilnadu, India.

***Corresponding Author:** R. Sujatha

*Email id: sujathanagarajan8082@gmail.com

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Introduction:

Achieving the full potential of magnesium-ion batteries still requires developing effective electrolytes for magnesium-ion conduction one source of magnesium ions that facilitates effective ion transport in the electrolyte is magnesium perchlorate. The solvent of choice, dimethylformamide, is essential for dissolving magnesium perchlorate and cellulose acetate to create a uniform and conductive electrolyte solution. It is anticipated that the electrolyte's distinct composition would solve issues with low conductivity and unstable performance, which are frequently present in magnesium-ion battery electrolytes [1-4]. The inquiry encompasses a thorough analysis of the thermal stability, electrochemical performance, and physicochemical characteristics of the electrolyte [5]. The viability of incorporating the created biopolymer electrolyte into workable magnesium-ion battery systems is also investigated in this study. The findings of this study have the potential to greatly develop the technology of magnesium-ion batteries, providing a reliable and effective energy storage option for a range of uses in the quickly changing fields of portable electronics and renewable energy[6].

Methodology:

It takes many processes to create a magnesium ion conducting biopolymer electrolyte with magnesium perchlorate and cellulose acetate and dimethylformamide (DMFO) as the solvent. Here is a generic approach that you may use. [7,8].

Resources:

The biopolymer known as cellulose acetate (CA) will serve as the electrolyte's structural support.

Magnesium Perchlorate : Magnesium salt to give magnesium ions for conduction.

Dimethylformamide (DMFO): A solvent used to dissolve magnesium perchlorate and cellulose acetate.

Stirring equipment : For mixing and homogenizing the solution.

Glassware: Stir bars, beakers, and flasks for preparation.

Gloves and safety equipment: To provide security when working with chemicals.

How to proceed:

Getting cellulose acetate Ready Resolution:

Weigh the cellulose acetate to the necessary amount. Transfer the cellulose acetate into a dry, clean container. Pour an adequate amount of DMFO into the container. Until the cellulose acetate is fully dissolved, keep stirring the liquid. It can take some time to complete this[9,10].

Adding magnesium per chlorate salt: Determine the necessary magnesium perchlorate weight. Stirring constantly, gradually add the magnesium perchlorate to the cellulose acetate and DMFO solution. Until the magnesium perchlorate is completely dissolved, keep stirring[11].

Homogenization: For reliable mixing, a magnetic stirrer or other such tool can be useful[12].

The Electrolyte Film Casting Process: Transfer the uniform mixture onto a spotless, level surface, such as a glass petri dish. To leave a solid electrolyte layer behind, let the solvent evaporate.

Drying: To guarantee consistent drying, place the film in a controlled setting. Depending on the thickness of the film and the surrounding circumstances, this might take some time[13].

Characterization: Assess the electrolyte film's conductivity using appropriate methods such as XRD, FTIR, impedance spectroscopy.[14]

Assemble the battery by cutting the electrolyte sheet to the appropriate dimensions. Assemble the battery by sandwiching the electrolyte sheet between suitable electrodes (anode and cathode)[15].

Performance testing: Evaluate the stability, capacity, and charge/discharge cycles of the battery.

This approach offers a broad framework; parameters may need to be modified in accordance with your particular needs and the outcomes of your experiments.[16].

Characterization:

To comprehend the electrolyte's performance and applicability for various battery systems, it is essential to characterize it. Some important characterisation strategies that can be used are listed below: In the cellulose acetate and magnesium perchlorate composite, functional groups may be identified and chemical bonds can be examined using FTIR[17]. This aids in verifying the biopolymer electrolyte's composition. Information on the electrolyte's crystalline structure may be obtained by XRD. It facilitates comprehension of the polymer chains' organization and the existence of any crystalline phases [18]. The thermal behaviour of the electrolyte, including phase transitions, glass transition temperature, and thermal stability, may be investigated using DSC. TGA is helpful in examining the biopolymer electrolyte's heat stability and breakdown behaviour. It can provide details on decomposition temperatures and weight loss.[19,20] Optically measure the electrolyte's ionic conductivity using impedance spectroscopy or other suitable methods. This is essential to comprehending how well the

electrolyte facilitates ion movement. When attempting to comprehend the redox behaviour of magnesium ions, they are especially helpful. This has significance in scenarios where the electrolyte could encounter mechanical strain[21,22]. This is crucial for determining how simple it will be to process and handle throughout battery manufacture. Examine the solubility of magnesium perchlorate in cellulose acetate and the DMFO solvent. Ensuring the stability and uniformity of the electrolyte solution is crucial these characterization methods provide you a thorough grasp of the mechanical, thermal, electrochemical, and structural characteristics of the magnesium ion-conducting biopolymer electrolyte, which is helpful information for future battery applications.

Result and Discussion:

It provides structural stability and adds to the overall mechanical strength of the electrolyte by acting as the polymer matrix. It works as the magnesium perchlorate salt, dissociating into magnesium ions (Mg^{2+}) and perchlorate ions (ClO_4^-), promoting ion conduction [23, 24]. This solvent is used to dissolve magnesium perchlorate and cellulose acetate, creating a homogenous electrolyte solution. Utilized to verify the development of the intended polymer matrix and examine the chemical structure of the electrolyte's constituent parts. Provide details regarding the electrolyte's structure and crystallinity. Used to verify homogeneity by examining the electrolyte's surface morphology. Check the electrolyte's capacity to conduct magnesium ions. This is an important battery performance metric. Analyse the battery's performance and electrochemical stability across several cycles of charge and discharge. Analyse voltage profiles to comprehend the battery's energy storage and release properties. Examine the electrolyte components' phase transitions and thermal stability [25,26]. Talk about how the findings stack up against those of other related research in the area. Emphasize the advantages and possible drawbacks of the established electrolyte system. Make recommendations for possible modifications or enhancements to increase battery performance.

XRD Analysis:

The prepared samples were analysed for XRD studies in order to investigate their crystalline/amorphous character. The XRD patterns for the prepared samples are displayed in Fig. 1.

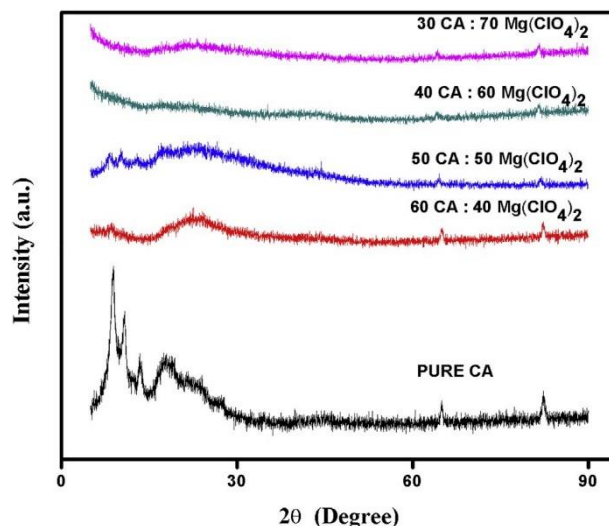


Figure 1: XRD patterns of the pure cellulose acetate and magnesium perchlorate doped cellulose acetate polymer electrolytes.

Pure cellulose acetate exhibits peaks at $2\theta = 9^\circ, 13^\circ, 18^\circ, 27^\circ$ and 65° which are consistent with the previous findings[12,27]. The amorphous character of the electrolytes is enhanced by the doping salt, as seen by the decreasing peak intensity as the magnesium perchlorate salt concentration increases. The Hodge et al. [28] criteria, which establishes a correlation between peak intensity and degree of crystallinity, was used to interpret this data. A maximum of amorphous nature is noted in the 40% cellulose acetate:60% magnesium perchlorate sample. Moreover, the salt recrystallizes with the further addition of magnesium perchlorate salt, which lessens the amorphous character of the polymer matrix.

FTIR Analysis:

The interactions between the salt and the polymer is studied by FTIR spectroscopy through the alteration of the vibrational modes of the electrolyte under study. In the wavenumber range of 400 to 4000 cm^{-1} . Figure 2 displays the Fourier Transform Infrared Spectroscopy spectra of the magnesium perchlorate doped cellulose acetate samples. Table 1 lists the relevant vibration frequencies that were allocated.

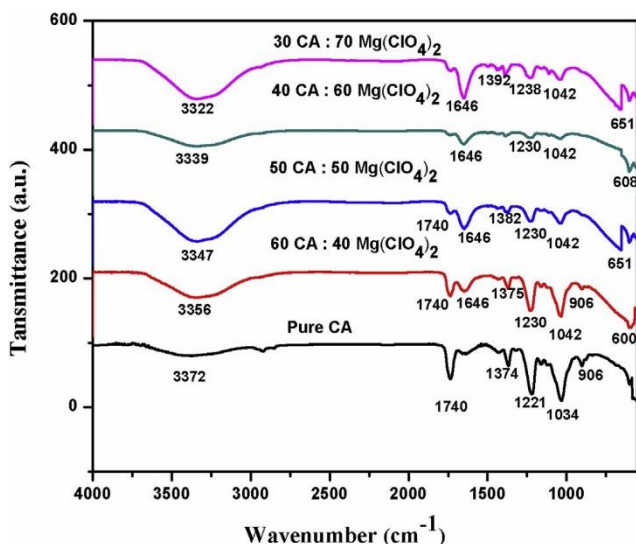


Figure 2: FTIR spectrum of the pure cellulose acetate and magnesium perchlorate doped cellulose acetate polymer electrolytes.

The absorption peak in pure cellulose acetate observed at 3372cm^{-1} is assigned to OH stretching and is been shifted to 3356cm^{-1} , 3347cm^{-1} , 3339cm^{-1} and 3322cm^{-1} for the samples 60%cellulose acetate:40% magnesium per chlorate, 50%cellulose acetate:50% magnesium perchlorate, 40% cellulose acetate:60% magnesium per chlorate, 30%cellulose acetate:70% magnesium per chlorate respectively. The C=O stretching vibration of the pure cellulose acetate is obtained at 1740cm^{-1} [29]. In addition of the salt to the polymer, the intensity of this vibration decreases [30] which is due to the dipole and ion interaction [31,32]. This peak remains the same for 60%cellulose acetate:40% magnesium per

chlorate and 50% cellulose acetate:50% magnesium per chlorate samples. The peak at 1646cm^{-1} in the salt doped samples is due to carbonyl group C=O stretching which is absent in pure cellulose acetate. The absorption peak observed at 1374cm^{-1} for pure cellulose acetate of medium intensity is due to the CH bending and is been shifted to 1375cm^{-1} , 1322cm^{-1} and 1392cm^{-1} for 60%cellulose acetate:40% magnesium per chlorate, 50%cellulose acetate:50% magnesium per chlorate and 30%cellulose acetate: 70% magnesium per chlorate. The peak at 1221cm^{-1} corresponding to CO stretching for the pure cellulose acetate is been shifted to 1230cm^{-1} for 60%cellulose acetate:40% magnesium per chlorate, 50%cellulose acetate:50 magnesium per chlorate, 40%cellulose acetate:60% magnesium per chlorate samples and at 1238cm^{-1} for 30% cellulose acetate:70% magnesium per chlorate [31]. The 1034cm^{-1} peak of pure cellulose acetate is attributed to COC stretching and is been shifted to 1042cm^{-1} for all the magnesium per chlorate doped samples. The existence of Cl^{-} ion in the magnesium per chlorate added samples is ascertained by the peak observed around 608cm^{-1} in all the samples [33].

The maximum ionic conductivity is favoured by the high ion mobility. This suggests that magnesium per chlorate may be able to act as the system's charge carrier. The conduction mechanism occurs when the weakly constrained Mg^{2+} ion hops over the C=O host polymer's coordinating site [34]. These findings provide an explanation for the host polymer's complex formation with the salt.

Table 1 FTIR assignments of the pure cellulose acetate and magnesium per chlorate doped polymer electrolytes

Wavenumbers (cm^{-1})					
Pure cellulose acetate	60%cellulose acetate:40% magnesium per chlorate	50%cellulose acetate:50% magnesium per chlorate	40%cellulose acetate:60% magnesium per chlorate	30%cellulose acetate:70% magnesium per chlorate	Assignments
3372	3356	3347	3339	3322	OH stretching
1740	1740	1740	-	-	C=O symmetric stretching
	1646	1646	1646	1646	C=O stretching (carbonyl group)
1374	1375	1382	-	1392	CH bending
1221	1230	1230	1230	1238	CO stretching
1034	1040	1042	1042	1042	COC stretching

DSC Analysis:

The differential scanning thermographs of the pure cellulose acetate and the magnesium per chlorate

doped cellulose acetate samples are shown in the fig3.

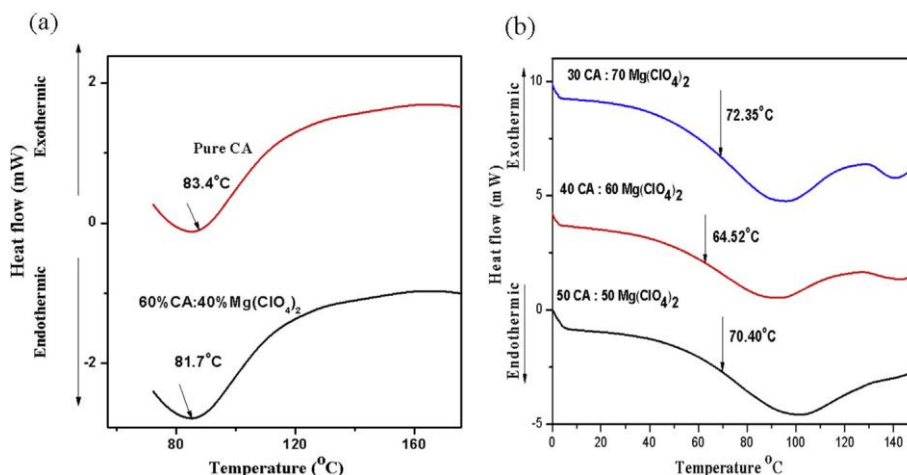


Fig 3. Differential Scanning thermographs of the pure cellulose acetate and the magnesium perchlorate doped cellulose acetate polymer electrolytes.

The pure cellulose acetate has a T_g value of 83.4°C. Monisha et al. had previously reported a T_g value that is comparable. At varying concentrations, the T_g exhibits a minor shift towards lower temperatures. Because of the magnesium salt's plasticizing impact on the biopolymer structure, the

lowering T_g value indicates an influence of the salt on softening the biopolymer. Magnesium ion's mobilization within the membrane serves a purpose [35]. The T_g values of the prepared samples are listed in the table 2.

Sl. No.	Samples	Glasstransition Temperature (T_g) (°C) Rounded off value
1	Pure Cellulose Acetate	83
2	60%cellulose acetate:40%magnesium per chlorate	82
3	50%cellulose acetate:50%magnesium per chlorate	70
4	40%cellulose acetate:60%magnesium per chlorate	64
5	30%cellulose acetate:70%magnesium per chlorate	72

Table 2: Glass transition temperatures of the pure cellulose acetate and magnesium perchlorate doped cellulose acetate polymer electrolytes

AC Impedance Analysis

A cole-cole plot showing different cellulose acetate compositions at room temperature with different

magnesium perchlorate concentrations is shown in the fig 4

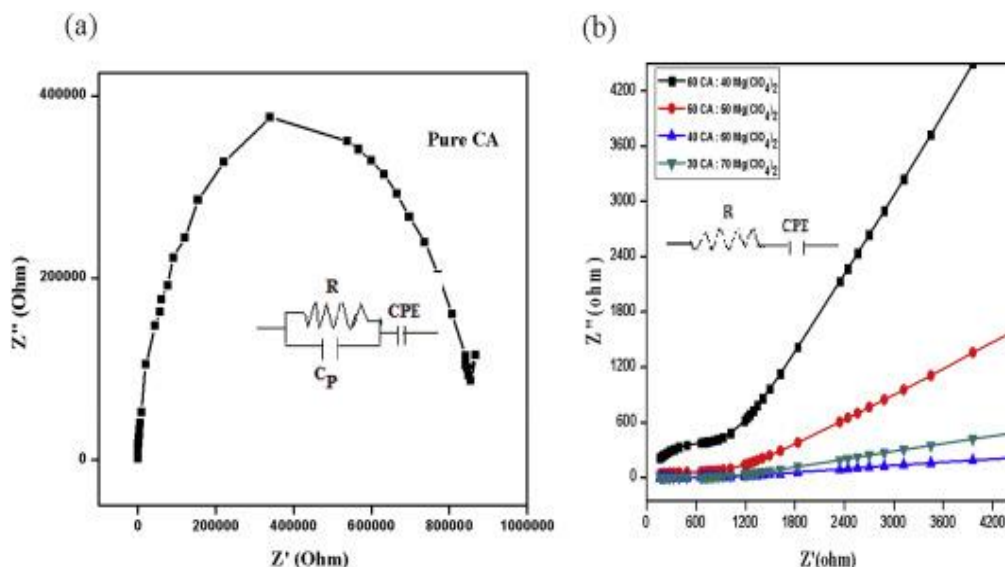


Fig 4. (a) Cole cole plot for pure cellulose acetate and (b) cole-cole plot for the magnesium perchlorate doped cellulose acetate polymer electrolytes

To calculate the ionic conductivity equation (1) is used[36]. The ionic conductivity values of the prepared samples for calculated using the equation (1) and the results are tabulated in table 3. The sample 40%cellulose acetate:60% magnesium per chlorate exhibit the maximum ionic conductivity of 4.13×10^{-4} S/cm[37].

$$\sigma = t/R_b A \quad (1),$$

where

t is the thickness of the highest conducting sample

A area of the highest conducting sample

The value of R_b (bulk resistance) is obtained from the cole-cole plot using Boukamp software[38]. The ionic conductivity of the pure cellulose acetate is 3.1×10^{-9} S/cm which is in accordance with the results reported earlier. On addition of magnesium per chlorate to the polymer cellulose acetate the salt being dissociated into Mg^{2+} ions and ClO_4^- ions due to which the charge carriers availability increases which is reflected in the ionic conductivity values of the prepared polymer electrolytes[39].

Sl.No.	Sample	ionic conductivity S/cm
1	Pure cellulose acetate	3.1×10^{-9}
2	60%cellulose acetate:40% magnesium per chlorate	4.88×10^{-6}
3	50%cellulose acetate:50% magnesium per chlorate	3.79×10^{-5}
4	40%cellulose acetate:60% magnesium per chlorate	4.13×10^{-4}
5	30%cellulose acetate:70% magnesium per chlorate	2.58×10^{-4}

Table 3: ionic conductivity values of the pure cellulose acetate and the magnesium per chlorate doped cellulose acetate polymer electrolytes.

Frequency dependent conductivity

Fig 5 represents the graph of log f versus log σ for the magnesium per chlorate doped cellulose acetate polymer electrolytes. From fig it is observed that as the number of charge carriers increases by the addition of the magnesium per chlorate to the polymer cellulose acetate the conductivity values

of the prepared electrolytes also increases[40]. The DC conductivity value is obtained by extending the middle frequency independent plateau to the log σ axis from the conduction spectra. These values are in good agreement between the values obtained from the Cole-Cole plot.

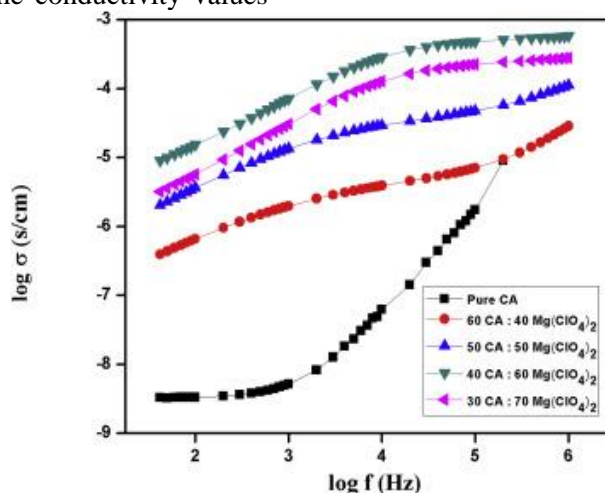


Fig 5 Frequency dependent conduction spectra of the pure cellulose acetate and magnesium per chlorate doped cellulose acetate polymer electrolytes

Transference number analysis

Wagners polarisation method:

Wagners polarization technique records the change in polarization current over time due to the ionic species[41] depletion in the biopolymer electrolyte. The formula for calculating the transference number is

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

where I_i denotes the starting current and I_f the final current.

This method involved applying a 1.5 V dc-potential across over time[43]. Because the ionic species in the biopolymer electrolyte are being depleted, the initial total current gradually drops until it approaches [44] electrode contact. Total transference number (t_{ion}) for the biopolymer with the highest conductivity 40%cellulose acetate: 60%magnesium per chlorate is determined to be 0.98 using the Eq. (2), which is near to unity, implying that only a minor contribution comes from the electrons.

Evans polarization method

The contribution of Mg^{2+} ions to the total conductivity has been calculated using a combination of ac and dc approaches. This method of polarizing the Mg/40%cellulose acetate:60% magnesium per chlorate/Mg cell included maintaining a constant voltage of $\Delta V=1.5V$. The transport number of Mg^{2+} is calculated using the formula

$$t_+ = I_s (\Delta V - R_o I_o) / I_o (\Delta V - R_s I_s) \quad [45] \quad (3)$$

here,

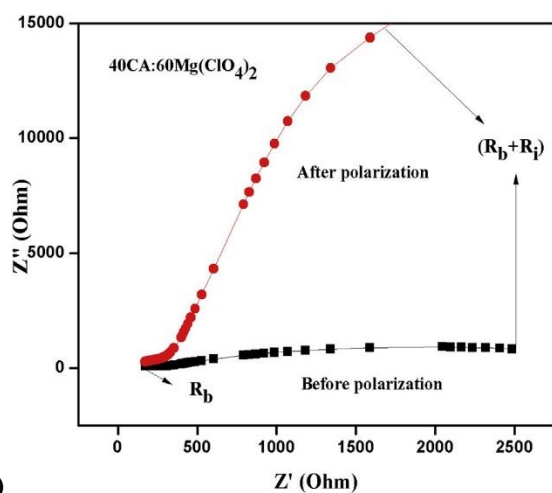
I_o is the initial current

I_s is the final current

R_o is the resistance before polarization of the cell

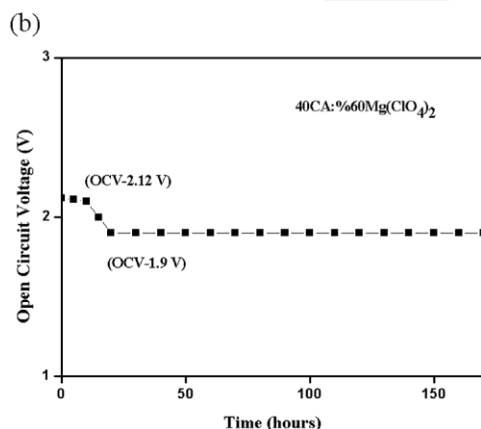
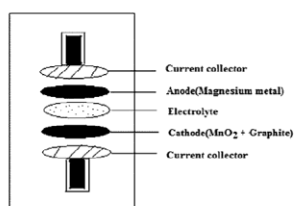
R_s is the resistance after polarization of the cell

The Mg^{2+} ions transport number for the cell Mg/40cellulose acetate:60% magnesium per chloride/Mg is found to be 0.31.

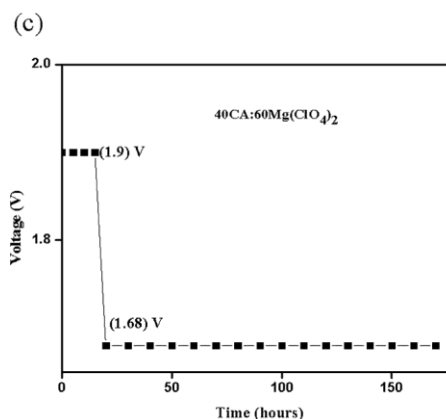


(i)

(a)

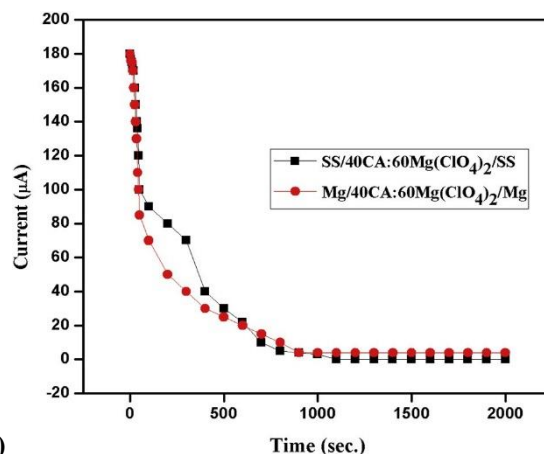


(b)



(c)

Fig 7 (a) schematic diagram of the fabricated magnesium battery (b) Variation of the voltage with time for the fabricated magnesium battery (c) discharge curve of the fabricated magnesium battery with 100KΩ load.



(ii)

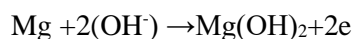
Fig 6 DC polarisation curve of (i) SS/40CA:60salt/SS cell (ii) Mg/40CA:60salt/Mg cell

Construction and performance of the Mg battery cell

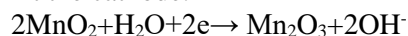
In order to create the magnesium primary battery, the highest conducting 40%cellulose acetate:60% magnesium per chlorate biopolymer electrolyte is being used. Pelletized magnesium metal is used as anode. Graphite and manganese dioxide in the perfect ratio are crushed into a powder, shaped into a pellet by applying 5 Torr of pressure, are the used materials. Fig 7(a) displays the setup of the battery containing the highest conducting sample of 40%cellulose acetate:60% magnesium per chlorate biopolymer electrolyte.

The initial open circuit voltage (OCV) is tracked throughout the time. The OCV was reported for the highest conducting biopolymer electrolyte 40% cellulose acetate:60% magnesium per chlorate is 2.12 V. The OCV decreased significantly to 1.9 V after one day, and it stays there for the next seven days. The cell formation processes at the electrodes cause a little interim dip in battery voltage following creation, as seen in Fig. 7b [45]. The following describes the chemical processes occurring in the battery cell:

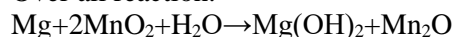
At the Anode:



At the cathode:



Over all reaction:



The battery discharge characteristics at room temperature is measured for the prepared battery with an external load of 100K Ω . After seven days of observation, it was discovered that the battery potential discharged under a constant load of 100 K Ω remained constant at 1.68 V. Table 4 lists the parameters of the battery cell.[46]

Cell parameters	Values
Cell area (cm ²)	1.23
Cell weight (g)	1.215
Cell diameter (cm)	1.3
Cell thickness (cm)	0.232
Open circuit voltage (V)	2.12

Table 4. cell parameters

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