DEVELOPMENT OF SOLID ELECTROLYTE FROM BIOMASS AND INVESTIGATION OF THEIR COMPATIBILITY IN FABRICATING ELECTROCHEMICAL DEVICES

Thesis submitted to Bharathiar University in partial fulfillment of the requirements for the award of the Degree of

DOCTOR OF PHILOSOPHY IN CHEMISTRY

By

Mrs. K. SUVARNNA, M.Sc., M.Phil.,

Under the guidance of

Dr. (Mrs.) S. JONE KIRUBAVATHY, M.Sc., M.Phil., Ph.D.,

Assistant Professor

DEPARTMENT OF CHEMISTRY

PSGR KRISHNAMMAL COLLEGE FOR WOMEN

College of Excellence, nirf 2022 – 6th Rank

An Autonomous Institution, Affiliated to Bharathiar University

Re-accredited with 'A++' Grade by NAAC, An ISO 9001:2015 Certified Institution

PEELAMEDU, COIMBATORE - 641 004

TAMIL NADU, INDIA

APRIL 2023

Chapter 9

CHAPTER 9

SUMMARY, CONCLUSIONS, AND FUTURE WORK

Biomaterials are any substance that can be synthetic or natural in origin and can be used for any period as a whole or a part of a system. They are also essential in developing an eco-friendly, energy-efficient technology and can act as a likely choice for developing a green and clean energy source for the next generation. The rapidly developing industrial and domestic needs highlighted the importance of environmentally friendly plant-based – biomaterials derived from sources free of ecological burden. These plant-based biomaterials possess various electroactive carboxylates, and hydroxyl groups in their structure, which makes them an ideal candidate for solid electrolytes. Hence an attempt has been made to develop a solid bio-electrolyte and also to construct an energy storage cell. On this basis, research for non-toxic, but biodegradable materials leads to these plant-derived materials. These materials include agricultural waste, plant byproducts, and much more. The development of a solid biopolymer electrolyte with an increased safety level and biodegradable nature is the need of the hour. The implementation of this biodegradable electrolyte in storage devices enables the conversion of waste to energy.

The present thesis work has been focused on the development of solid biopolymer electrolyte membranes from bio-based materials and investigating the efficiency of the bio-electrolytes prepared by doping with magnesium, lithium, and ammonium salts for the fabrication in battery devices as an electrolyte.

- ❖ In the initial part of the work, three biomass has been identified and segregated based on the presence of ample electroactive components like – COOH, – OH, –NH_2 groups present in their structural composition.
- ❖ These electroactive groups can easily act as a coordinating site for the cation added as the ionic dopant and help in the ion transport thus aiding the prepared membranes to act as an efficient bio-electrolyte.
- ❖ Further, magnesium chloride, lithium chloride, and ammonium formate are designated as the charge carriers for providing Mg^{2+}, Li^{+}, and H^{+} ions respectively.
- ❖ Three biopolymer membranes from the three different biomass, corn silk extract (CSE), seaweed extract (SME), and the plant gum (SG) by blending with polyvinyl alcohol (PVA) in an appropriate ratio by solution casting technique.

- The biopolymer membranes thus developed CSBP, SMBP, and SGBP are then investigated for their efficiency in ionic conduction by doping with three ionic dopants $MgCl_2$, LiCl, and NH_4HCO_2, respectively.

- The ionic carriers provide Mg^{2+}, Li^{+}, and H^{+} ions for ionic conduction and thus Mg-ion, Li-ion, and proton-conducting bio-electrolytes are synthesized from each of the three biomasses.

- The synthesized bio-electrolytes have been then utilized for the fabrication of the battery by sandwiching between a standard anode and a cathode.

- In the process of this work, melezitose one of the components present in corn silk extract has been investigated for its ability to ionic conductivity with magnesium perchlorate as the ionic dopant.

The introductory prospects of the present work plan in Chapter I discuss the different synthetic and biopolymer electrolytes used in energy storage devices and an insight into the evolution of different biodegradable sources used for the preparation of solid electrolytes. This also discusses the choice of the host bio-mass, the choice of the salts for the electrolyte preparation, and the essential attributes for biodegradable materials to be used as electrolytes for battery applications. Chapter II provides an elaborate background discussion of the different liquid, gel, and solid electrolyte sources such as synthetic polymer and biopolymer electrolytes, various biodegradable sources, and composites which are employed for the fabrication of different energy storage systems. The review of literature relevant to solid electrolytes and present developments in the field of the present work are also elaborated.

Chapter III provides the details of the chemicals and materials used, and methods adopted for the preparation of solid bio-membrane and bio-electrolytes from all three biomasses. Collection of Corn-Silk biomass, its extraction, and preparation of solid bio-membrane from Corn-Silk extract is also reported. The optimization of the composition of the bio-membrane prepared from the biomasses is performed based on the impedance plots. This optimized bio-membrane is utilized for bio-electrolyte preparation.

The characterization techniques such as Gas Chromatography-Mass Spectroscopy, Fourier Transmission-Infra Red Spectroscopy, X-Ray Diffraction Analysis, Differential Scanning Calorimetry, Linear Sweep Voltammetry, Electrochemical Impedance Spectroscopy, and Transference number measurement are discussed.

The next Chapter IV deals with the preparation and characterization of solid bio-membrane from Corn-Silk extract. The improvement in the flexibility and film-forming ability of the membrane has been enhanced by blending PVA into the extract. The development of bio-electrolyte for the fabrication of Magnesium, Lithium, and Ammonium batteries with the usage of $MgCl_2$, LiCl, and NH_4HCO_2 salts as the ionic dopant.

- ❖ The study starts with the development of a bio-electrolyte from the prepared bio-membrane composition (0.9g CSE + 1g PVA) and adding an ionic dopant as in Figure 9.1.
- ❖ Solution casting technique has been used for the preparation of flexible and free-standing bio-electrolyte films with good ionic conductivity, and considerable electrochemical stability for the composition CSMC 0.45 (0.9g CSE + 1g PVA + 0.45wt % $MgCl_2$), CSLC 0.5 (0.9g CSE + 1g PVA + 0.5wt% LiCl), and CSAF 0.5 (1g PVA + 0.9g CSE + 0.5wt% NH_4HCO_2).
- ❖ The increase in amorphous nature with the complex formation between the prepared bio-membranes and the added salts has been evaluated using XRD, and FTIR analysis.
- ❖ The increase in amorphous nature increases the flexibility of the membrane which has been confirmed by the lowering of the glass transition temperature (T_g) in thermal analysis technique differential scanning calorimetry.
- ❖ Wagner's polarization technique has been used to evaluate the transference number analysis for the highest conducting membranes CSMC 0.45, CSLC 0.5, and CSAF 0.5 and found to be 0.99, 0.98, and 0.98 respectively. The prepared bio-membranes and the salt-incorporated solid electrolytes have been optimized by the AC Impedance technique.

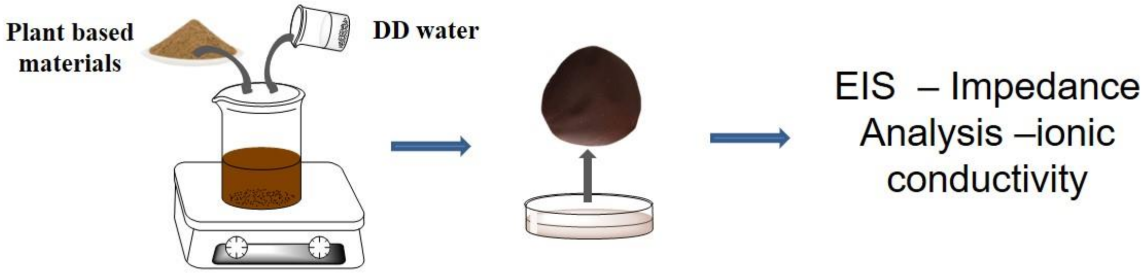


Figure 9.1: General Scheme of preparation of the biopolymer membrane

The next Chapter V deals with the preparation of solid bio-membrane from the seaweed *Sargassum Muticum* extract and then bio-electrolyte with the incorporation of $MgCl_2$, LiCl, and NH_4HCO_2 salts and their characterization.

- ❖ The XRD studies establish that the low crystalline nature of the membranes SMMC 0.7 (1g SME + 0.8g PVA + 0.7wt% $MgCl_2$), SMLC 0.6 (1g SME + 0.8g PVA + 0.6wt% LiCl), and SMAF 0.7 (1g SME + 0.8g PVA + 0.7wt% NH_4HCO_2).
- ❖ Complex formation between the seaweed extract, polyvinyl alcohol, and the added charge carrier has been made evident from the FTIR technique. Thermal properties of the bio-electrolytes by differential scanning calorimetry (DSC) are supported with the lowest glass transition temperature (T_g) for the membranes SMMC 0.7, SMLC 0.6, and SMAF 0.7 i.e., 45.4°C, 35.4°C, and 44.7°C.
- ❖ Linear sweep voltammetry is carried out to understand the working potential range for the bio-electrolytes prepared. The transference number measurement performed by Wagner's polarization technique provides a value of 0.97, 0.98, and 0.98 for the electrolytes SMMC 0.7, SMLC 0.6, and SMAF 0.7 affirming the contribution of ions to the total current.
- ❖ Electrochemical impedance analysis has been performed for the prepared bio-electrolytes and optimized for maximum ionic conductivity. In comparison with the corn silk biomass, this seaweed biomass produces membranes with good ionic conductivity such as SMMC 0.7 (2.22×10^{-3} Scm^{-1}), SMLC 0.6 (4.11×10^{-3} Scm^{-1}), and SMAF 0.7 (2.83×10^{-3} Scm^{-1}).

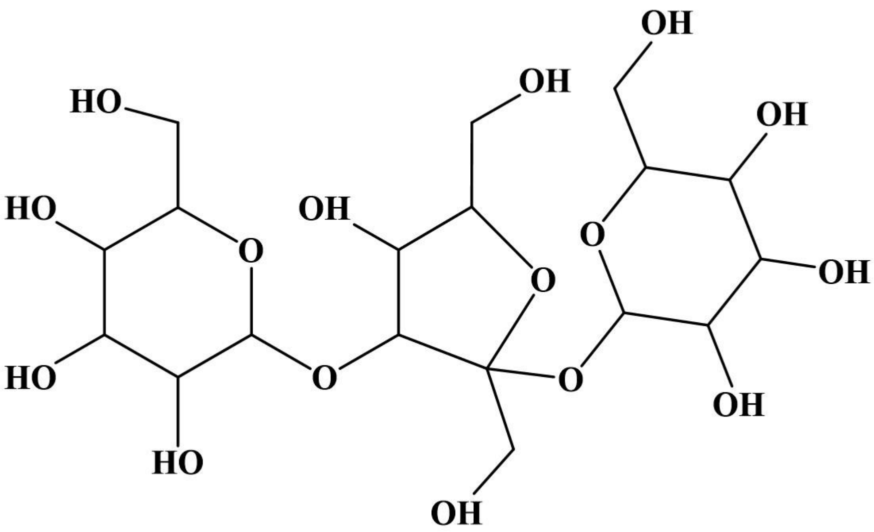
The third work on biomass *Salmalia Malabarica* has been discussed in Chapter VI. The preparation of solid bio-membrane from this exudate of composition 1g SG + 0.8g PVA

(SGBP) has been selected for the bio-electrolyte preparation with magnesium chloride, lithium chloride, and ammonium formate and characterized.

- ❖ The bio-electrolyte has been found to possess the highest conductivity SGMC 0.7 (7.2×10^{-3} S cm^{-1}) at room temperature compared to the membranes prepared from all the biomasses.
- ❖ The amorphous nature of the bio-electrolytes and the complex formation of the gum with the PVA and added ionic salts are affirmed by the XRD and FTIR spectroscopic analysis. This study also confirms the low crystallinity value for SGMC 0.7 compared to other $MgCl_2$ dopped membranes.
- ❖ The amorphous nature of the membrane SGMC 0.7, as expected possesses the lowest glass transition temperature which facilitates the easy movement of Mg^{2+} ions throughout the bio-electrolyte. This enhances the flexible nature by reducing the T_g value for SGMC 0.7 to 35.59°C and increases the ionic conductivity to 7.2 $\times 10^{-3}$ S cm^{-1} which is the highest of all the bio-electrolytes prepared in this complete work.
- ❖ The transference number analysis for the membranes SGMC 0.7, SGLC 0.5, and SGAF 0.7 has been calculated to understand the ionic contribution of the electrolyte membranes to the total current which has a value of 0.98, 0.99, and 0.98 respectively.

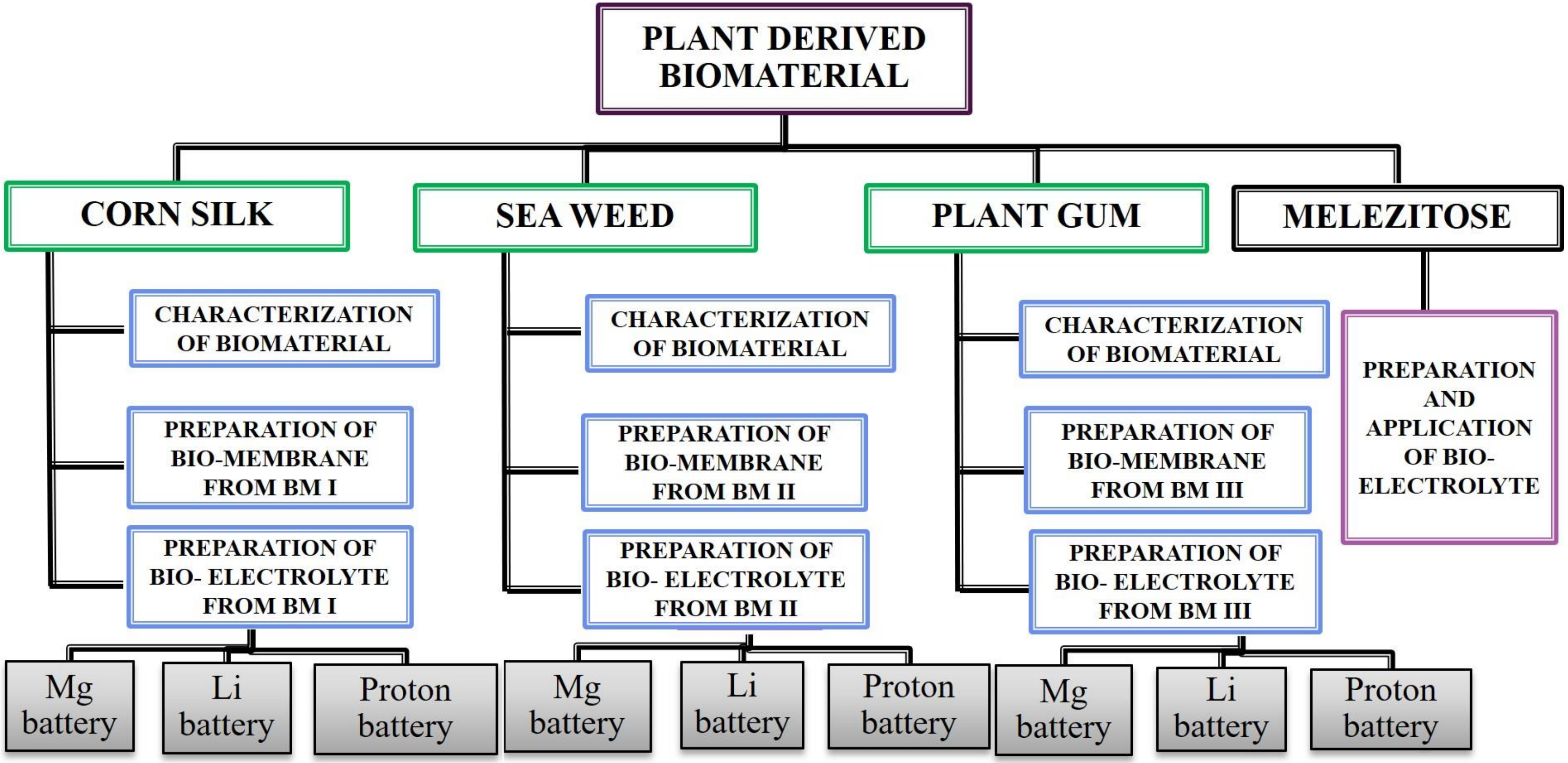
  Linear sweep voltammetry has also been performed to enunciate the applicability of the prepared membranes to the fabrication of devices like batteries.

The next Chapter VII discusses the development of a bio-membrane based on Melezitose and magnesium salt incorporated bio-electrolyte. Melezitose has been identified as a component present in the extract of Corn silk biomass, its structural composition and its novelty in the field of solid electrolytes aroused the interest to explore them for the preparation of solid bio-electrolyte. The prepared bio-electrolyte has been then characterized and then analyzed for its applicability for fabricating devices. The moisture-absorbing ability of the melezitose was so high that it has not been used for the fabrication of batteries.



Structure of Melezitose

- The last Chapter VIII brings about the fabrication of an ion-conducting battery constructed with the highest conducting bio-electrolyte membrane and open circuit voltage validates the application of this bio-membrane as a promising solid electrolyte for energy storage devices.
- A comparison of the fabricated batteries from the individual biomass has been performed based on their characteristic analytics like OCV, ionic conductivity, discharge current, and time.
- A final comparison has been established among the magnesium-ion, lithium-ion, and proton conducting batteries of the three biomasses which reveals the third biomass to possess better performance among the three biomass.


PLANT DERIVED BIOMATERIAL
CORN SILK
SEA WEED
PLANT GUM
MELEZITOSE
CHARACTERIZATION OF BIOMATERIAL
PREPARATION OF BIO-MEMBRANE FROM BM I
PREPARATION OF BIO- ELECTROLYTE FROM BM I
CHARACTERIZATION OF BIOMATERIAL
PREPARATION OF BIO-MEMBRANE FROM BM II
PREPARATION OF BIO- ELECTROLYTE FROM BM II
CHARACTERIZATION OF BIOMATERIAL
PREPARATION OF BIO-MEMBRANE FROM BM III
PREPARATION OF BIO- ELECTROLYTE FROM BM III
PREPARATION AND APPLICATION OF BIO-ELECTROLYTE
Mg battery
Li battery
Proton battery
Mg battery
Li battery
Proton battery
Mg battery
Li battery
Proton battery

FUTURE PROSPECTS

The results from the present investigation propose a great deal of scope to facilitate further research to enhance the performance of the prepared bio-electrolytes and electrode materials for the construction of devices.

- Establishing attention more on to the practical applicability of the bio-electrolyte films developed and assembling cells that are economical and energy efficient.
- The development of composite biopolymer electrolytes with the nanoparticles developed from the biomasses will be focused to handle the demanding needs of energy storage devices.
- Improving the output efficiency of the battery with different electrode materials.
- High-Temperature studies, mechanical stability analysis, and surface structure analysis will be focussed.
- Improving the composition of the prepared bio-electrolytes for its utilization in Fuel cell applications.
- Construction of sodium-ion conducting batteries and Zinc-air batteries using the biomasses studied.