

## *Chapter 2*

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## CHAPTER 2

### REVIEW OF LITERATURE

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Biomass and its derived materials are enriched with polyphenols, carbohydrates, lipids, and proteins in common which have the potential benefits as electrolytes. The finding of some organic bio-active molecules in these materials gave an insight into the idea of the development of solid bio-electrolyte for electrochemical applications. These biomass-derived materials are biodegradable and sustainable and biocompatible. This work aims to develop solid electrolytes derived from biodegradable bio-based materials which can be further employed in energy storage devices like batteries for a simple and reliable source of energy. The present-day batteries use organic liquid electrolytes which have the risk of explosion or leakage. These liquid electrolytes were then surpassed by polymer gel electrolytes, solid polymer electrolytes, and ceramic electrolytes. An electrolyte should be stable during the entire electrochemical operation that is expected to happen at the electrodes. Also, the electrolyte must possess high ionic conductivity but not electronically conductive which otherwise may lead to short-circuiting.

Solid-state batteries employ solid electrolytes and are the current state of the art. In this pursuit, research for non-toxic, but abundant materials lead to these plant-derived materials. These materials include biomass materials, 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 these biodegradable electrolytes in storage devices enables the conversion of waste to energy.

The key component in an energy storage device for its better performance of ionic conduction is its electrolyte. The progress in the development of solid electrolytes has gone through diverse stages. Primarily, liquid electrolytes are used as ionic conductors in batteries due to high ionic conductivity [1–6]. Later, to overcome its disadvantages, greater efforts are put forward to develop electrolytes such as polymer electrolytes [7–9], gel polymer electrolytes [10–12], composite polymer electrolytes [13–15], and solid biopolymer electrolytes [16,17].

#### **2.1 Transition from liquid to solid electrolytes**

Zang et al [18] have reviewed several advancements in liquid electrolytes and have discussed their chemical compatibility and their problems with solutions to meet their performance in batteries. Quartarone et al reported the role of liquid electrolytes as ionic

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conductors, their chemistries with electrode surface like corrosion, safety issues due to the exothermic release of the gaseous by-products and the need to focus on alternate electrolytes for batteries [19]. Lin et al explained the state of art demand for electrolyte systems by mentioning the actualities of the organic liquid electrolytes and the need to develop new host materials and discussed the new concepts of fluorine-free electrolytes, pseudo-concentrated electrolytes to enhance safety and better electrochemical performance [20]. Michael stitches et al discussed the release of potentially harmful HF species when  $\text{LiPF}_6$  is used as the ionic conductor and its effect on health in case of its leakage. His team was able to provide valuable insight into the need to develop battery electrolytes that are highly tolerant to water contaminations [21]. Yonatan Horowitz et al were able to explore the need for hybrid electrolytes to all-liquid to all-solid electrolytes and pressed the importance of polymer electrolytes in batteries [22].

## 2.2 Polymer electrolytes

Polymer electrolyte membrane possesses good ionic conduction properties and hence its application is widely extended in electronic devices, electrochemical devices such as fuel cells, dye-sensitized solar cells, rechargeable batteries, memory devices, and electrochemical sensors [23–31]. Albeit coming in the same classification as solid electrolytes, these polymer electrolytes have improved properties like blocking Li dendrites, virtuous ionic conductivity, chemical stability, and ease of fabrication. Goodenough et al also emphasized the situation for the storage of electrical energy and provided an insight into the development of Na-ion batteries with varied solid polymer electrolytes to eliminate the challenges of handling the lithium sources [32].

Strauss and his co-workers were addressing the key limitations of the organic electrolytes and the pathway to the development of single-cation-conducting polymer electrolyte systems in electrochemical batteries. They also discussed the different strategies to improve the ionic conductivity and diversified applications of these solid ion-conducting polymer electrolytes [33].

Kazunori Takada in his work detailed the intensive studies on the development of solid electrolytes such as sulfide-based electrolyte system, and oxide-based electrolyte system which produces high ionic migration due to the large ionic radius. He also detailed the study for power density enhancement and ion transport across interfaces for the development of solid-state

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batteries for practical applications [34]. Yonatan Horowitz et al compared the three types of electrolytes liquid, solid, and ceramic with their mechanisms for ionic conduction. They have highlighted the perspective of ceramic solid electrolytes over other electrolytes while providing an overview of the current electric vehicle ventures and the challenges faced during the incorporation of solid-state batteries in them [35].

### **2.2.1 Gel polymer electrolytes**

Gel polymer electrolytes combine the advantages of both liquid and solid electrolytes with improved physicochemical properties and find applications in diversified fields like batteries, supercapacitors, dye-sensitized solar cells, and sensors. Jianxun Dai et al in their work on gel polymer electrolyte (GPE) briefed them as ionic conducting organic material with rich functional groups which helps them to act as humidity sensors for monitoring respiration by producing a strong electronic signal due to the change in humidity [36]. This GPE finds its application in batteries as a single-ion conducting electrolyte as reported by Kuirong Deng and his co-workers. They have discussed the pivotal properties and the methods of preparation to improve the mechanical strength, ionic conductivity, and the need for a sustainable host for battery applications. Deng has also discussed the current status and challenges faced in the research of the development of gel polymer electrolytes for commercial applications [37]. A similar application of the gel polymer electrolytes in Lithium-ion and Magnesium ion conducting batteries was reported by Dong Zhou et al and Xin Tang [38, 39]. Saisai Wang et al developed a PVdF-HFP gel polymer electrolyte for dendrite-free lithium batteries [40].

Jian Hou and his co-workers [41] reported the synthesis of a gel separator from poly (ethylene glycol) methacrylate oligomer and a commercial liquid electrolyte. Their physical and electrochemical properties are characterized and the cycle performance of the fabricated coin-type cell was also analyzed. Mengjin Jiang et al, have addressed the problems faced in fabricating a supercapacitor by conceiving and implementing an effective technique of electrodepositing polyvinyl alcohol potassium borate GPE directly on the active carbon electrode surface [42].

Lina Yue et al in their work used sulfonated bacterial cellulose nanofibers as a template along with polyaniline and developed a composite GPE membrane. These membranes were biocompatible, with high ionic conductivity and good electrochemical stability [43]. Zehua Liu et al developed a GPE for Na-ion conducting battery application. In their work, sodium-

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conductive  $\beta$ -Alumina nanoparticles were incorporated into poly (vinylidene fluoride-co-hexafluoropropylene)/poly(methyl methacrylate) GPE and it was characterized and then fabricated as a sodium ion conductive cell with ionic conductivity of  $2.39 \times 10^{-3} \text{ S cm}^{-1}$  [44]. Gel polymer electrolyte also acts as a promising candidate in the fabrication of Dye-sensitized solar cells with comparable power conversion efficiency, high stability, and superior ionic migration in a cost-effective technique [45–47].

### **2.2.2 Composite polymer electrolyte**

Composite polymer electrolytes (CPE) are chemically stable membranes developed with the incorporation of inorganic fillers to enhance the ionic conductivity which possesses a high dielectric constant to hinder the aggregate formation of the ion pairs. The aforementioned properties enable these composite electrolytes applied in varied applications. Rakhi Sood et al, has given insight into the preparation of composite membrane for fuel cell, water electrolyzers, and batteries. They have also discussed the Mirai, a fuel cell vehicle by Toyota on a commercial scale with Hyundai and Honda following the same for transport applications. They also elaborated on the technique of electrospinning and explained their different processing methods from the perspective of industrial application [48].

Seokwoo Kim and his co-workers were able to prepare a new CPE with flame-retardant properties. The incorporation of  $\text{Mg}(\text{OH})_2$  into the PVdF-co-HFP- based electrolyte has a significant role in enhancing the flame retarding nature. With 40%  $\text{Mg}(\text{OH})_2$  in the electrolyte has increased its porosity, toughness, and flame-retarding properties without compromising its electrochemical performance in Li-ion batteries [49]. Good enough and his co-workers have synthesized a three-dimensional poly (ethylene glycol) methyl ether acrylate (CPMEA) polymer electrolyte and it is sandwiched in a polymer/ceramic/polymer membrane arrangement to form a Li-ion cell which is stable even above  $270^\circ\text{C}$ , possesses superior long-term electrochemical stability and were able to reduce the interfacial resistance at the electrode/electrolyte interface [50].

### **2.2.3 Biopolymers**

The next technological step was the search for more sustainable and environmentally friendly materials for the current environmental crisis, waste management, safety, and recycling issues. This can be met with the use of biocompatible and biodegradable materials obtained from natural sources for food and medical industries. These materials, so-called

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Biopolymers are either natural (starch, cellulose) or synthetic (polyvinyl alcohol, polylactic acid) in origin, but is largely explored in recent years. Biopolymers have placed an important landmark with their widespread applications in drug-delivery systems [51], food packaging [52], pharmaceutical science [53], wound healing [54], tissue scaffolds [55], and more [56].

#### ***2.2.4 Synthetic biopolymer as electrolyte***

Synthetic polymers have been developed to replace liquid electrolytes with solvent-free electrolytes for improved safety and compact fabrication. Many synthetic polymers have been explored to serve the purpose of creating a thin film electrolyte for battery applications. Poly (trimethylene carbonate) electrolyte has been reported by Bing Sun et al, as a new host material for Li-ion batteries. They have synthesized this high molecular weight polymer by ring-opening polymerization which achieved an ionic conductivity in the order of  $10^{-7}$  S  $\text{cm}^{-1}$  at  $60^\circ\text{C}$ . Their study also confirmed that post-functional modification of the polymer may enhance the performance of even three-dimensional batteries [57].

Another polymer polyethylene oxide has been largely utilized and modified for the preparation of electrolytes with lithium salt as a dopant [58–62]. Similarly, polyvinyl alcohol is the next polymer studied for battery applications. This polymer has been studied by blending with different ratios of another polymer (polyvinyl propylene) or dopants or plasticizers and their effect on ionic conductivity was investigated by different research groups [63–67].

#### ***2.2.5 Natural biopolymer as electrolyte***

These biopolymers are renewable and obtained from natural sources like vegetable oils, plant biomass, microbes-algae, fungus, agricultural waste, and also seaweed, and aquatic species. The application of these biopolymers as thin films as the solid electrolyte is of current state-of-art. Anandha Jothi et al synthesized a Corn starch/Polyvinylpyrrolidone electrolyte with Ammonium acetate as an ionic dopant with an ionic conductivity of  $1.09 \times 10^{-6}$  S  $\text{cm}^{-1}$  and fabricated a proton battery with an output circuit voltage of 0.89 V with a discharge time of 63 hours [68]. A biopolymer electrolyte based on chitosan with  $\text{V}_2\text{O}_5$  as filler for its application in magnesium batteries was prepared by Adlin Helen and co-workers. The open circuit voltage for the maximum conducting electrolyte was found to be 2.45 V and their transference number measurements confirm that the biopolymer electrolyte is an ionic conductor [69]. Similarly, Prasanna et al investigated chitosan as a potential binder for  $\text{LiFePO}_4$  cathode electrodes. The enhanced properties of the chitosan binder were compared with that of

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the PVDF binder by XRD and Fe-SEM analysis. The chitosan-based binder had better discharge capacity, and charge transfer resistance compared to the PVDF binder [70].

Noor and Isa have investigated the biopolymer carboxymethyl cellulose and successfully doped Ammonium thiocyanate into the membrane. They have also studied the thermal and transport properties of the membrane along with the electrochemical stability window that came out to be 1.6 V [71]. Ndruru et al, have prepared a lithium-ion conducting electrolyte with methylcellulose as the biopolymer by using the solution casting technique. Different weight ratios of  $\text{LiClO}_4$  as 0%, 5%, 10%, 15%, and 20% were used to produce an ionic conductivity of  $3.66 \times 10^{-5} \text{ S cm}^{-1}$  with good mechanical and thermal stability [72].

Sohaimy and Isa in their work on Carboxymethyl cellulose doped with Ammonium formate synthesized a biopolymer electrolyte which was then characterized using FT-IR and XRD. The results indicated the disruption in the crystalline nature of the biopolymer and the salt [73]. Selvalakshmi et al, have fabricated agar-agar-based ammonium chloride-doped biopolymer electrolytes with ionic conductivity of  $4 \times 10^{-3} \text{ S cm}^{-1}$  and characterized them using FT-IR, XRD, and AC impedance spectroscopy. She has also studied the Arrhenius behavior and its dielectric properties of the membrane. Later a primary proton battery was constructed with an output voltage of 1.89V and a fuel cell was also fabricated with an output current of 541mV [74]. Pectin-based biopolymer was used for the preparation of electrolyte for Na – ion conducting battery with an average output voltage of 0.4 V and the ionic conductivity of the membrane was found to be  $4.2 \times 10^{-6} \text{ S cm}^{-1}$  [75]. Similarly, pectin with lithium perchlorate as an ionic dopant was also studied and produced an ionic conductivity of  $3.89 \times 10^{-4} \text{ S cm}^{-1}$  and the fabricated battery had an OCV of 1.65 V [76].

Tamarind seed polysaccharide (TSP) has been used as a gelling agent and thickening agent in the food, packaging, and textile industries. This biopolymer was also explored for its candidature as an electrolyte membrane for the construction of batteries. Premalatha et al, doped LiBr with TSP and obtained an ionic conductivity of  $4.83 \times 10^{-4} \text{ S cm}^{-1}$  and the primary lithium battery with an OCV of 1.63 V was also constructed [77]. Whereas, Perumal et al, doped  $\text{Mg}(\text{ClO}_4)_2$  with TSP producing an ionic conductivity of  $5.66 \times 10^{-4} \text{ S cm}^{-1}$  at ambient temperature, and an Mg-ion conducting a battery of OCV 2.36 V was constructed [78]. Another polysaccharide alginate was also studied for its electrochemical properties. Fuzlin et al prepared a new type of  $\text{H}^+$  carrier membrane with alginate doped with glycolic acid and

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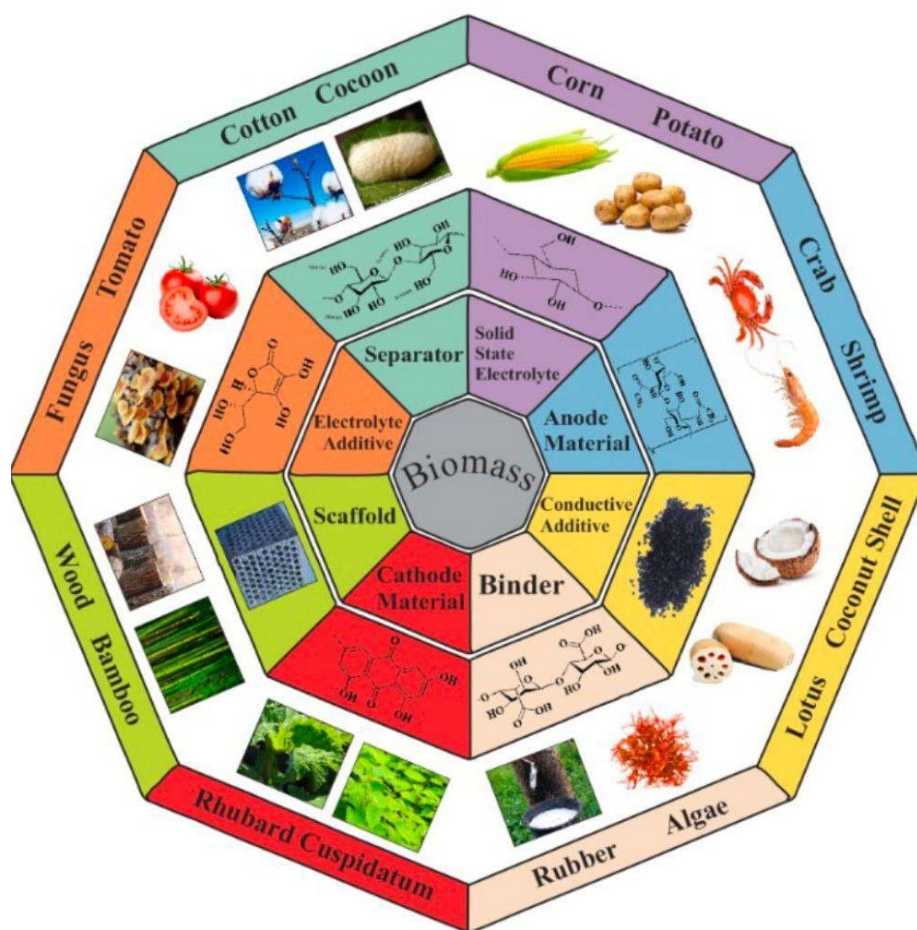
plasticizer, ethylene carbonate. The ionic conductivity of the optimized membrane was  $9.06 \times 10^{-4} \text{ S cm}^{-1}$  [79]. Another group Rasali et al had developed a biopolymer electrolyte by doping  $\text{NH}_4\text{NO}_3$  with alginate and achieved an ionic conductivity of  $5.56 \times 10^{-5} \text{ S cm}^{-1}$  [80].

### 2.3 Present developments in host materials

In particular, many biopolymers are explored with different blend compositions and modification of the preparation techniques and the next present move has been concerned with an eco-friendlier and sustainable and biodegradable host material. The terms bio-electrolyte, bio-battery, and bio-based materials, bio-inspired electrolytes are the currently coined terms for the use of biomass like plant parts, plant by-products, plant exudates, and agricultural and aquatic waste as the host materials since these materials are the source of the biopolymers already studied. These biomaterials are selected since the sourced biopolymers exhibited excellent chemical and mechanical stability and also optimum ionic conductivity during the analysis thus provoking the idea to apply directly the bio-based host materials for the electrochemical applications and many researchers were successful in executing this idea.

Spent honeycomb biomass has been used as a sustainable source of activated carbon as an anode material for Li-ion batteries and ultracapacitors in aqueous and non-aqueous electrolytes by Duraisamy et al. The coin cell of the type CR-2032 Li-ion battery produced a discharge capacity of 140mAh/g at a C/5 rate and the ultracapacitor delivered an energy density of 72Wh/kg. the fabricated battery and ultracapacitor were used to light a green LED bulb for more than 3hrs and 20 minutes respectively [81]. Bagasse waste from sugarcane was used as the source of carbon material by Feng et al and synthesized the activated carbon by hydrothermal carbonization followed by the KOH activation process. The bagasse-derived supercapacitor exhibits 20Wh/kg energy density at 182Wh/kg power density which makes them suitable for high-performance storage devices [82]. Some of the biomass and its varied applications are shown in Figure 2.1.





**Figure 2.1: Different Biomass and its applications**

Cassava peel, is another source of carbon material, whereas waste coffee grounds, pig skin, silkworm cocoon, green bristlegrass seeds, bamboo char, cotton T-shirts, and pistachio shell plant leaves are the other sources for bio-mass derived active carbon materials used for electrodes for electrochemical devices [83–91]. Another part of the research includes the utilization and development of polysaccharides from the biomasses for the preparation of electrolytes for energy storage applications. Cellulose-derivative was obtained from a kenaf fiber-based biopolymer and its electronic and transport properties were studied by Rani et al [92]. In another work chitosan, a biopolymer was extracted from shrimp shell, kappa-carrageenan from red seaweed extract, cellulose from oil palm empty fruit bunch, and polyhydroxyalkanoate from microbial stains are other biomaterials used for the synthesis of electrolytes [93–96].

Gum of plants called exudate is another group of biomaterials used for the preparation of electrolyte and electrode materials such as gum Arabic, gum Acacia, Xanthan gum, sesbania gum, and Tragacanth gum [97–106] for investigation for electrochemical storage devices. Erman Taer and his co-workers derived activated carbon from the green stem of Cassava. They used ZnO<sub>2</sub> for chemical activation for the development of a porous carbon monolith. The optimized porous carbon demonstrated a nanofiber structure suitable for supercapacitor applications [107]. Chinnaiah et al incorporated *Withania somnifera* leaf extract into the sodium alginate biopolymer to prepare a solid electrolyte with an electrochemical stability window of -0.4 V to 0.4 V and ionic conductivity of  $2.80 \times 10^{-6}$  S cm<sup>-1</sup> [108].

Other bio-based materials used include, a medicinal plant, *Centella Asiatica* as proton conducting solid electrolyte [109], latex of *Calotropis gigantea* is combined along with poly (vinylidene fluoride)-co-hexafluoropropylene by Neha Taneja [110], Aloe vera extract for anode material to the lithium-ion battery by Perumal [111], fallen *Camellia* flower - derived carbon plates for electrochemical storage [112], tea factory waste as an electrode for hydrogen production and supercapacitor applications [113], jute fibre has been used as a sustainable electrode material [114], Chestnut shell was used as a source of activated carbon for the anode material with high porosity by Hong et al [115].

In our present investigation, we have selectively chosen different biomass materials for the development of solid bio-electrolyte and the fabrication of Magnesium, Lithium, and Ammonium (H<sup>+</sup>) – ion-conducting batteries. The materials under investigation are

1. Corn Silk from Corn (*Zea Mays*) – a biowaste from the corn plant.
2. *Sargassum Muticum* – an invasive seaweed.
3. Gum of *Salmalia Malabarica* – a plant exudate.

We have developed a bio-membrane from the ethanol extract of Corn Silk and *Sargassum Muticum* whereas the gum was used as such for the bio-membrane preparation. Subsequently, magnesium, lithium, and ammonium salts are incorporated in each membrane to develop three different ion-conducting from each biomaterial. Thus, the above-synthesized membranes are optimized and the construction of the respective battery and its characterization was performed.

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**References**

- [1] A. Manthiram, *Journal of Physical Chemistry Letters* 2 (2011) 176–184.
- [2] Y. Yamada, J. Wang, S. Ko, E. Watanabe, A. Yamada, *Nat Energy* 4 (2019) 269–280.
- [3] K. Xu, *Chem Rev* 104 (2004) 4303–4417.
- [4] M. Becker, R.S. Kühnel, C. Battaglia, *Chemical Communications* 55 (2019) 12032–12035.
- [5] L. Smith, B. Dunn, *Science* (1979) 350 (2015) 918.
- [6] M. Gauthier, T.J. Carney, A. Grimaud, L. Giordano, N. Pour, H.H. Chang, D.P. Fenning, S.F. Lux, O. Paschos, C. Bauer, F. Maglia, S. Lupart, P. Lamp, Y. Shao-Horn, *Journal of Physical Chemistry Letters* 6 (2015) 4653–4672.
- [7] A. Manthiram, X. Yu, S. Wang, *Nat Rev Mater* 2 (2017).
- [8] J. Janek, W.G. Zeier, *Nat Energy* 1 (2016).
- [9] D.T. Hallinan, N.P. Balsara, *Annu Rev Mater Res* 43 (2013) 503–525.
- [10] S. Wang, L. Zhou, M.K. Tufail, L. Yang, P. Zhai, R. Chen, W. Yang, *Chemical Engineering Journal* 415 (2021).
- [11] Hou, J.; Park, I.K.; Cha, W.J.; Lee, C.H. A Gel Polymer Electrolyte Reinforced Membrane for Lithium-Ion Batteries via the Simultaneous-Irradiation of the Electron Beam. *Membranes* 11 (2021) 219.
- [12] D. Zhou, Y.B. He, Q. Cai, X. Qin, B. Li, H. Du, Q.H. Yang, F. Kang, *J Mater Chem A Mater* 2 (2014) 20059–20066.
- [13] D. Zhou, D. Shanmukaraj, A. Tkacheva, M. Armand, G. Wang, *Chem* 5 (2019) 2326–2352.
- [14] L. Chen, Y. Li, S.P. Li, L.Z. Fan, C.W. Nan, J.B. Goodenough, *Nano Energy* 46 (2018) 176–184.
- [15] S. Li, S.Q. Zhang, L. Shen, Q. Liu, J. bin Ma, W. Lv, Y.B. He, Q.H. Yang, *Advanced Science* (2020) 7.
- [16] J.C. Barbosa, R. Gonçalves, C.M. Costa, S. Lanceros-Méndez, *ACS Omega* 7 (2022) 14457–14464.
- [17] M. Hema, P. Tamilselvi, G. Hirankumar, *Ionics (Kiel)* 23 (2017) 2707–2714.
- [18] S.S. Zhang, *J Power Sources* 231 (2013) 153–162.
- [19] E. Quartarone, P. Mustarelli, *Chem Soc Rev* 40 (2011) 2525–2540.

- 
- [20] Y. Lin, S. Huang, L. Zhong, S. Wang, D. Han, S. Ren, M. Xiao, Y. Meng, *Energy Storage Mater* 34 (2021) 128–147.
- [21] M. Stich, M. Göttliger, M. Kurniawan, U. Schmidt, A. Bund, *Journal of Physical Chemistry C* 122 (2018) 8836–8842.
- [22] Y. Horowitz, C. Schmidt, D. hwan Yoon, L.M. Riegger, L. Katzenmeier, G.M. Bosch, M. Noked, Y. Ein-Eli, J. Janek, W.G. Zeier, C.E. Diesendruck, D. Golodnitsky, *Energy Technology* (2020) 8.
- [23] W.Q. Ding, F. Lv, N. Xu, M.T. Wu, J. Liu, X.P. Gao, *ACS Appl Energy Mater* 4 (2021) 4581–4601.
- [24] M. Dosi, I. Lau, Y. Zhuang, D.S.A. Simakov, M.W. Fowler, M.A. Pope, *ACS Appl Mater Interfaces* 11 (2019) 6166–6173.
- [25] E. Ercan, J.Y. Chen, P.C. Tsai, J.Y. Lam, S.C.W. Huang, C.C. Chueh, W.C. Chen, *Adv Electron Mater* (2017) 3.
- [26] G. Jiang, T. Cumberland, J. Zhang, S. Sy, S. Delaat, Z. Mao, H. Jin, A. Yu, S. Wang, Z. Chen, *Sens Actuators B Chem* (2021) 329.
- [27] L. Mazzapioda, S. Panero, M.A. Navarra, *Polymers (Basel)* (2019) 11.
- [28] D.S. Liu, H. Ryu, U. Khan, C. Wu, J.H. Jung, J. Wu, Z. Wang, S.W. Kim, *Nano Energy* (2021) 81.
- [29] M. Noorkami, J.B. Robinson, Q. Meyer, O.A. Obeisun, E.S. Fraga, T. Reisch, P.R. Shearing, D.J.L. Brett, *Int J Hydrogen Energy* 39 (2014) 1439–1448.
- [30] H. Chae, D. Song, Y.G. Lee, T. Son, W. Cho, Y.B. Pyun, T.Y. Kim, J.H. Lee, F. Fabregat-Santiago, J. Bisquert, Y.S. Kang, *Journal of Physical Chemistry C* 118 (2014) 16510–16517.
- [31] J. Theerthagiri, R.A. Senthil, M.H. Buraidah, J. Madhavan, A.K. Arof, *Ionics (Kiel)* 21 (2015) 2889–2896.
- [32] J.B. Goodenough, K.S. Park, *J Am Chem Soc* 135 (2013) 1167–1176.
- [33] E. Strauss, S. Menkin, D. Golodnitsky, *Journal of Solid State Electrochemistry* 21 (2017) 1879–1905.
- [34] K. Takada, in: *AIP Conf Proc*, American Institute of Physics Inc., 2016.
- [35] Y. Horowitz, C. Schmidt, D. hwan Yoon, L.M. Riegger, L. Katzenmeier, G.M. Bosch, M. Noked, Y. Ein-Eli, J. Janek, W.G. Zeier, C.E. Diesendruck, D. Golodnitsky, *Energy Technology* 8 (2020).
- [36] J. Dai, H. Zhao, X. Lin, S. Liu, T. Fei, T. Zhang, *Sens Actuators B Chem* 304 (2020).
-

- 
- [37] K. Deng, Q. Zeng, D. Wang, Z. Liu, Z. Qiu, Y. Zhang, M. Xiao, Y. Meng, *J Mater Chem A Mater* 8 (2020) 1557–1577.
- [38] D. Zhou, Y.B. He, Q. Cai, X. Qin, B. Li, H. Du, Q.H. Yang, F. Kang, *J Mater Chem A Mater* 2 (2014) 20059–20066.
- [39] X. Tang, R. Muchakayala, S. Song, Z. Zhang, A.R. Polu, *Journal of Industrial and Engineering Chemistry* 37 (2016) 67–74.
- [40] S. Wang, L. Zhou, M.K. Tufail, L. Yang, P. Zhai, R. Chen, W. Yang, *Chemical Engineering Journal* (2021) 415.
- [41] Hou, J.; Park, I.K.; Cha, W.J.; Lee, C.H. A Gel Polymer Electrolyte Reinforced Membrane for Lithium-Ion Batteries via the Simultaneous-Irradiation of the Electron Beam. *Membranes* 11 (2021) 219.
- [42] M. Jiang, J. Zhu, C. Chen, Y. Lu, Y. Ge, X. Zhang, *ACS Appl Mater Interfaces* 8 (2016) 3473–3481.
- [43] L. Yue, Y. Xie, Y. Zheng, W. He, S. Guo, Y. Sun, T. Zhang, S. Liu, *Compos Sci Technol* 145 (2017) 122–131.
- [44] Z. Liu, X. Wang, J. Chen, Y. Tang, Z. Mao, D. Wang, *ACS Appl Energy Mater* 4 (2021) 623–632.
- [45] C.Y. Tan, F.S. Omar, N.M. Saidi, N.K. Farhana, S. Ramesh, K. Ramesh, *Solar Energy* 178 (2019) 231–240.
- [46] M.O.S. Lobregas, D.H. Camacho, *Electrochim Acta* 298 (2019) 219–228.
- [47] M. Thomas, S. Rajiv, *J Photochem Photobiol A Chem* 394 (2020).
- [48] R. Sood, S. Cavaliere, D.J. Jones, J. Rozière, *Nano Energy* 26 (2016) 729–745.
- [49] S. Kim, T. Han, J. Jeong, H. Lee, M.H. Ryou, Y.M. Lee, *Electrochim Acta* 241 (2017) 553–559.
- [50] W. Zhou, S. Wang, Y. Li, S. Xin, A. Manthiram, J.B. Goodenough, *J Am Chem Soc* 138 (2016) 9385–9388.
- [51] Z. Belhadj, M. Ying, X. Cao, X. Hu, C. Zhan, X. Wei, J. Gao, X. Wang, Z. Yan, W. Lu, *Journal of Controlled Release* 255 (2017) 132–141.
- [52] L. Pinto, M.A. Bonifacio, E. de Giglio, E. Santovito, S. Cometa, A. Bevilacqua, F. Baruzzi, *Food Packag Shelf Life* 28 (2021).
- [53] Z. Pedram Rad, J. Mokhtari, M. Abbasi, *Materials Science and Engineering C* 93 (2018) 356–366.
-

- 
- [54] J. Devalliere, K. Dooley, Y. Yu, S.S. Kelangi, B.E. Uygun, M.L. Yarmush, *Biomaterials* 141 (2017) 149–160.
- [55] A. Balasso, A. Subrizi, S. Salmaso, F. Mastrotto, M. Garofalo, M. Tang, M. Chen, H. Xu, A. Urtti, P. Caliceti, *European Journal of Pharmaceutical Sciences* 161 (2021).
- [56] J. Baranwal, B. Barse, A. Fais, G.L. Delogu, A. Kumar, *Polymers (Basel)* 14 (2022).
- [57] B. Sun, J. Mindemark, K. Edström, D. Brandell, *Solid State Ion* 262 (2014) 738–742.
- [58] Y. Jiang, X. Yan, Z. Ma, P. Mei, W. Xiao, Q. You, Y. Zhang, *Polymers (Basel)* 10 (2018).
- [59] H. Cheng, C. Zhu, B. Huang, M. Lu, Y. Yang, *Electrochim Acta* 52 (2007) 5789–5794.
- [60] W. Huang, Q. Pan, H. Qi, X. Li, Y. Tu, C.Y. Li, *Polymer (Guildf)* 128 (2017) 188–199.
- [61] Q. Lu, J. Fang, J. Yang, G. Yan, S. Liu, J. Wang, *J Memb Sci* 425–426 (2013) 105–112.
- [62] A.J. Butzelaar, M. Gauthier-Jaques, K.L. Liu, G. Brunklaus, M. Winter, P. Theato, *Polym Chem* 12 (2021) 4326–4331.
- [63] V. Parameswaran, N. Nallamuthu, P. Devendran, A. Manikandan, E.R. Nagarajan, *J Nanosci Nanotechnol* 18 (2017) 3944–3953.
- [64] R. Manjuladevi, S. Selvasekarapandian, M. Thamilselvan, R. Mangalam, S. Monisha, P.C. Selvin, *Ionics (Kiel)* 24 (2018) 3493–3506.
- [65] V. Duraikkan, A.B. Sultan, N. Nallaperumal, A. Shunmuganarayanan, *Ionics (Kiel)* 24 (2018) 139–151.
- [66] G. Xu, Y. Zhang, R. Rohan, W. Cai, H. Cheng, *Electrochim Acta* 139 (2014) 264–269.
- [67] A.R. Polu, R. Kumar, H.W. Rhee, *Ionics (Kiel)* 21 (2015) 125–132.
- [68] M.A. Jothi, D. Vanitha, K. Sundaramahalingam, N. Nallamuthu, *Int J Hydrogen Energy* 47 (2022) 28763–28772.
- [69] P.A. Helen, K. Ajith, M.I. Diana, D. Lakshmi, P.C. Selvin, *Journal of Materials Science: Materials in Electronics* 33 (2022) 3925–3937.
- [70] K. Prasanna, T. Subburaj, Y.N. Jo, W.J. Lee, C.W. Lee, *ACS Appl Mater Interfaces* 7 (2015) 7884–7890.
- [71] N.A.M. Noor, M.I.N. Isa, *Int J Hydrogen Energy* 44 (2019) 8298–8306.
- [72] S.T.C.L. Ndruru, D. Wahyuningrum, B. Bundjali, I.M. Arcana, *Journal of Engineering and Technological Sciences* 52 (2020) 28–50.
- [73] M.I.H. Sohaimy, M.I.N. Isa, *Polymers (Basel)* 14 (2022).
- [74] S. Selvalakshmi, D. Vanitha, P. Saranya, S. Selvasekarapandian, T. Mathavan, M. Premalatha, *Journal of Materials Science: Materials in Electronics* (2022).
-

- 
- [75] M. Vahini, M. Muthuvinayagam, M.I.N. Isa, *Polymer Science - Series A* 61 (2019) 823–831.
- [76] P. Perumal, P. Christopher Selvin, S. Selvasekarapandian, P. Sivaraj, K.P. Abhilash, V. Moniha, R. Manjula Devi, *Polym Degrad Stab* 159 (2019) 43–53.
- [77] M. Premalatha, T. Mathavan, S. Selvasekarapandian, S. Monisha, S. Selvalakshmi, D. Vinoth Pandi, *Ionics (Kiel)* 23 (2017) 2677–2684.
- [78] P. Perumal, K.P. Abhilash, P.Sivaraj, P.C. Selvin, *Mater Res Bull* 118 (2019).
- [79] A.F. Fuzlin, M.A. Saadiah, Md.M. Hasan, Y. Nagao, I.I. Misnon, A.S. Samsudin, *Int J Hydrogen Energy* 47 (2022) 7846–7860.
- [80] N.M.J. Rasali, Y. Nagao, A.S. Samsudin, *Ionics (Kiel)* 25 (2019) 641–654.
- [81] E. Duraisamy, A. Prasath, V. Sankar Devi, M.N.M. Ansari, P. Elumalai, *Energy Storage* 2 (2020).
- [82] H. Feng, H. Hu, H. Dong, Y. Xiao, Y. Cai, B. Lei, Y. Liu, M. Zheng, *J Power Sources* 302 (2016) 164–173.
- [83] Y. Gong, D. Li, C. Luo, Q. Fu, C. Pan, *Green Chemistry* 19 (2017) 4132–4140.
- [84] A.E. Ismanto, S. Wang, F.E. Soetaredjo, S. Ismadji, *Bioresour Technol* 101 (2010) 3534–3540.
- [85] E. Duraisamy, A. Prasath, V. Sankar Devi, M.N.M. Ansari, P. Elumalai, *Energy Storage* 2 (2020).
- [86] W. Zhou, S. Lei, S. Sun, X. Ou, Q. Fu, Y. Xu, Y. Xiao, B. Cheng, *J Power Sources* 402 (2018) 203–212.
- [87] B. Liu, Y. Liu, H. Chen, M. Yang, H. Li, *J Power Sources* 341 (2017) 309–317.
- [88] X. Xia, Y. Zhang, D. Chao, Q. Xiong, Z. Fan, X. Tong, J. Tu, H. Zhang, H.J. Fan, *Energy Environ Sci* 8 (2015) 1559–1568.
- [89] Y. Zhou, J. Ren, Y. Yang, Q. Zheng, J. Liao, F. Xie, W. Jie, D. Lin, *J Solid State Chem* 268 (2018) 149–158.
- [90] H. Yan, Y. Li, X. Guo, M. Zhou, H.-Q. Wang, Y. Dai, J.-C. Zheng, *J Electrochem Soc* 165 (2018) A2075–A2083.
- [91] T.E. Rufford, D. Hulicova-Jurcakova, Z. Zhu, G.Q. Lu, *Electrochem Commun* 10 (2008) 1594–1597.
- [92] M.S.A. Rani, A. Ahmad, N.S. Mohamed, *Polymer Bulletin* 75 (2018) 5061–5074.
- [93] C. Naceur Abouloula, M. Rizwan, V. Selvanathan, C.I. Abdullah, A. Hassan, R. Yahya, A. Oueriagli, *Ionics (Kiel)* 24 (2018) 3827–3836.
-

- 
- [94] V. Dall'Asta, V. Berbenni, P. Mustarelli, D. Ravelli, C. Samori, E. Quartarone, *Electrochim Acta* 247 (2017) 63–70.
- [95] P. Perumal, P.C. Selvin, *Journal of Solid State Electrochemistry* 24 (2020) 2249–2260.
- [96] M. Nithya, M. Alagar, B. Sundaresan, Development of Red Seaweed Extracted Film for Energy Saving Batteries, Article, 2012.
- [97] Z. Wang, X. Xu, C. Chen, T. Huang, A. Yu, *J Power Sources* 539 (2022) 231604.
- [98] A. Pawlicka, F.C. Tavares, D.S. Dörr, C.M. Cholang, F. Ely, M.J.L. Santos, C.O. Avellaneda, *Electrochim Acta* 305 (2019) 232–239.
- [99] R.D. Knuth, F.A. Knuth, G.K. Maron, R.D.C. Balboni, M.L. Moreira, C.W. Raubach, P.L.G. Jardim, N.L. v Carreno, C.O. Avellaneda, E.C. Moreira, S.S. Cava, *J Appl Polym Sci* 139 (2022) e52400.
- [100] D.V. Carvalho, N. Loeffler, M. Hekmatfar, A. Moretti, G.T. Kim, S. Passerini, *Electrochim Acta* 265 (2018) 89–97.
- [101] Y. Huang, J. Zhang, J. Liu, Z. Li, S. Jin, Z. Li, S. Zhang, H. Zhou, *Mater Today Energy* 14 (2019).
- [102] V. Sharma, N. Arora, R. Kumar, S. Singh, S. Verma, *Polymer Bulletin* 79 (2022) 8865–8882.
- [103] M. Nandhinilakshmi, D. Vanitha, N. Nallamuthu, K. Sundaramahalingam, P. Saranya, *Journal of Materials Science: Materials in Electronics* 33 (2022) 21172–21188.
- [104] L. Xu, H. Sitinamaluwa, H. Li, J. Qiu, Y. Wang, C. Yan, H. Li, S. Yuan, S. Zhang, *J Mater Chem A Mater* 5 (2017) 2102–2109.
- [105] S. Monisha, J. Gajendiran, G. Boopathi, M. Premalatha, A. Saranya, S. Gnanam, U. Rajesh Kumar, *Mater Lett* 321 (2022) 132408.
- [106] J. I, V. K, K. S, M. S, A. G, P. Moni, J.S. D, *Journal of Solid State Electrochemistry* 25 (2021) 2371–2383.
- [107] E. Taer, N. Yanti, W.S. Mustika, A. Apriwandi, R. Taslim, A. Agustino, *Int J Energy Res* 44 (2020) 10192–10205.
- [108] K. Chinnaiyah, T. Theivashanthi, K. Kannan, M.S. Revathy, V. Maik, H. Parangusan, S.C. Jeyaseelan, K. Gurushankar, *J Inorg Organomet Polym Mater* 32 (2022) 583–595.
- [109] R. Hemalatha, M. Alagar, P. Rameshbabu, A. Azhagu Parvathi, R. Hepzi Pramila Devamani, *Mater Today Proc* (2021).
- [110] N. Taneja, K. Dujearic-Stephane, N. Agrawal, A. Kumar, P. Singh, Bharti, M. Gupta, Y. Kumar, *High Perform Polym* (2022) 0(0).
-



- [111] P. Perumal, P. Sivaraj, K.P. Abhilash, G.G. Soundarya, P. Balraju, P.C. Selvin, *Journal of Science: Advanced Materials and Devices* 5 (2020) 346–353.
- [112] D. Guo, C. Zheng, W. Deng, X. Chen, H. Wei, M. Liu, S. Huang, *Journal of Solid State Electrochemistry* 21 (2017) 1165–1174.
- [113] S. Özarıslan, M. Raşıit Atelge, M. Kaya, S. Ünalın, *Fuel* 305 (2021) 121578.
- [114] P. Manasa, Z.J. Lei, F. Ran, *J Energy Storage* 30 (2020).
- [115] P. Hong, X. Liu, X. Zhang, S. Peng, T. Zou, Z. Wang, Y. Yang, R. Zhao, Y. Chen, Y. Wang, *Int J Energy Res* 44 (2020) 5385–5396.

## AIM & SCOPE OF THE PRESENT INVESTIGATION

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### *Aim of the present investigation:*

- ❖ To obtain eco-friendly and sustainable solid-state electrolyte from bio-derived materials.
- ❖ To prepare thin solid biopolymer membranes from three different biomass.
- ❖ To develop three bio-electrolyte membranes with three different ionic dopants, magnesium chloride, lithium chloride and ammonium formate.
- ❖ To optimize the prepared bio-electrolyte membranes with high ionic conductivity and to characterize the membranes for their application to electrochemical devices.
- ❖ To investigate the compatibility of the developed bio-electrolyte membranes by electrochemical techniques for the construction of respective ion-conducting batteries.
- ❖ To fabricate Mg-ion, Li-ion and proton conducting batteries from all three biomass by sandwiching the prepared bio-electrolyte between the respective standard anode and cathode.

### *Scope of the present investigation:*

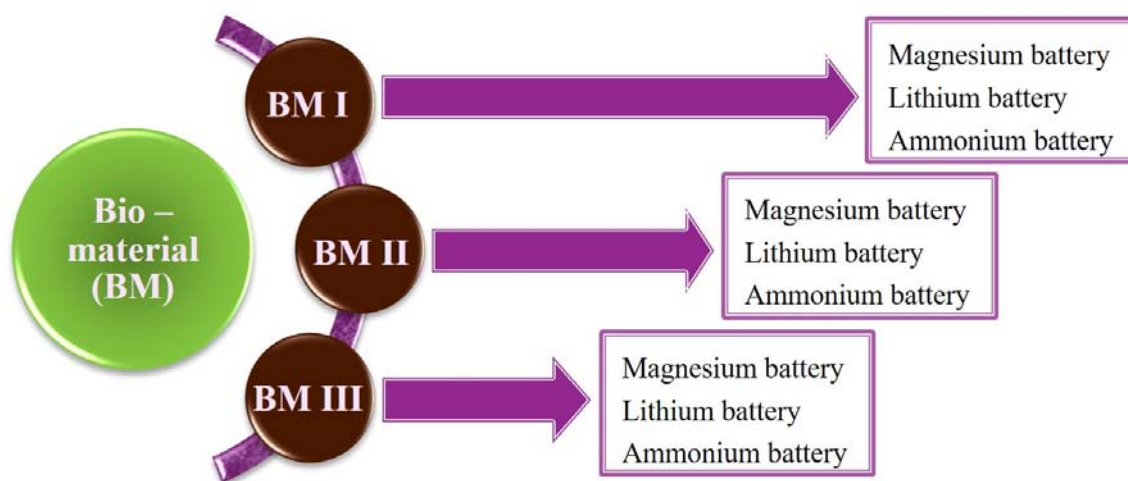
Solid biopolymer membranes synthesized from the biomass-derived materials and then ionic salt doped bio-electrolyte by amalgamation has been emerged as an alternate solution for the organic liquid electrolyte used in present day batteries. These bio-electrolytes possess high ionic conductivity at ambient temperature, good electrochemical stability, cost effective and environmental-friendly properties desirable for battery applications. Hence, we have chosen the extract and gum from three different biomass-derived biomaterials respectively.

1. Corn Silk, a plant biowaste.
2. *Sargassum Muticum*, an invasive seaweed.
3. *Salmaalial Malabarica* gum, a plant exudate.

The chosen biomass-derived materials with their extract and gum are entirely novel for this investigation. From the literature, it's obvious this bio-based electrolyte for energy storage

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batteries are entirely novel. In this regard, the present investigation focuses on the development of solid electrolyte from biomass by doping with three different salts – magnesium chloride, lithium chloride and ammonium formate as mentioned in Figure 1.7. These solid bio-electrolytes has been characterized and their compatibility for the fabrication of ion-conducting battery with the ionic dopants has been explored.



**Figure 1.7: Scope of the Present Investigation**

The systems prepared and studied for the present investigation and its designations are provided in Tables 1.1 to 1.10.

**SYSTEM I**

**Table 1.1: Designation and sample composition of blend bio-membrane (0.9g CSE + 1g PVA) and MgCl<sub>2</sub> incorporated corn silk bio-electrolyte**

<b>Composition</b>	<b>Code</b>
Corn Silk Ethanol Extract	CSE
0.9g CSE + 1g PVA	CSBP(Bio-membrane)
0.9g CSE + 1g PVA + 0.3wt % MgCl <sub>2</sub>	CSMC 0.3
0.9g CSE + 1g PVA + 0.4wt % MgCl <sub>2</sub>	CSMC 0.4
0.9g CSE + 1g PVA + 0.45wt % MgCl <sub>2</sub>	CSMC 0.45
0.9g CSE + 1g PVA + 0.5wt % MgCl <sub>2</sub>	CSMC 0.5

**SYSTEM II**

**Table 1.2: Designation and sample composition of LiCl incorporated corn silk bio-electrolyte**

<b>Composition</b>	<b>Code</b>
0.9g CSE + 1g PVA + 0.3wt% LiCl	CSLC 0.3
0.9g CSE + 1g PVA + 0.4wt% LiCl	CSLC 0.4
0.9g CSE + 1g PVA + 0.5wt% LiCl	CSLC 0.5
0.9g CSE + 1g PVA + 0.6wt% LiCl	CSLC 0.6

**SYSTEM III**

**Table 1.3: Designation and sample composition of NH<sub>4</sub>HCO<sub>2</sub> incorporated corn silk bio-electrolyte**

<b>Composition</b>	<b>Code</b>
0.9g CSE + 1g PVA + 0.4wt% NH <sub>4</sub> HCO <sub>2</sub>	CSAF 0.4
0.9g CSE + 1g PVA + 0.5wt% NH <sub>4</sub> HCO <sub>2</sub>	CSAF 0.5
0.9g CSE + 1g PVA + 0.6wt% NH <sub>4</sub> HCO <sub>2</sub>	CSAF 0.6

**SYSTEM IV**

**Table 1.4: Designation and sample composition of blend bio-membrane (1g SME + 0.8g PVA) and MgCl<sub>2</sub> incorporated seaweed bio-electrolyte**

<b>Composition</b>	<b>Code</b>
<i>Sargassum Muticum</i> Ethanol Extract	SME
1g SME + 0.8g PVA	SMBP
1g SME + 0.8g PVA + 0.5wt% MgCl <sub>2</sub>	SMMC 0.5
1g SME + 0.8g PVA + 0.6wt% MgCl <sub>2</sub>	SMMC 0.6
1g SME + 0.8g PVA + 0.7wt% MgCl <sub>2</sub>	SMMC 0.7
1g SME + 0.8g PVA + 0.8wt% MgCl <sub>2</sub>	SMMC 0.8

**SYSTEM V**

**Table 1.5: Designation and sample composition of LiCl incorporated seaweed bio-electrolyte**

<b>Composition</b>	<b>Code</b>
1g SME + 0.8g PVA + 0.4wt% LiCl	SMLC 0.4
1g SME + 0.8g PVA + 0.5wt% LiCl	SMLC 0.5
1g SME + 0.8g PVA + 0.6wt% LiCl	SMLC 0.6
1g SME + 0.8g PVA + 0.7wt% LiCl	SMLC 0.7

**SYSTEM VI**

**Table 1.6: Designation and sample composition of NH<sub>4</sub>HCO<sub>2</sub> incorporated seaweed bio-electrolyte**

<b>Composition</b>	<b>Code</b>
1g SME + 0.8g PVA + 0.5wt% NH <sub>4</sub> HCO <sub>2</sub>	SMAF 0.5
1g SME + 0.8g PVA + 0.6wt% NH <sub>4</sub> HCO <sub>2</sub>	SMAF 0.6
1g SME + 0.8g PVA + 0.7wt% NH <sub>4</sub> HCO <sub>2</sub>	SMAF 0.7
1g SME + 0.8g PVA + 0.8wt% NH <sub>4</sub> HCO <sub>2</sub>	SMAF 0.8

**SYSTEM VII**

**Table 1.7: Designation and sample composition of blend bio-membrane (1g SG + 0.8g PVA) and MgCl<sub>2</sub> incorporated Salmalia gum bio-electrolyte**

<b>Composition</b>	<b>Code</b>
<i>Salmalia Malabarica</i> Gum	SG
1g SG + 0.8g PVA	SGBP
1g SG + 0.8g PVA + 0.5wt% MgCl <sub>2</sub>	SGMC 0.5
1g SG + 0.8g PVA + 0.6wt% MgCl <sub>2</sub>	SGMC 0.6
1g SG + 0.8g PVA + 0.7wt% MgCl <sub>2</sub>	SGMC 0.7
1g SG + 0.8g PVA + 0.8wt% MgCl <sub>2</sub>	SGMC 0.8

**SYSTEM VIII**

**Table 1.8: Designation and sample composition of LiCl incorporated Salmalia gum bio-electrolyte**

<b>Composition</b>	<b>Code</b>
1g SG + 0.8g PVA + 0.3wt% LiCl	SGLC 0.3
1g SG + 0.8g PVA + 0.4wt% LiCl	SGLC 0.4
1g SG + 0.8g PVA + 0.5wt% LiCl	SGLC 0.5
1g SG + 0.8g PVA + 0.6wt% LiCl	SGLC 0.6

**SYSTEM IX**

**Table 1.9: Designation and sample composition of NH<sub>4</sub>HCO<sub>2</sub> incorporated Salmalia gum bio-electrolyte**

<b>Composition</b>	<b>Code</b>
1g SG + 0.8g PVA + 0.5wt% NH <sub>4</sub> HCO <sub>2</sub>	SGAF 0.5
1g SG + 0.8g PVA + 0.6wt% NH <sub>4</sub> HCO <sub>2</sub>	SGAF 0.6
1g SG + 0.8g PVA + 0.7wt% NH <sub>4</sub> HCO <sub>2</sub>	SGAF 0.7
1g SG + 0.8g PVA + 0.8wt% NH <sub>4</sub> HCO <sub>2</sub>	SGAF 0.8

**SYSTEM X**

**Table 1.10: Designation and sample composition of blend bio-membrane (1g Melezitose + 0.8g PVA) and Mg (ClO<sub>4</sub>)<sub>2</sub> incorporated Melezitose bio-electrolyte**

<b>Composition</b>	<b>Code</b>
1g Melezitose	MZ
1g Melezitose + 0.8g PVA	MZP
1g Melezitose + 0.8g PVA + 0.4wt% Mg (ClO <sub>4</sub> ) <sub>2</sub>	MMP1
1g Melezitose + 0.8g PVA + 0.5wt% Mg (ClO <sub>4</sub> ) <sub>2</sub>	MMP2
1g Melezitose + 0.8g PVA + 0.7wt% Mg (ClO <sub>4</sub> ) <sub>2</sub>	MMP3
1g Melezitose + 0.8g PVA + 0.8wt% Mg (ClO <sub>4</sub> ) <sub>2</sub>	MMP4
1g Melezitose + 0.8g PVA + 0.84wt% Mg (ClO <sub>4</sub> ) <sub>2</sub>	MMP5

Thus, the prepared solid bio-electrolytes has been characterized by XRD, FTIR, DSC, AC impedance spectroscopy, Transference number measurements and Linear Sweep Voltammetry. As aforesaid, the bio-electrolyte membranes are fabricated with in a cell for an ion-conducting battery with the three respective ionic providers Magnesium Chloride, Lithium Chloride and Ammonium formate respectively are studied and its performance has been reported.

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