ABSTRACT

The rechargeable magnesium metal batteries (MMBs) are one of the emerging alternatives of lithium-ion batteries (LIBs) as they show a high volumetric capacity, non-toxic nature, a divalent charge of Mg-ions. Moreover, its dendrites free and one of the most abundant elements in the earth crust. However, MMBs are at a very early stage of research due to lack of high ionic conductivity and high electrochemically stable, electrolytes system. The ionic conductivity, electrochemical stability and thermal stability of the electrolyte system is an essential parameter for improving battery performance and safety. Herein, an attempt has been made to prepare different electrolytes-separator systems using polymer and glass-ceramic as a membrane. The three different polymers (1) PVDF, (2) PVDF-*co*-HFP and (3) PAN are used as polymer membrane for the present study. All polymer membranes are prepared by electrospinning techniques, which is one of the most efficient techniques to prepare nonwoven porous mat with bead free and uniformly distributed nanofibers. The β-phase of PVDF is achieved by electrospinning process which is polar and electroactive with a high dipole moment. The electrospun mats are immersed in magnesium perchlorate ($Mg(ClO_4)_2$) and propylene carbonate (PC) solution to form the gel polymer electrolyte (GPE). The physical and electrochemical characterization is carried out by various techniques to investigate the performance of GPE.

The ionic conductivity of electroactive PVDF based GPE is found to be 1.49 mS cm^{-1} at 30 °C, which is higher than commercially available polypropylene (PP) Celgard. The electrochemical stability of the EGPE is stable up to a high voltage of 5.0 V against Mg^{+2}/Mg. Later, to improve the ionic conductivity, PVDF-*co*-HFP (high amorphous phase) is used as a polymer membrane in GPE. The effect of the crystalline phase and surface structure of electrospun PVDF-*co*-HFP membranes are principally reviewed.

The ionic conductivity and electrochemical stability of PVDF-*co*-HFP copolymer electrolyte membranes are found to be 1.62 mS cm^{-1} and 5.5 V, respectively. To further enhance the thermal stability as well as ionic conductivity of GPE, polyacrylonitrile (PAN) is used as a polymer membrane. The achieved ionic conductivity of PAN-based GPE is 3.28 mS cm^{-1}, electrochemical stability is 4.6 V. They also have shown excellent interfacial stability with magnesium metal. The results showed that the PAN-based GPE has superior ionic conductivity and thermal stability than the PP Celgard membrane.

Subsequently, an attempt has been made to compare the physical and electrochemical characteristics of glass-ceramic and PP Celgard membranes as separators in the Magnesium metal battery, using magnesium bis(trifluoromethanesulfonimide) and PC as an organic electrolyte. The characterizations like X-ray diffraction, field emission electron microscopy, electrolyte uptake, ionic conductivity, electrochemical stability, thermal stability and transference number are thoroughly examined for both the membranes. The glass-ceramic electrolyte system showed significantly higher ionic conductivity of 9.22 mS cm^{-1} at room temperature as compared to the PP Celgard membrane (6.55×10^{-3} mS cm^{-1}). Additionally, the glass-ceramic electrolyte system showed higher thermal and electrochemical stability.

In summary, the increase in ionic conductivity, thermal and electrochemical stability is achieved by proper selection of polymers, synthesis process and proper selection of electrolyte (salt and solvent) which creates an excellent possibility for commercial MMBs.

***Keywords**: Electrolyte-separator system, Gel polymer electrolyte, Magnesium metal battery, β-phase PVDF, Glass-ceramic membrane, Ionic conductivity, Electrochemical stability, Thermal stability.*