Synthesis and characterization of PEO and PVDF based polymer electrolytes with Mg(NO$_3$)$_2$ ionic salt as ionic conductivity improver

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Abstract. The demand for solid polymer electrolytes is increasing continuously because of their better mechanical properties, stability, and strength while compared with liquid or gel electrolytes. However, the polymers are having poor ionic conductivity that can be improved by adding ionic salt during solid electrolyte production. Further, not all the electrolytes are compatible with polymers also the concentration of ionic salt beyond some limit not only decrease the ionic conductivity of solid electrolyte but also decrease the strength as well. In the present work, the mixture of two different polymers (10% PEO and 90% PVDF) is selected as the parent polymer for the production of solid polymer electrolytes. Mg(NO$_3$)$_2$ is used as ionic salt to increase the ionic conductivity and other properties of electrolytes. The concentration of Mg(NO$_3$)$_2$ is taken in 10%, 15%, and 20% (w/w) to the parent polymer, and the effects are analyzed on ionic conductivity. It is found that the addition of Mg(NO$_3$)$_2$ improves the ionic conductivity of electrolytes with a higher rate initially but the rate of increase of ionic conductivity decreases after 15%. Further, better thermal conduction and other properties are observed for the electrolyte having a 15% Mg(NO$_3$)$_2$ concentration. The detailed results are given in the present work.

Keywords: Ionic conductivity, Mg(NO$_3$)$_2$, PEO+PVDF, Solid Polymer Electrolytes

1. Introduction
The energy demand all over the world is increasing continuously as all countries are developing at a faster rate [1,2]. A major part of this energy demand is fulfilled by fossil fuels in the present scenario [3,4]. However, all the fossil fuels are available in a limited amount which forces the researchers to work in the direction of some alternative source of energy [4–7]. Also, the combustion of all the fossil fuels releases various harmful emissions such as carbon monoxides, hydrocarbons, oxides of nitrogen, particulate matter, soot, etc [8,9]. All these emissions results in the greenhouse effect, various skin and breathing diseases [10]. On the other hand, most of the natural energy resources like solar energy, wind energy, tidal energy, etc. are clean and renewable and also available in a tremendous amount. Effectively use of these natural resources cut down the dependency over the fossil fuels and provide self-sustainability to the developing country such as India, which does not have enough fossil fuels resources and heavily depended on the import of fossil fuels from other countries. Therefore, the use of natural energy resources helps to overcome most of the energy-related problems. However, it is not a simple task as it looks on paper, due to irregular availability and fluctuating intensity of the energy resources. Moreover, we can regulate the demand by storing the energy when the intensity is higher and can supply
when these natural resources are having low density or unavailability [11]. In all the storage devices, batteries are most reliable, economical, and easy to use. However, the higher weight-to-energy ratio, limitation in operating conditions, and danger to operate at higher operating temperature make their usage limited. Most of these limitations are associated with electrolytes and can be improved by modifying by providing enough strength to the electrolyte that not only makes usage of battery safe but also improves the range of the operating parameters [12,13].

The research is going on the improvement of electrolytes of the battery storage system, especially for lithium-ion batteries. In that direction, solid electrolytes showed better performance and improved operating parameters as compared to liquid electrolytes [14]. The chances for the formation of dendrites are more for the liquid electrolytes that decrease drastically once liquid electrolytes are replaced with solid electrolytes [15]. The formation of dendrites leads to an explosion in the battery [13]. Therefore, solid electrolytes provide a promising solution to the safe operation of the battery with improved battery life. The solid electrolytes are classified into organic and inorganic electrolytes depending upon the compound used for production. Furthermore, both types of electrolytes have their advantages and limitations like inorganic electrolytes have good ionic conductivity and a wide range of operating temperatures, on the other hand, organic electrolytes have better compatibility with electrodes [16,17].

In contrast, organic electrolytes have a poor operating temperature range and inorganic electrolytes are brittle that makes them difficult to process. Therefore an effort is put to develop composite-based solid electrolytes that provide better ionic conductivity and strengthen the battery. The ionic conductivity of the electrolytes can be improved by dropping the nanoparticles in the electrolytes during the development of the electrolyte. In the present research, the combination of 90% of poly(vinylidene fluoride) (PVDF) + 10% of poly(ethylene oxide) (PEO) is used as the host polymer and Mg(NO$_3$)$_2$ is selected as ionic salt. The solid electrolytes are prepared with different concentrations of Mg(NO$_3$)$_2$ in the parent polymer to check the strength and ionic conductivities of the prepared electrolytes. The thermal properties of the prepared solid polymer electrolytes are analyzed with Calorimetry-Thermogravimetric analysis (DSC-TGA) however the X-ray diffraction is conducted to analyze the structural properties of the prepared electrolytes.

2. Experimental

2.1. Materials

The PEO (molecular weight 900,000 g/mol), PVDF (molecular weight 534,000 g/mol), and Mg(NO$_3$)$_2$ are obtained from Sigma-Aldrich, USA. Whereas, dimethylformamide (DMF) is purchased from Pon Pure Chemicals Group, Chennai, India. All the polymers are vacuum dried before use. The other chemicals used in the research are purchased from local institute vendors.

2.2. Synthesis of Polymer Electrolytes

Primarily, the mixture of PEO and PVDF is prepared in 10% and 90% proportions respectively. The mixture is taken as parent polymer for the production of solid electrolytes. The solution cast technique is opted to produce solid polymer electrolytes. In this technique, the parent polymer mixture is taken in the airtight conical flask and DMF is pouring into it. The solution is then put on a magnetic stirrer for continuous agitation. The temperature of the solution is maintained at 70°C throughout the reaction with the help of an electric heater mounted over the magnetic stirrer system. The solution is allowed to react for 10 hours undisturbed. After that the ionic salt Mg(NO$_3$)$_2$ is added to the solution. The concentration of Mg(NO$_3$)$_2$ is taken 10%, 15%, and 20% for different electrolytes. The concentration of parent polymer and ionic salt is taken by (100-x)(PEO+PVDF) + x Mg(NO$_3$)$_2$, where x is 0, 10, 15, and 20. After adding the Mg(NO$_3$)$_2$ into the solution, the solution is further put for the stirring process for another 10-12 hours. The temperature of the solution is maintained during this step is also 70°C. The consistency of the solution is checked after 10 hours and put for agitation for another 2 hours if a homogeneous mixture is not observed. The solution is then poured into a glass Petri dish and put into a vacuum oven.
at 40°C for 60 hours for drying. The polymer film is obtained after the drying process. The prepared solid polymer electrolytes are stored in an airtight container for further study. The complete process of production of solid polymer electrolyte is shown in figure 1.

![Image of production process]

**Figure 1.** Schematic diagram of the solid electrolyte production process

| Notification | Nomenclature                              |
|--------------|-------------------------------------------|
| BP           | 90% PVDF + 10% PEO                       |
| 0.9BP-0.1IS  | 90% BP + 10% Mg(NO$_3$)$_2$               |
| 0.85BP-0.15IS| 85% BP + 15% Mg(NO$_3$)$_2$               |
| 0.8BP-0.2IS  | 80% BP + 20% Mg(NO$_3$)$_2$               |

### 2.3. Characterization of Solid Polymer Electrolytes

The prepared solid polymer electrolytes are tested to analyze the various characteristics such as phase structure, electrochemical properties, thermal properties, etc. The phase structures are characterized using an X-ray diffractometer (XRD) with a scanning range of 10° to 60°. Whereas, thermogravimetric analyzer and Autolab are used to measure the thermal stability and ionic conductivity of solid polymer electrolytes. The thermal stability of electrolytes is measured in a nitrogen atmosphere with a heating rate of 10°C per minute. The operating range for the process is from atmospheric temperature to 700°C. The ionic conductivity of the electrolyte is also measured under a controlled nitrogen environment. To measure the ionic conductivity of the electrolyte, the electrolyte is kept in between two electrodes made up of stainless steel. The frequency range of current varies during the experiment is from 10 Hz to 1 MHz. The following formula is used to measure the ionic conductivity (σ) of the electrolyte:

\[
\sigma = \frac{t}{R_b A}
\]

Where; t is the thickness of electrolyte, $R_b$ is bulk resistance and A is the cross-sectional area of the electrolyte.
The ionic conductivity variation is studied in the temperature range of 300K to 353K similar to the study conducted by Wang et al. [15].

3. Results and Discussions

X-ray diffraction is used to analyze the crystalline structure of all the prepared solid polymer electrolytes. The XRD patterns of all the solid polymer electrolytes (i.e. BP, 0.9BP-0.1IS, 0.85BP-0.15IS, and 0.8BP-0.2IS) are represented in figure 2. It can be observed that none of the prepared electrolytes has any sharp phase peak that shows the homogeneity among all the materials. The possession of OH group and fluoride present in the PEO skeleton by PVDF molecules is one of the reasons for no sharp peak in the crystallinity structure. The crystalline structure of Mg(NO$_3$)$_2$ in the solid polymer electrolyte disappeared also the intensity at 20.3° decreases this is a clear indication of complete mixing of ionic salt in the parent polymer. Very similar patterns are also observed by Nidhi & Kumar [18] in their research. Further, the increase in the concentration of ionic salt in the electrolyte solution decreases the peak of the parent polymer.

![Figure 2. XRD analysis of all prepared electrolytes](image)

The ionic conductivity of the parent polymer-based electrolyte is very poor that is improved by adding Mg(NO$_3$)$_2$ ionic salt in the solid electrolyte. It is observed that an increase in the concentration of Mg(NO$_3$)$_2$ in the solid polymer electrolyte increases the ionic conductivity of the electrolyte. The highest ionic conductivity of 767 S/m is noticed for 0.8BP-0.2IS and the lowest ionic conductivity of 817 S/m is observed for the parent polymer solid electrolyte. The ionic conductivity of all the prepared solid electrolytes at room temperature is shown in figure 3. The enhancement of ionic conductivity of electrolytes with an increase in ionic salt concentration is due to an increase in charge carrier in the electrolyte. However, the rate of increase of ionic conductivity decreases above 15% of Mg(NO$_3$)$_2$. The prime reason for the decrease in rate is ion pair formation which is strengthened by ion aggregation [19].
Figure 3. Ionic conductivity of all prepared electrolytes at room temperature

To measure the electric properties of all prepared solid polymer electrolytes the impedance plot is performed. The relationship used to perform the impedance is the same as used by Nidhi & Kumar [18]. At a particular frequency, the impedance is inversely proportional to the product of resistance and capacitive reactance and provides information regarding the elements. Furthermore, the lower impedance elements are more dominant in the impedance spectra at a higher frequency and vice-versa for the low frequency. It is mainly due to the interception of a semicircle that provides the material a bulk resistance at the real axis. The impedance plot of all the prepared solid polymer electrolytes is given in figure 4. All the impedance plots are generated at room temperature only.

Figure 4. Impedance plots of all the prepared electrolytes.

The ionic conductivity of the solid electrolyte varies with temperature changes. At higher temperatures, the ions present in the solid electrolytes have higher activation energy that makes them unstable and the ions start jumping within the vacant site available in the electrolyte. Therefore, the ionic conductivity of solid electrolytes increases with an increase in temperature however the strength of the solid electrolyte decreases. The effect of temperature on the ionic conductivity of prepared electrolytes is also analyzed in the present study. The temperature range taken for the analysis is from room temperature (30°C) to 100°C with a fraction of 10°C. The results obtained for ionic conductivity of all the prepared solid
electrolytes are shown in figure 5. Also the activation energy of all the solid polymer electrolytes are calculated at room temperature and represented in figure 6.

**Figure 5.** Ionic conductivity of all the prepared electrolytes w.r.t. operating temperature

**Figure 6.** Activation Energy of all prepared electrolytes at room temperature.

### 4. Conclusions
In the present work, the solid polymer electrolytes are prepared with 10%PEO + 90% PVDF (by w/w). The effect of the concentration of ionic salt Mg(NO₃)₂ on the ionic conductivity and other properties of solid polymer electrolytes are analyzed in the present research. The major finding observed in the present work are as follows:

- No sharp peaks are observed in any of the prepared electrolytes which indicates the compatibility of polymers and ionic salt with each other.
- The ionic conductivity of the solid electrolyte improves with an increase in the concentration of Mg(NO₃)₂ in the polymer.
The ionic conductivity of all prepared solid electrolytes increases with an increase in operating temperature.

The addition of Mg(NO$_3$)$_2$ in the electrolyte improves the activation energy of the electrolyte.

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