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Study of the Thermal Stability and Ionic Conductivity of Polystyrene-Co-Acrylonitrile Based Composite Solid Polymer Electrolytes Incorporated with different Lithium Salts

S. V. Ganesan
Department of Chemistry
Saraswathi Narayanan College, Madurai, Tamil Nadu, India

M. Selvamurugan
Department of Energy Science
Alagappa University, Karaikudi, Tamil Nadu, India

M. Thamima
Department of Energy Science
Alagappa University, Karaikudi, Tamil Nadu, India

S. Karuppuchamy
Department of Energy Science
Alagappa University, Karaikudi, Tamil Nadu, India

K. K. Mothilal
Associate Professor and Head
Research and PG Department of Chemistry
Saraswathi Narayanan College, Madurai, Tamil Nadu, India

Abstract

In the present study, a series of poly(styrene-co-acrylonitrile) (SAN) polymer electrolytes and SAN- poly(vinyl alcohol) (PVA) polymer blend electrolytes were prepared with different lithium salts using a solvent casting technique. TG & DSC studies were carried out to investigate the thermal stability of the polymer blend electrolytes. Ionic conductivities of these electrolytes were measured by AC impedance spectroscopy. Results for conductivity studies have shown that the polymer with SAN/PVA complex with 5 % LiBr exhibits the highest conductivity of $8.7 \times 10{-}5$ *S/cm at 70°C. The temperature dependence of the polymer electrolyte films obeys Arrhenius relation.*

Keywords: Polymer Blend Electrolytes, FT-IR, Thermal Studies, Li Ion Battery, PVA

Introduction

Pioneer work with the lithium battery began in 1912 under G.N. Lewis. However, until the early 1970s the first non-rechargeable lithium battery became commercially available. Lithium is the lightest weight, highest voltage, and greatest energy density of all metals. The first published interest in lithium batteries began in the works of Harris in 1958. The work eventually led to the development and commercialisation of a variety of primary lithium cells during 1970s.

The original design of the Li-ion polymer battery is invented in 1970s; the researcher uses a dry solid polymer electrolyte only in the battery system. This electrolyte resembles a plastic-like film and act as a separator that does not conduct electricity but allows an exchange of ions between anode to cathode. The polymer electrolyte offers simplifications with respect to fabrication, safety, light weight and flexibility. There is no leaking problem and any danger of flammability because no liquid or gelled electrolyte is used. With the provision of a thin film of electrolyte system, the form, shape and size of the battery can be fabricated easily at lower production cost (Mahendran and Rajendran, 2003).

Although using the solid polymer electrolyte in a lithium ion polymer battery has several advantages, but it still suffers from poor conductivity. Due to its high internal resistance, the battery cannot deliver the current to modern communication devices or spinning up the hard drives of mobile computing equipment. Even though heating the cell to 60°C or higher temperature will eventually increase the conductivity to acceptable levels but this requirement is unsuitable for practical applications.

Therefore, research continues to develop a solid Li-ion polymer battery that performs at room temperature. A solid Li-ion polymer is commercially available in 2005. It is expected to be very stable and would run 1000 full cycles with higher energy densities. In order to build up a small Li-ion polymer battery system, gelled electrolyte has been invented. Most of the commercial Li-polymer batteries used today for mobile phones are a hybrid and contain gelled electrolyte. With the implementation of gelled electrolyte, the characteristics and performance are similar to the solid type where these polymer electrolytes are used to replace the porous separator and to enhance ion conductivity.

A polymer electrolyte plays an important role due to the safety and environmental issues. A polymer electrolyte acts as a separator between anode and cathode to prevent internal short circuit and at the same time, provide good ionic conductivity. The polymer electrolytes have more advantages compared to the conventional liquid electrolyte such as; it is not flammable and has no leakage problem.

Numerous works have been carried out to minimize the semi-crystalline nature of PVA. Blending is one of the most relevant techniques that completely redefine the physical and chemical properties of PVA(3). The polymer electrolytes with plasticizers are known as second generation polymer electrolytes(4). The addition of plasticizers may also improve the salt-solvating power and high ion mobility to the polymer electrolytes(5).

In the present work, new plasticized polymer electrolytes composed of the SAN, SAN/PVA blend, propylene carbonate (PC) as a plasticizer, and various lithium salts have been studied.

The polymer electrolytes PVA/SAN-PC-LiX and SAN-PC-LiX, (X=Cl-, Br-, CO_3^{2}-) are prepared using a solvent casting technique. The prepared polymer electrolyte films are characterized by *AC* impedance, TG and DSC studies.

Experimental

All polymer complexes were prepared using solution casting techniques(6, 7). The polymers Poly (Styrene-co-acrylonitrile) (SAN) (Sigma-Aldrich) (M_w = 165000), Polyvinyl alcohol (PVA) (Sigma-Aldrich) (M_w = 146000), propylene carbonate (Alfa-Aesar) and different lithium salts that include lithium chloride, lithium bromide and lithium carbonate (Alfa-Aesar) were purchased and used as such without any further purification. The polymers were dried at 373 K in vacuum for 12 h before use. The solvent THF/DMF was distilled and dried over molecular sieves (4A^o) before use. The plasticizer and the lithium salt (LiX) with X = Br^-, Cl^-, and CO_3^{2-} in appropriate quantities (wt %) were mixed separately in THF and then transferred to beaker containing SAN in THF. The polymer blends along with plasticizer and lithium salts are stirred at room temperature for 48 h or until slurry of polymer electrolyte is homogenous. The same procedure is repeated for PVA/SAN-PC-LiX in solvent THF. This homogenous blend of plasticised polymer with lithium salt is cast on to Teflon coated glass plate and dried over vacuum at 60 ^{o}C for 12 h to remove any traces of solvent.

X-ray diffraction (XRD) analysis was carried out using an X'Pert proPANalytical diffractometer using CuKα as source. Fourier Transform Infra Red (FT-IR) measurements were made using BRUKER Optik GmbH spectrometer in 4000 – 500cm^{-1} under transmittance mode. Thermal stability of the sample was measured using thermo gravimetric Analysis (VA instruments) with a heating range from room temperature to 1000 ^{o}C at the rate of 10^{o}C per minute. Ionic conductivity of the electrolyte was measured using FRA2 µ AUTOLAB - III with signal amplitude of 10 mV in the frequency range 40 Hz - 100 kHz. The bulk electrical conductivities of the polymer complexes were calculated from the impedance plots in the temperature range 303 -343 K.

Results and Discussion

Conductivity Studies

The conductivity studies are performed using typical ac impedance technique employing FRA2 µ AUTOLAB III to characterize the electrical properties of the material and their interfaces with the electrodes. In the present study, ionic conductivity of SAN and SAN/PVA based polymer blend electrolytes with different lithium salts are explored. The bulk electrical resistance value (R_b) is calculated from the intercept made by the spike on the real axis (Z') in impedance plot (8). The ionic conductivity (σ) is calculated using the equation:

$$\sigma = L / Rb\ A$$

were L = thickness of the sample, A = surface area of the sample film, and R_b = bulk resistance.

The conductivity values of both PVA/SAN and SAN with LiBr electrolytes are higher than those of the Li_2CO_3 and LiCl electrolytes over the temperature range studied. Fig. 1 shows the temperature dependence conductivity of PVA-SAN-PC-LiX [LiCl (P1)—Li_2CO_3 (P2)—LiBr (P3)]. It is evident that the polymer composite containing lithium bromide showed better conductivity compared to those containing other lithium salts. The temperature dependence of the ionic conductivity data of PVA/SAN and SAN complexes show that the conductivity can be well described by the familiar Arrhenius equation(9). The conductivity value of the LiBr electrolyte is higher than those of the Li_2CO_3 and LiCl electrolytes over the temperature range studied. This suggests that the ionic conductivity is affected by the diffusion rate of the ions, which in turn depends on the size of Br– ion. The degree of dissociation of the various salts has been previously reported in liquid electrolytes(10). The ionic conductivity enhancement observed in the PVA–SAN–PC–LiBr system evidently results from the combined effect of salt and plasticizer(11). The optimum conductivity value was 2.62×10^{-5} S cm^{-1} for PVA–SAN–PC– LiBr at room temperature. The ionic conductivity of the polymer electrolytes show temperature dependence (Arrhenius behaviour), where, it increases with increasing temperature(12, 13). The presence of plasticizer PC helps to trap the ions and enhance conductivity and stability of the film. The incorporation of PVA enhances the amorphous nature of the film leading to enhancement of conductivity. Among the counter ions, the bromide shows enhanced conductivity compared to chloride and carbonate as evident from Figure 1. This increase in conductivity with bromide anion compared to chloride anion in PVA-SAN-PC-Li salt system may be due to large size of the anion and greater ionic dissociation of bromide ion than chloride ion in THF solvent. Due to this effect the Li+ ions are completely free from anion and are attached to polymer chain leading to enhanced conductivity.

Thermal Studies

The thermal stability of the polymer electrolyte is an important parameter to promise suitable performance in lithium ion batteries especially when it is operated at elevated temperature. In order to study the thermal stability of the prepared samples, Thermo-Gravimetric analysis is carried out for A3 and P3 samples. It is seen from Figure 2 that the polymer electrolyte (A3) is stable up to 70°C up to which no degradation or loss of any kind takes place from the sample. The weight loss % of 31.74 at 123°C indicates that polymer electrolyte degrades and it is solvent free (THF). The weight loss % at this temperature may be due to melting of the polymer blend. Further degradations at 239°C, 348.65°C and 422.18°C are due loss of various components of the polymer electrolyte namely PC, SAN and LiBr. In short, the polymer electrolyte is thermally stable up to 70°C which is quite enough for battery applications. The TG Analysis of polymer electrolyte P3 (PVA+SAN+PC+LiBr) (Figure 3) shows sample is stable up to 42°C beyond which there occurs loss. This weight loss pertaining to 13% at 79°C is due to the solvent (THF) trapped and further degradation starts only beyond 264°C. The weight loss ends at 287°C corresponds to 37% is definitely due to degradation of the polymer, plasticizer component of the electrolyte. Thus the sample P3 is stable up to 264°C. The introduction of PVA into sample A3 has increased its stability from 70°C to 264°C shows that the choice of hybrid solid polymer electrolyte increases both the ionic conductivity as well as thermal stability(14, 15). The DSC curve of the composite polymer electrolyte P3 film is shown in Figure 4. From the Figure 4, it is evident that two small endothermic peaks centered at 107.5°C and 142.19°C correspond to the melting of PVA / SAN and Lithium ion, and a single exothermic peak centered at 303.6°C related to a thermal decomposition reaction of polymer electrolyte(16).

Conclusion

Polymer electrolyte films were prepared using SAN, PVA, PC and lithium salts comprising of chloride, bromide, carbonate as counter anions. Thermogravimetric analysis reveals the sample (A3) is stable up to 123°C beyond which degradation of the polymer electrolyte starts. The presence of solvent THF has had its effect on conductivity as evidenced in thermal studies where the sample (P3) is stable up to 264°C after removal of trace solvent THF at 79°C. The polymer PVA-SAN-PC-LiBr (P3) shows maximum conductivity of 8.72×10^{-5} Scm^{-1} at 70°C. The study of the effect of temperature variation on conductivity reveals that there is increase in conductivity with increase in temperature.

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Figure Captions

1. **Figure 1**: Temperature dependent variation of conductivity of sample: P1, P2, and P3.
2. **Figure 2**: TG analysis of sample A3 (SAN+PC –LiBr).
3. **Figure 3**: TG analysis of sample P3 (PVA+SAN+PC – LiBr).
4. **Figure 4**: DSC curve of PVA/SAN-PC- LiBr (P3).

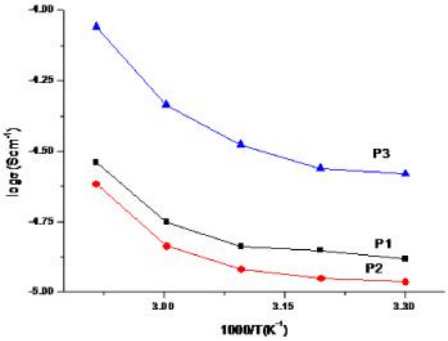

Figure 1: Temperature dependent variation of conductivity of sample: P1, P2, and P3.

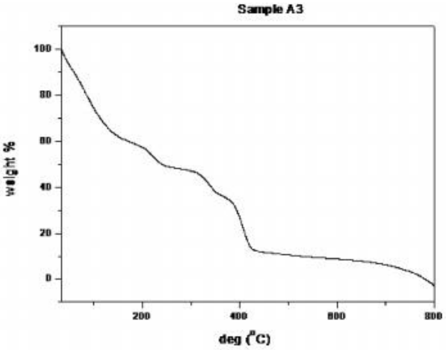

Figure 2: TG analysis of sample A3 (SAN+PC –LiBr)

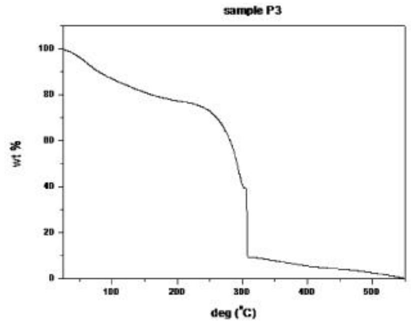

Figure 3: TG analysis of sample P3 (PVA+SAN+PC – LiBr)

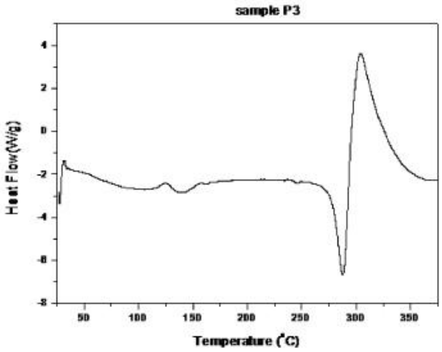

Figure 4: DSC curve of PVA/SAN-PC- LiBr (P3)