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Research Article

Solid polymer electrolytes as a prospective class of electrolytes

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Abstract

Electrolytes have been identified as one of the most influential components for the performance of electrochemical devices. In literature, there are several generations in the field of electrolytes and among them Solid Polymer Electrolytes (SPEs) have received a great interest. The first ever SPE has been introduced to the world around 1973. Thereafter, so many modifications have been done in order to uplift the characteristics of SPEs. In general, SPE is a blend of a polymer, a salt and solvent/s. With respect to SPEs, there are some special features of interest encompassing ionic conductivity, transference number etc. Various characterization techniques are being practiced to evaluate those properties and some of them are Electrochemical Impedance Spectroscopy (EIS), Cyclic voltammetry (CV) test, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Looking back at the past as well as the present day of SPEs, it can envisage that they will appear in future with a huge number of reforms.

Key words: Solid polymer electrolytes, Ionic conductivity, Electrochemical impedance spectroscopy, Cyclic voltammetry, Natural rubber

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1. INTRODUCTION

Electrolytes play a pivotal role in electrochemical devices mainly serving as the medium for facilitating ion conduction between the anode and the cathode. Besides, they take care of avoiding short circuiting between those two electrodes guaranteeing safer operation. Upon physical state of electrolytes, there are two major categories of electrolytes as solid and liquid[1]. They both owe various merits and demerits when employing in applications. To overcome crucial issues such as low conductivity, leakage and evaporation, a substantial amount of methodologies have been practiced by experts in multidisciplinary areas to explore novel electrolytes with significant higher performance. As a result, SPEs have been emerged as a prospective class of electrolytes upon the pioneering contribution by Wright et al in 1973[2]. A SPE is a membrane prepared via dissolution of salts in a polymer matrix with high molecular weight[3]. The first ever SPE reported by Wright et al was consisted with polyethylene oxide (PEO) as the host polymer and sodium thiocyanate (NaSCN) as the salt. Due to the unending enthusiasm blended with the dedication of the researchers in the field of polymers, SPEs have undergone a gigantic, incomparable progress towards improving their characteristics. As a result, several generations are recorded as key mile stones in the history of SPEs.

In this review article, the evolution, the approaches launched to improve ~~of~~ SPEs, the current state and features of interest of SPEs will be discussed in brief followed by common characterization methods. Lastly, future predictions and conclusions are presented.

2. EVOLUTION OF SOLID POLYMER ELECTROLYTES

In 1973, Wright et al came up with the first ever SPE comprising PEO and NaSCN and in addition, they reported the semi crystalline structure of complexes between PEO and alkali metals[2]. As time passes, it was realized that conductivity of a SPE should be higher than 10^{-4} Scm^{-1} to be used for device applications. Hence, the electrochemical properties of these systems were studied later and correlation between the ionic conductivity and the amorphous phase was highlighted[4].

Next generation came up with modified SPEs with the main target of breaking crystalline nature of the structure. This has been motivated mainly by the realization of the fact that crystallinity hinders the ionic conductivity[5,6]. Some of the modification methodologies include cross-linked polymer matrices, blended polymers and comb branched copolymers [7-9]. But, many of those approaches were also not able to reach the accepted conductivity levels.

Introduction of composite SPEs gave a new insight for conventional SPEs and unlocked another important era. A remarkable attention was focused on using plasticizers for SPEs[10,11]. Those plasticizers such as ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC) were capable of introducing amorphous nature to the SPEs while lowering glass transition temperature and paving path for high conductivity. Simultaneously, the mechanical properties were affected negatively which pose some limitations for practical applications. With the untiring efforts of researchers to raise the conductivity while maintaining mechanical properties, addition of fillers was practiced. As fillers, nanoscale additives like silicon dioxide (SiO_2), titanium dioxide (TiO_2) have been considered[12,13]. They slightly reduce conductivity but the assistance for sustaining good mechanical properties is well compensated.

Another key milestone in the history of SPEs is the introduction of gel polymer electrolytes (GPEs) for the first time by Feuillade and Perche in 1975 as an alternative and a parallel approach to improve SPEs[14,15]. A GPE is consisted of a polymer matrix wherein a liquid electrolyte with a salt/s and solvent/s are encapsulated in it. Upon continuous discoveries and progress of SPEs and GPEs, it has been found that presence of plasticizers and solvents create some negative issues while enhancing properties.

Ionic liquids (ILs) have opened a new chapter in the history of SPEs as they have proved to be suitable substitutes for plasticizers and solvents [16,17]. In some occasions, they have been able to replace the salts serving a dual role.

In the new millennium, hybrid inorganic-organic SPEs have been able to draw the world wide attention as a class of very attractive SPEs. They exhibited excellent mechanical, thermal, chemical and electrochemical stability and high conductivity at room temperature which was of pressing importance to increase the suitability for applications[18-20].

3. CURRENT STATE OF SPES WITH NOVEL APPROACHES

The major legacy of the present day world is indeed the concept of green technology and low cost. This has addressed the necessity for shifting of SPEs towards natural polymer materials which satisfy at once those two contradicting properties of safety and cheap price. At present different types of natural polymers have received a notable attention in preparation of SPEs.

3.1 Starch based SPEs

Starch, a form of energy storage in plants, is the largest amount of carbohydrate in human diets and is found in substantial quantities in staple foods such as potatoes, wheat, corn, and rice[21,22]. It is a polymeric carbohydrate composed of repeating glucose monomers joined by glycosidic linkages forming a stable helix structure[23,24]. SPEs have been made when starch is plasticized with glycerol. This has several beneficial properties such as biodegradability, non-toxicity and high ionic conductivity. Mattos et al have investigated a system of amylopectin rich starch, glycerol (30% of the starch mass) and lithium perchlorate ($LiClO_4$) with [O]/[Li] = 10 and have characterized through ionic conductivity (σ) measurements, scanning electron microscopy, thermal analysis, and spectroscopy in the UV–Vis–NIR region[25]. The results showed that the amylopectin rich starch plastisized with glycerol showed the highest σ of 1.1×10^{-4} Scm^{-1} at 30 °C.

3.2 Cellulose based SPEs

Cellulose is a biodegradable natural polymer which can be obtained from all plants. According to the literature reviews, samples with Hydroxyl Ethyl Cellulose (HEC) with different quantities of glycerol and addition of lithium trifluoro methanesulfonate ($LiCF_3SO_3$) have been prepared in the form of transparent films with very good adhesive properties [26, 27]. The best σ values of 1.07×10^{-5} Scm^{-1} at 30 ^{0}C and 1.06×10^{-4} Scm^{-1} at 83 ^{0}C were reported for the samples of HEC plasticized with 58% of glycerol. These results showed that plasticized HEC is a very good material to be used for the preparation of SPEs.

3.3 Chitosan based SPEs

Chitosan is a natural biopolymer with the chemical name of poly[(1,4)-N-acetylD-glucose-2-amine)] which has received an upsurge of interest from academia and industry over the past decades. Structure of chitosan is shown in fig. 1.

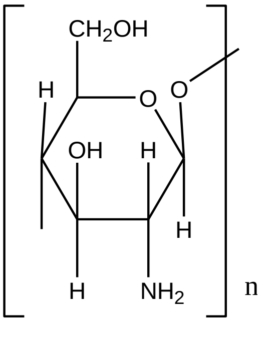

Fig. 1 Structure of chitosan

It also has been used as a polymer host in solid/composite polymer electrolytes for batteries and capacitors by several groups[28,29]. A lithiumtrifluoromethanesulfonate / EC / chitosan-based electrolyte was studied by Osman and Arof in 2003[30]. When ethylene carbonate (EC) was used as a plasticizer in this composite SPE, it has been reported that the ionic conductivity improved due to the interaction between the lithium salt and the plasticizer.

3.4 Gelatin based SPEs

Gelatin is a synthesized biopolymer which is also a polysaccharide. The molecular structure of gelatin is shown in fig. 2.

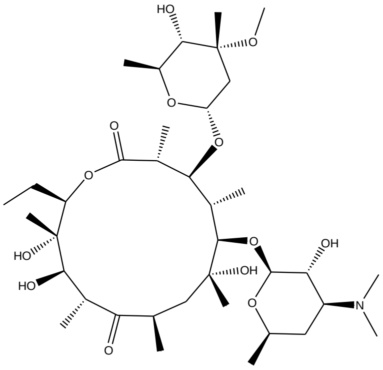

Fig. 2 Molecular structure of gelatin

When the gelatin-based SPE containing acetic acid are cross-linked with formaldehyde and plasticized with glycerol, σ values are found to be increased from 4.5×10^{-5} to 3.6×10^{-4} Scm^{-1} [31]. As the temperature increases from room temperature to 80 °C, the films are found to be mechanically stable. These gelatin based SPEs are very attractive for electrochemical device applications including electrochromic smart windows[32,33].

3.5. Natural rubber (NR) based SPEs

The growing interest in the exploitation of new raw materials for the development of high quality SPEs makes Natural Rubber (NR) a material of choice among polymers. This is due to its low cost and wide availability. NR having the monomer isoprene ($(C_5H_8)_n$) shown in fig.3 is obtained from the latex of several rubber yielding plants such as *Hevea brasiliensis* and *Parthenia argentatum*. But, it is to be noted that much preference is on the latex obtained from *Hevea brasiliensis*[34]. The rubber produced from latex contains relatively small quantities of protein (~2.2%), carbohydrates (~0.4%), natural lipids (~2.4%), glycolipids and phospholipids (~1.0%), inorganic materials (~0.2%), other compounds (~0.1%)[35]. The molar masses of rubber molecules range from 50,000 to 3,000,000 $gmol^{-1}$ [36]. There are several ongoing research activities in progress in the field of NR based SPEs during recent years.

They offer high σ and can provide good electrode–electrolyte contact which makes it suitable to be implemented in electrochemical devices. However, NR is an elastomeric, insulating polymer. Hence, modifications are needed to form it to serve as a host polymer in SPEs. Modified natural rubber (MNR) has a low glass transition temperature (T_g), soft elastomer characteristics at room temperature and possess adhesive properties[37].

Two types of modifications are being done to NR for enhancing their properties. They are grafting a methyl group and epoxidizing which are called Methyl Grafted Natural Rubber (MGNR) and epoxidized natural rubber (ENR) respectively.

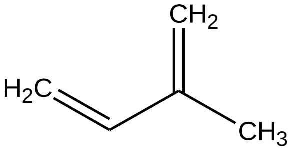

Fig. 3 Monomer of isoprene

It has been found that grafting methyl groups for the NR backbone upgrades the quality of NR to be competing as a polymer network in SPEs. Depending on the amount of methyl groups introduce to the backbone, resultants are labeled as MG49, MG30 etc. MG-49 is more free standing, flexible and has a good elasticity. MG49 also has oxygen atom with a lone pair of electrons acting as electron donor atoms in the structure of the polymer host. The interaction between the oxygen atoms and lithium ions of the metal salt forms a coordinate bond and generates polymer-salt complexes. A large number of studies on various MGNR have been reported in literature[37-39]. However, MGNR based SPEs with presence of plasticizers has shown enhanced ionic conductivity[34, 40]. Natural rubber-g-methyl methacrylate/poly(methyl methacrylate) (NR-g-MMA/PMMA) blends had been prepared by a melt-mixing system[41]. The mechanical properties and the fracture behavior of GNR/PMMA blends were evaluated as a function of the graft copolymer composition and the blend ratio. The tensile strength, tear strength and hardness increased with an increase in PMMA content. The tensile fracture surface examined by scanning electron microscopy disclosed that the graft copolymer acted as an interfacial agent and gave a good adhesion between the two phases of the blend.

To improve the stability, NR is sometimes chemically modified by introducing hydrophilic groups along the isoprene backbone or by epoxidization which yields Epoxidized Natuarl Rubber (ENR). The presence of polar epoxide groups in ENR provides rubber a compatibility with high polar fillers. ENR is commercially available in 25 mole % epoxidation (ENR 25) and 50 mole % epoxidation (ENR 50). The epoxy groups of ENR, which are randomly distributed, provide sites for chemical modifications or crosslinking with suitable compounds[42, 43]. ENR appears as a masticated sheet after it is passed into the two-roll mill machine about six times. Properties are improved depending on the degree of epoxidation. Epoxidation is found to be increasing the polarity of natural rubber [44]. ENR can be prepared by using peracid formed by the reaction of acetic or formic acid with hydrogen peroxide. It produces rubber with randomly dispersed epoxide groups along the polymer backbone[45]. However, ENR suffers a drawback due to sticky nature which disables easy peeling off from substrate[46,47].

4. FEATURES OF INTEREST

4.1 Ionic conductivity(σ)

From fundamentals, conductivity is defined as the degree to which a specified material conducts electricity and is calculated as the ratio of the current density in the material to the electric field which causes the flow of current[48]. There are two types of conductivities namely ionic and electronic. Ionic conductivity arises due to the motion of ionic charge whereas electronic conductivity is mainly due to electrons. For electrolytes, it is always needed to have higher ionic conductivity so as to make provision for ion conduction as well as for avoiding short circuiting. In general, SPEs should possess ionic conductivities beyond 10^{-4} $\mathrm{Scm^{-1}}$ at ambient temperature. It is a well accepted fact that ionic conductivity is totally depending on the charge mobility as well as the charge concentration[48]. For the mobility, viscosity of the medium is greatly responsoble as under higher viscosity, moving of charges become more difficult. With respect to charge concentration, there are two contradictory effects due to high and low concentrations. At high charge concentrations, ionic conductivity is expected to increase. But at higher charge concentration, there is a chance for the formation of neutral ion clusters leading to zero contribution for conductivity. And also, mobility can go down due to high population of charges. At low charge concentrations, again the conductivity is low due to the unavailability of sufficient number of charges. So, in each SPE, there is a certain value for charge concentration to achieve the highest conductivity. Ionic conductivity is normally symbolised with σ and it correlated to as,

$$\sigma=(1/R_b)(t/A) \tag{1}$$

Here, R_b is the bulk resistance of polymer electrolyte, t is the film thickness and A is surface area of electrolyte[49].

σ of SPEs is truly depending on temperature and its variation with temperature basically follows two behaviours. They are Arrhenius and Vogel Tamman Fulcher behaviours[50-52].

4.2 Transference number

Transference number is defined as the ratio of the current flowing when a steady state current is passing through a cell following establishment of a stable concentration gradient, to the current flowing in the absence of a concentration gradient. There are two types of transference numbers. They are ionic/electronic transference number and cationic/anionic transference number. They all are symbolizing the contribution of ions, electrons, anions and cations to the conductivity[53].

4.3 Thermal, chemical and electrochemical stability

To operate in an appropriate temperature range, SPEs must possess good thermal stability. It is mainly because the devices which use SPEs have to be operated in diverse temeprature ranges. The solid state electrochemical devices are fabricated by sandwiching the SPE membranes between appropriate cathode and anode materials. In order to avoid undesired chemical reactions proceeding at the electrode/electrolyte interfaces, SPEs should possess a high chemical stability. In addition, they have to be stable through a wide potential window. In other words, there should not be any current change within a certain potential window. Preferably, a electrochemical stability domain is expected to extend from 0 V to as high as 4–5 V[54].

4.4 Durability

Durability is a crucial factor for the continuous and constant operation of devices. It is exceptionally high in SPEs when compared to liquid and solid electrolytes. This is due to the retention of all components of a SPE without undergoing deterioration and also due to the good compatibility of SPEs with many electrodes. Unstable charge/discharge cycles are present if the durability is poor which affects the efficiency of devices very much.

5. CHARACTERIZATION METHODS

5.1 Electrochemical impedance spectroscopy (EIS)

EIS is a technique that is used to study the electrical properties of materials and their interfaces over a wide range of frequencies and temperatures. The bulk and interface contribution can be separated using this method. It can also be used to study the ion conduction mechanism and dielectric relaxation in SPEs. Frequency response analyzer is the main device that is being used to get required data for calculating conductivities at different frequencies.

σ is found via EIS using impedance measurements with an electrochemical cell consisting of the SPE film sandwiched between two electrodes**.** EIS could be used to measure the impedence. The impedance (Z) of a circuit is its opposition to the current, so for example in a circuit composed purely of resistors, the impedance is exactly equivalent to the circuit resistance. It can be represented by

$$Z=V/I \tag{2}$$

where V is the voltage and I is the current.

After gathering impedacne data, a graph is plotted with real part of impedacne (Z') and imagianry part of impedance (Z'') for the whole frequency range which is known as a Nyquist plot[55].

Fig. 4 shows a typical Nyquist plot, where the value of the first point of intersection at high frequency region between the arc and the x-axis represents the value of the bulk electrolyte resistance of SPE (R_b).

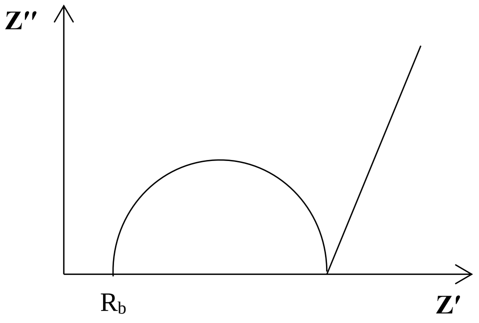

Fig. 4 Typical Nyquist plot

5.2 DC polarization test

In electrochemistry, polarization is a collective term for certain mechanical side-effects (of an electrochemical process) by which isolating barriers develop at the interface between electrode and electrolyte[56].

Measuring the ionic conductivity of a SPE yield limited information since no indication is given of what species are carrying the current nor is there any measure of what proportion of current is carried by a particular species. Greater insight into ion transport in such systems may be obtained by polarizing the electrolyte with a dc potential under conditions where transport of one of the constituents of the salt is suppressed. This phenomenon is called as a polarization test. A constant dc potential is applied across the sample and the current is monitored as a function of time remove. With this test, total ionic transference number (t_{ion}) can be calculated using DC polarization test according to the equation [57,58].

$$t_{ion}=(I_i-I_t) / I_t \quad (3)$$

I_i is the initial current and I_t is the steady current. If the ionic transference number (t_{ion}) of a SPE is close to unity, it highlights the dominant ionic contribution on conductivity. This means that the particular SPE is suitable for electrochemical applications. Interestingly, many of SPEs possess t_{ion} value very much close to unity[57,58].

Cationic transference number (t_c) can be calculated by using the following equation,

$$t_c=I_c /(I_c +I_a) \quad (4)$$

where, I_c is the current carried by cations and I_a is the current carried by anions. Allowed values of transport numbers are believed to lay exclusively in the range from 0 to 1[59,60].

5.3 Linear sweep voltammetry (LSV) and cyclic voltammetry (CV)

A typical linear sweep voltammogram is shown in fig. 5.

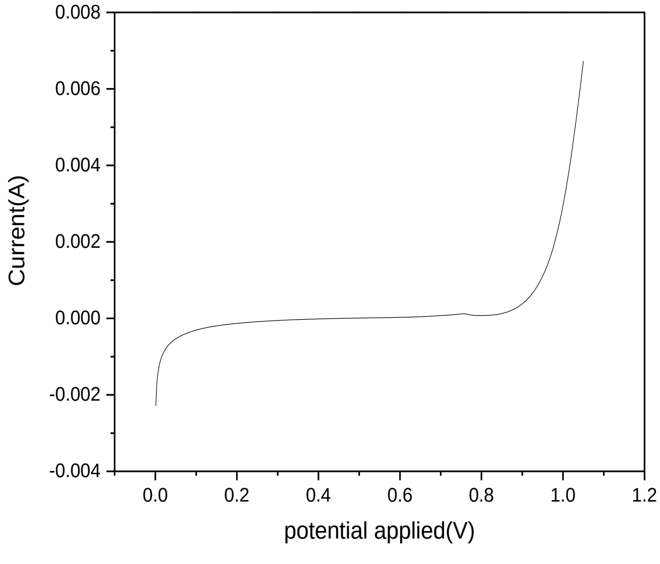

Fig. 5 Linear sweep voltammogram

In LSV, a fixed potential range is employed much like potential step measurements. However in LSV, the voltage is scanned from a lower limit to an upper limit as shown above[61].

CV is an electrochemical technique which measures the current that develops in an electrochemical cell during charge and discharge processes[62,63]. It could be performed by varying the potential between a working electrode and a reference electrode while measuring the resulting current between the working and counter electrodes. The potential of the working electrode is controlled with respect to the reference electrode such as a saturated calomel electrode (SCE) or a silver/silver chloride electrode (Ag/AgCl). The current can be considered as the response to the potential excitation signal. A graph can be drawn between potential and current. It is known as a cyclic voltammogram which is a useful tool for identifying several details of a particular system[64]. A typical cyclic voltammogram is shown in fig. 6.

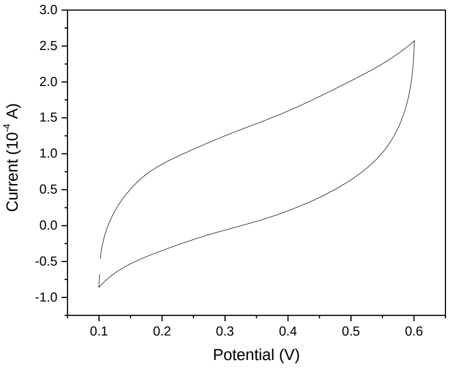

Fig. 6 A typical cyclic voltammogram

Cycling is done at a specific rate called as the scan rate. It serves as a determinant of the performance of the system under investigation. Modern instrumentation enables switching potentials and scan rates to be easily varied.

5.4 Scanning electron microscopy (SEM)

SEM provides surface morphological information of SPE films[65]. The scanning electron microscope which is one of the most versatile instruments is being used to perform SEM studies[66]. Image formation in the SEM is depending on the acquisition of signals produced from an electron beam and specimen interactions. These interactions can be divided into two major categories namely elastic interactions and inelastic interactions [67, 68]. Elastic scattering results from the deflection of the incident electron by the specimen atomic nucleus or by outer shell electrons of similar energy. This kind of interaction is characterized by negligible energy loss during the collision and by a wide-angle directional change of the scattered electron. Incident electrons that are elastically scattered through an angle of more than 90° are called backscattered electrons (BSE), and yield a useful signal for imaging the sample.

Inelastic scattering occurs through a variety of interactions between the incident electrons and the electrons and atoms of the sample and results in the primary beam electron transferring substantial energy to that atom. The amount of energy loss depends on whether the specimen electrons are excited singly or collectively and on the binding energy of the electron to the atom. As a result, the excitation of the specimen electrons during the ionization of specimen atoms leads to the generation of secondary electrons (SE), which are conventionally defined as possessing energies of less than 50 eV and can be used to image or analyze the sample[66]. A SEM image is shown in fig. 7.

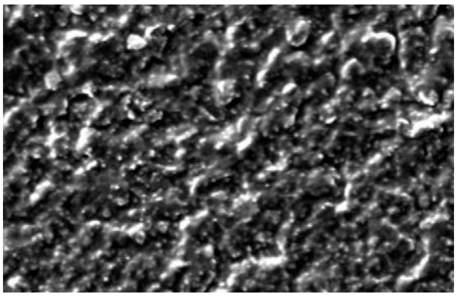

Fig. 7 A SEM image

5.5 X-Ray diffraction (XRD)

XRD is a powerful nondestructive technique for characterizing materials. X-ray diffractometer is the device used for this technology which produces the so-called diffractogram. It provides information on structures, phases, preferred crystal orientations and other structural parameters such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample[69]. XRD analysis is used to determine the structure and crystallization of polymer-salts complex by observing the appearance and disappearance of peaks. A sketch of a XRD pattern is given in fig. 8.

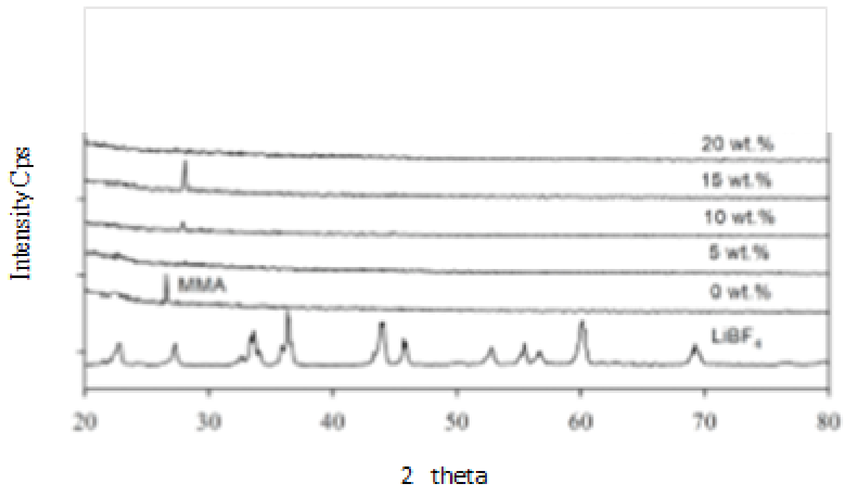

Fig. 8 XRD patterns of a SPE

5.6 Differntial scanning calorimetry (DSC)

DSC is an effective analytical tool for characterizing the physical properties of a polymer. It enables determination of melting, crystallization, mesomorphic transition temperatures, corresponding enthalpy and entropy changes, characterization of the glass transition and other effects which show either changes in heat capacity or latent heat. In addition to its simplicity and universality, the energy characteristics (heat capacity CP and its integral over temperature T), measured via calorimetry, have a clear physical meaning even though sometimes interpretation may be difficult[70].

The DSC set-up is composed of a measurement chamber and a computer. Two pans are heated in the measurement chamber. The sample pan contains the material being investigated. A second pan, which is typically empty, is used as a reference. The computer is used to monitor the temperature and regulate the rate at which the temperature of the pans changes. A typical heating rate is around 10 ^{0}Cmin^{-1}. A differential scanning calorimetry graph is shown in fig. 9.

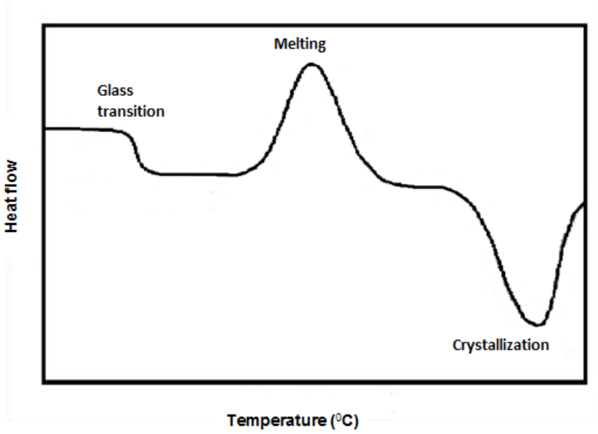

Fig. 9 Differential scanning calorimetry graph

7. PREDICTIONS FOR FUTURE

SPEs are promising alternatives to liquid and solid electrolytes and have received tremendous attention in energy storage system research in both academia and industry. Moreover, some companies have made efforts toward commercialization to promote the practical applications. Although substantial progress has been obtained, it is necessary to bear in mind that some fundamental issues concerning SPEs must be addressed before they meet the requirements for practical applications; the optimization of the ionic conductivity and the interfacial compatibility, for instance. Furthermore, fundamental knowledge as well as new design technologies is urgently needed to accelerate the industrialization process. Some new device architectures and technological applications with SPEs are still at an early stage and require better evaluation procedures. In the field of polymer nano composite materials, the influence of several parameters remains unexplored. Specifically, the role of the size, shape of the nanoparticles and their alignment remains to be clarified. Molecular-scale details regarding conductivity across conductive ceramics and polymer electrolyte interfaces has not been discussed largely. Moreover, there is still an open question of whether the polymer-nano particle interactions can indeed be tuned to achieve a simultaneous enhancement in conductivity and mechanical properties. To address such questions, more realistic force fields and models are essenial.

8. CONCLUSIONS

The storage of electrical energy is far more important in this century than it was in the previous decades. The necessity will be doubled during the next few years to come. This is mainly due to the high rising usage of multi-purpose appliances. In par with that, the use of SPEs in various devices has advanced much in recent years.

Since the introduction, SPEs have gone through a large number of developing stages in terms of improving their characteristics. Present day world has a high concern over green technology. Hence, it is very much needed to develop materials for SPEs which enable to raise the level of safety. On the other hand, due to economical constraints exist in many countries; money value is an important factor. Novel approaches are really important to address the low cost while maintain good performance. If SPEs are revitalized with more and more attractive features using suitable materials, demand on them will be doubled in the future. It is therefore the central focal point of attention of researchers in the fields like electrochemistry and material science to exploringe new SPEs with improved properties.

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