iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 7 **Issue:** XII **Month of publication:** December 2019

DOI: http://doi.org/10.22214/ijraset.2019.12116

www.ijraset.com

Call: 08813907089 | E-mail ID: ijraset@gmail.com

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.177
Volume 7 Issue XII, Dec 2019- Available at www.ijraset.com

A Comparative Review of Characterization of Polymer Electrolytes for Energy Storage Application

Richa Sharma[1], Dr. Aarti Verma[2]
[1]*Assistant Professor,* [2]*Professor, RCET, Bhilai.*

Abstract: ***In this review article, the recent progress in poly (ethylene oxide) based polymer electrolytes are comparatively studied based on the characterization of the poly(ethylene oxide) for its application in energy storage devices. Requirements for the polymer host, salt, solvent, nanofiller, and ionic liquid are elaborated in detail followed by the comparison of polymer electrolytes obtained by complexation of silver trifluoromethane sulfonate [$AgCF_3SO_3$] (also known as silver triflate) with PEO and PEO blend of Lithium trifluoromethanesulfonate with linear formula CF_3SO_3Li based on influence of addition of additives to improve electrical conductivity and crystallinity of the PEO matrix.***

Keywords: Polymer Electrolytes, Polyethylene Oxide, Electrical Conductivity, DSC, Battery

I. INTRODUCTION

Polymer electrolytes can be categorized as compounds formed via the dissolution of salt into polar and excessive molecular weight polymers [1]. Poly(ethylene oxide) based polymer electrolytes have numerous benefits which include high safety, ease of fabrication, low capital cost, high energy density, excellent electrochemical stability, and exquisite compatibility with salts/acids, however, possess low ionic conductivity at moderate temperatures, which limit their use in potential applications.[2] Poly(ethylene oxide) , PEO, is one of the most investigated polymer for solid-state electrolytes in the technology of lithium ion batteries.[3-4] PEO-based SPE is the most preferred polymer host in the research system due to its flexible backbone and ability to solvate lithium ions, with the coordination number dependent upon the salt concentration and identity of the anion.

The main advantage of PEO is high solvation strength. For this reason it can form complex easily with many alkalis salts and gives a right away path for cation migration due to the presence of (–CH2–CH2–Ö–)n in the polymer backbone. But the low conductivity value (10^{-7}-10^{-6} S cm^{-1}) and poor mechanical properties of PEO at the ambient temperature restrict their use in devices. in order to triumph over the disadvantage, the most common approach is changing of the morphology using the nanofiller/plasticizer/ionic liquid and salt with large anion within the polymer matrix. Polymer mixing is one of the exceptional followed techniques to improve the properties of host polymer and is a physical mixing of individual polymers together. This offers in hand superior properties than individual polymer and can be effortlessly controlled by varying the composition of polymer used. Further improvement in electrical and mechanical properties can be achieved by means of addition of nanofiller and plasticizer. [5] Many attempts have been made to enhance the ionic conductivity of polymer electrolytes by the use of copolymers, salts, polyelectrolytes and addition of plasticizers [6-8]

II. PROPERTIES

A. Properties of a solvent

An excellent solvent is essential for the better dissolution of salt and polymer thru dipole-dipole interactions. The solvent must possess simple traits which include high dielectric constant for better dissolution of salt, low viscosity for faster ionic movements, high electrochemical stability window, inert towards cell components and the principle one is it should offer ionic conductive solid electrolyte interface layer on electrodes. The high dielectric constant of solvent is a crucial parameter as it prevents the formation of the ion pairs because; ion pairs do not play any role in ionic conductivity. The solvent must completely swell and stretch the polymer chains within it so that more favourable interplay can arise between the cation and electron donor group of the host polymer. [6]

B. Properties of Salt

In order to fulfil the criterion of faster ion transport and high ionic conductivity salt plays a vital role. The salt must possess desirable properties such as; low lattice energy for more dissociation of salt, lower cation size for faster movement in the polymer matrix etc. One important requirement is the stability of anion towards electrodes and non-toxic nature. Also the high ionic conductivity and voltage stability window of the salt directly affects the overall conductivity of the electrolyte. As the mobility of ion plays an important role in determining conductivity so salt with smaller cation size and larger anion size are beneficial for obtaining optimal performance of an electrolyte.

©IJRASET: All Rights are Reserved

C. Properties of Ionic Liquid

The ionic liquids are molten salts with large anion at room temperature and bulky anion also supports the dissociation of salt in a polymer matrix which affects the electrochemical properties. On, the basis of their composition there are three types of ionic liquids aprotic, protic and zwitter, used for lithium batteries/super capacitor, fuel cells and ionic-liquid-based membranes, respectively [7-8]. The addition of ionic liquids in the polymer salt system also enhances the interfacial contact of electrodes with electrolyte and enhances the properties of the system.

D. Properties of Plasticizers

Plasticizers are the low molecular weight substances and when added in the polymer matrix increases its flexibility. The addition of plasticizer increases the free volume required for transport by penetrating between polymer chains. Since plasticizers are of a small size so they effortlessly penetrate between the polymer chains. This modifies the polymer chain arrangement by disrupting the cohesive force between polymer chains. This increases the segmental motion of polymer chains and more free volume is created. As for immediate ion transport, polymer matrix must possess high amorphous content. So to achieve the above the incorporation of plasticizer is the excellent approach which makes a significant enhancement of the amorphous phase as well as higher dissociation of salt into free cations and anions.[9]

E. Properties of Nanofiller

The addition of nanofiller in polymer electrolyte enhances the conductivity and also improves the mechanical properties such as physical strength of polymer electrolytes. The filler acts as a solid plasticizer that enhances the transport properties and reduces the crystallinity, glass transition temperature due to increase in the dielectric constant.

In the present study Poly(ethylene oxide) based nano-composite plasticized polymer electrolytes containing triflic acid and the effect of silver triflate on ion conducting characteristics of the PEO based composite polymer electrolyte[16] has been compared with the characteristic results of LiYrifl salt concentration on electrical conductivity an thermal properties of hot pressed Li+ ion conducting PEO composite electrolytes.[15]

III.COMPARISON

In an experiment to comprehend the effective interaction of polyethylene oxide (PEO) polymer matrix in conjunction with silver triflate ($AgCF_3SO_3$) dopant salt, dissolution of PEO is achieved by using dimethyl formamide (DMF) as the common solvent. [16]

Silver triflate possess properties that make it suitable to be chosen as a dopant, like it is non-susceptible to atmospheric humidity, non-hazardous and highly resistive to oxidation process. $AgCF_3SO_3$ salt with high lattice energy is expected to improve the performance in terms of electrochemical stability and high ionic conductivity. [10]

Lithium trifluoromethanesulfonate (LiTrifl) with linear formula CF3SO3Li is widely used as ion source and plasticizer and Lithium ion is the stronger Lewis base of the group as it accepts the single pairs on oxygen quickest and simply along with highest relative exposed positive charge.[11-14]

Aim of nano-filler addition is the reducing the crystallizing ability of the polymer without reducing the mechanical properties of the PEO composite. The carbon nanoparticles network-polymer composite exhibits electron tunnelling conductivity, which show that the CNTs and GRs network offers a promising application as filler material for creating super conductive composite.

A. Electrical conductivity

By using electrochemical impedance spectroscopy (EIS) the electrical conductivity for $(PEO)_x$: $AgCF_3SO_3$ (Where x= 50, 60, 70, 80 and 90 respectively) at room temperature for various compositions are obtained as listed in table.

Table 1. Values of room temperature electrical conductivity estimated for $(PEO)_{50}$:$AgCF_3SO_3$, $(PEO)_{60}$: $AgCF_3SO_3$, $(PEO)_{70}$: $AgCF_3SO_3$, $(PEO)_{80}$: $AgCF_3SO_3$ and $(PEO)_{90}$: $AgCF_3SO_3$ complexes.[16]

Compositions of $(PEO)_x$:$AgCF_3SO_3$	Electrical conductivity at room temperature
50:1	1.2×10^{-5} Scm^{-1}
60:1	2.9×10^{-5} Scm^{-1}
70:1	2.4×10^{-5} Scm^{-1}
80:1	6.2×10^{-6} Scm^{-1}
90:1	7.7×10^{-6} Scm^{-1}

©IJRASET: All Rights are Reserved

In comparison with pure PEO polymer electrolyte film the salt added $(PEO)_{60}$:Ag CF_3SO_3 composite polymer electrolyte film shows an increase in magnitude by five orders.

Conductivity results of the PEO/CNT and PEO/GR composite show, that addition of 0.05% GR increase conductivity of pure PEO from $7.8 \cdot 10^{-12}$ S/cm to $82.4 \cdot 10^{-12}$ S/cm. It can be concluded, that addition of only 0.05% GR increase conductivity of pure PEO by 10 times. At the same time, the opposite situation is with addition of 0.05% CNT, because conductivity decreased by 18 times from $7.8 \cdot 10^{-12}$ S/cm to $0.42 \cdot 10^{-12}$ S/cm. This behaviour can be explain by crystallinity degree increase and decrease of free Li+ ion mobility. Conductivity results of the PEO/CNT/LiTrifl composites show, that addition of LiTrifl increase electrical conductivity in all PEO/CNT/LiTrifl composites cases. Addition of 5% LiTrifl increase electrical conductivity of pure PEO from $7.8 \cdot 10^{-12}$ S/cm to $54.3 \cdot 10^{-12}$ S/cm (by 7 times), addition of 15% LiTrifl to $40.9 \cdot 10^{-12}$ S/cm (by 5 times) and addition of 25% LiTrifl to $32.8 \cdot 10^{-12}$ S/cm (by 4 times).

Addition of LiTrifl increase electrical conductivity in all PEO/GR/LiTrifl composites cases. Addition of 0.5% LiTrifl increase electrical conductivity of pure PEO from $7.8 \cdot 10^{-12}$ S/cm to $99.3 \cdot 10^{-12}$ S/cm (by 13 times), addition of 1.5% LiTrifl to 273·10-12 S/cm (by 35 times) and addition of 2.5% LiTrifl to $571 \cdot 10^{-12}$ S/cm (by 73 times).[15]

B. Differential Scanning Calorimetric (DSC) Data

The DSC curve of pure PEO displays a step change at 210 K [- 63°C] which may be attributed to the glass transition temperature (Tg) of the polymer host. Upon incorporation of silver triflate (AgTr) salt into the matrix of PEO the value of T g reaches a maximum value of 221 K [54°C] for the $(PEO)_{60}$:$AgCF_3SO_3$ complex and this type of increase in glass transition temperature may provide the desirable flexibility of polymer backbone chain in the case of PEO polymer thereby facilitating rapid movement of ionic species which would in turn enhance the electrical conductivity.[16]

For Lithium trifluoromethanesulfonate (LiTrifl), the experiment tests the lowest and the highest content of the CNT and GR filler to see the main characteristic changes in polymer composite electrolyte thermal properties.

It was observed that PEO reached 80% of the theoretically possible crystallinity. The addition of only 0.05% CNT or GR to pure PEO, decrease melting temperature from 66.7°C by 0.5°C and 0.8°C respectively. But addition of 0.5% CNT to PEO increase its melting temperature by 1.2°C, therefore electrical conductivity in this case decreased.

The addition of LiTrifl decrease melting temperature of PEO/0.05%CNT/LiTrifl composite from 66.2°C to 60.2°C, but addition of LiTrifl to PEO/0. 5%CNT/LiTrifl decreased *Tm* only to 60.8°C, further addition of LiTrifl increase melting temperature

The addition of LiTrifl decrease melting temperature of PEO/0.05%GR/LiTrifl composite from 65.9°C to 62.1°C, but addition of salt to PEO/0.5%GR/LiTrifl decrease it only to 63.4°C. Bulk PEO melting temperature is lower than PEO film melting temperature. The difference between bulk (*Tm*=65°C) and film (*Tm*=66.7°C) PEO melting temperatures is equal to 1.7°C. We can suggest that this difference exist because of free volume theory and kinetic theory for structural relaxation, where dynamic displacements in film are higher than in bulk polymer.[15]

IV. CONCLUSIONS

In all the PEOs (PEO)60:AgCF3SO3, PEO/CNT/LiTrifl and PEO/GR/LiTrifl increase of the doping salt content increases the electrical conductivity. The highest electrical conductivity is of (PEO)60:AgCF3SO3 which was 2.9×10-5 Scm-1 as compared to PEO/CNT/LiTrifl and PEO/GR/LiTrifl with electrical conductivity of 81.8 ×10-9 Scm-1 and 1.01 × 10-9 Scm-1. The DSC analysis indicates that the addition of salt induces change in melting temperature and decreases the degree of crystallinity whereas the Addition of LiTrifl as plasticizer to PEO/CNT and PEO/GR system decrease crystallinity and thus decrease melting temperature. On the basis of this comparative review promising candidate for application in solid state batteries may be selected which possesses optimum electrical conducting composition and have satisfactory performance under low current drain.

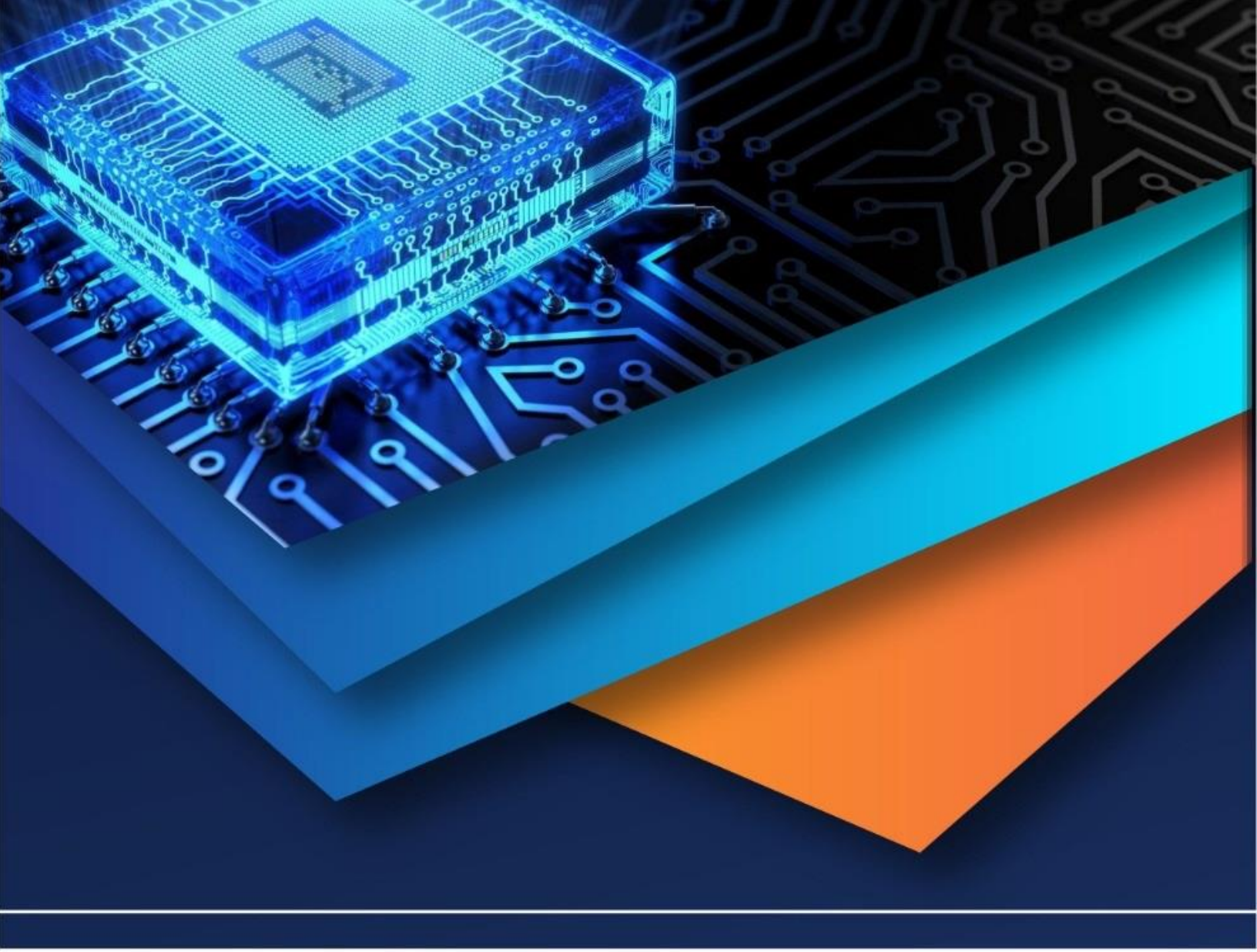
REFERENCES

[1] D. E. Fenton, J. M. Parker, P. V. Wright, Complexes of alkali metal ions with poly(ethylene oxide), Polymer, 1973, 14, p 589
[2] G. MacGlashan, Y.G. Andreev, P.G. Bruce, The Structure of the polymer electrolyte Poly(ethylene oxide)6:LiAsF6, Nature, 398 (1999), p792–794
[3] F. M. Gray, Polymer Electrolytes RSC Materials Monographs, Cambridge, 1997.
[4] Chem. Rev. Special issue on batteries and fuel cells, 2004,104,10, p 4243-4244
[5] Arya A, Sharma AL, Sharma S, Sadiq M, Role of low salt concentration on electrical conductivity in blend polymeric films Journal of Integrated Science and Technology, 2016, 4, p 17-20
[6] Liang B, Tang S, Jiang Q, Chen C, Chen X, Li S and Yan X 2015 Preparation and characterization of PEO-PMMA polymer composite electrolytes doped with nano-Al2O3 Electrochimica Acta, 169, p 334-341

©IJRASET: All Rights are Reserved

[7] Armand M, Endres F, MacFarlane D R, Ohno H and Scrosati B 2009 Ionic-liquid materials for the electrochemical challenges of the future Nature Materials 8 p 621-629.
[8] Lu J, Yan F and Texter J 2009 Advanced applications of ionic liquids in polymer science Progress in Polymer Science, 34, p 431-448
[9] Pradhan D K, Choudhary R N P, Samantaray B K, Karan N K and Katiyar R S 2007 Effect of plasticizer on structural and electrical properties of polymer nanocomposite electrolytes Int J Electrochem Sci, 2 ,p 861-871.
[10] Gondaliya, N.; Kanchan, D. K.; Sharma, P.; Jayswal, M. S.; Polym. Compos., 2012, 33, 2195. DOI: 10.1002/pc.22362
[11] Chandra An, Chandra Ar and Thakur K 2013 Indian J. of Pure & Applied Physics., 51 44-8
[12] Dey A, Karan S and De K S 2013 Indian J. of Pure & Applied Physics. 51 281-8
[13] Brandell D. 2005 Understanding ionic conductivity in crystalline polymer electrolytes. Acta Universitatis Upsaliensis. Digital Comprehensive summaries of Uppsala dissertations from the faculty of science and technology 34. p 63
[14] Gadjourova Z, Andreev Y G, Tunstall D P and Bruce PG 2001 Nature 412 520
[15] A Jurkane and S Gaidukov, Preparation and characterization of hot-pressed Li+ ion conducting PEO composite electrolytes , IOP Conf. Ser.: Mater. Sci. Eng. 111 012016, 2016
[16] S. Amudha, S. Austin Suthanthiraraj, Silver ion conducting characteristics of a polyethylene oxide-based composite polymer electrolyte and application in solid state batteries, Adv. Mater. Lett. 2015, 6(10), 874-882

©IJRASET: All Rights are Reserved



10.22214/IJRASET

45.98

IMPACT FACTOR: 7.129

IMPACT FACTOR: 7.429

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Call : 08813907089 (24*7 Support on Whatsapp)