Caliphate Journal of Science & Technology (CaJoST)

ISSN: 2705-313X (**PRINT**); 2705-3121 (**ONLINE**) **Research Article**

Open Access Journal available at: https://cajostssu.com and https://www.ajol.info/index.php/cajost/index

DOI: https://dx.doi.org/10.4314/cajost.v4i1.11

Article Info

Received: 2nd July 2020

Revised: 9th September 2021

Accepted: 11th September 2021

Department of Physics, Sokoto State University, Sokoto.

***Corresponding author's email:**

yaroko53@gmail.com

Cite this: *CaJoST*, 2022, 1, 87-92

Potassium Hydroxide Doped With (Poly(Methyl Methacrylate) (PMMA) Polymer as Electrolyte for Electrolytic Double layer Supercapacitor (EDLC) Application

Ibrahim Zakariya'u* and Abubakar A. Sifawa

The prime objective of the present paper is to develop polymer electrolyte doped with salt. A solution cast technique was adopted to develop a solid polymer electrolyte of polymer (Poly (methyl methacrylate) (PMMA) as host polymer and salt potassium hydroxide, KOH as dopant. Incorporation of salt increases the amophosity and homogeneity, decreases the surface roughness. Moreover, doping of salt (KOH) increases the overall conductivity of polymer electrolyte film. Electrochemical impedance spectroscopy (EIS) reveals the enhancement in conductivity (4 orders of magnitude) by salt doping. FTIR shows the complexation and composite nature of films. Polarized optical microscopy (POM) shows reduction in crystallinity which is further confirmed by Differential scanning calorimetry (DSC). Fabricated electrochemical double-layer supercapacitor using maximum conducting polymer salt electrolyte and symmetric carbon nanotubes electrodes shows specific capacitance of 21.86.

Keywords: Polymer electrolyte, conductivity, DSC, FTIR.

1. Introduction

In the 20th century, most of the polymers have been used as structural materials or electric insulators. In the past 20 years these polymers have been tailored to ion conductor, when combined with some inorganic or organic salts their ionic conductivity can be up to the mark used as an electrolyte[1]. So, polymer electrolyte are basically the alkali salt dissolved in polymer.

The ionic solids which have high conductivity at room temperature are known as solid electrolyte. The conduction is due to the movement of ions through voids, or empty crystallographic positions, in their crystal lattice structure. The cation or anion of the structure must be free to move in the structure as charge carrier. The drawbacks of liquid electrolyte lead to the polymer electrolyte, although the liquid electrolyte has high conductivity and electrochemical performance for Edlc Application. But there are still lot of drawbacks in liquid electrolyte like leakage, volatile nature and flammable organic solvent, difficulty in fabrication and corrosion [2-3]. Polymer electrolytes exhibits the advanced features which overcomes the counterparts of liquid electrolyte like light weight, low volatility, leakage-free, mechanically stable, flexible geometry and good compatibility with electrodes[4-5].

Many polymers have been studied and reported in polymer electrolytes like poly (ethylene oxide) PEO[6-8], poly (acrylonitrile) (PAN)[9-10], poly (vinylidenefluoride) (PVDF)[11-13], Biodegradable natural polymers such as chitosan [14-16], starch [17-18], cellulose [19-20], and natural rubber [21-23] have also been extensively studied.

Poly(methyl methacrylate) (PMMA), is one of the most thermoplastic polymer used in various applications in nanotechnology, photovoltaics, sensors, batteries, actuators to named few[24]. The polymer PMMA commercially known as Plexiglas, acrylate or Perspex and due to its physical and mechanical properties, high young's modulus and hardness ratio, is one of the most popular thermoplastics [25].

In past years researchers have reported a lot of work in polymer electrolyte like PMMA based polymer electrolyte using solvent EC-PC mixed with dopant LiBF4 salt[26], PVC-PMMA blend polymer electrolyte with different plasticizer's which shows increase in mechanical and ionic conductivity[27], PAN-PMMA blend polymer

electrolyte with LiClO4 salt[28], the host polymer PMMA containing different salt Li, Na, Mg, and Zn perchlorates and PC as plasticizers, the resistivity of PMMA based polymer electrolyte with a smaller cation is higher than that containing larger cation[29], the ionic conductivity of polymer electrolyte decrease on adding the polymer in electrolyte[30].

Our present research has focused on developing a PMMA polymer doped with salt KOH in order to enhance the ionic conductivity.

2. Experimental Details

2.1 Materials Used

The polymer poly(methyl methacrylate) (PMMA), was purchased from Sigma Aldrich, USA while potassium hydroxide (KOH) and other solvents were purchased from Qualikems Fine Chem Pvt. Ltd.,Vadodara, India.

2.2 Electrolyte Preparation

The solution cast method was adopted to make polymer electrolyte film which produces a polymer film of varying thickness ranging from several micrometers up to several millimeters. Initially PMMA was dissolved in acetone and allowed to be mix uniformly for 2 hours. Now, in prepared solution a certain amount of salt KOH by varying its concentration added into a PMMA polymer solution. Again, allowed to be mix uniformly and was kept for whole night to make a homogenous viscous solution polymer-salt. At last finally, the prepared solution was kept for drying in polypropylene petri dishes at room temperature followed by vacuum drying to remove the remaining traces of solvent and detail conductivity, optical microscopy, FTIR and DSC measurement have been done of salt KOH doped PMMA electrolyte.

3. Results and Discussion

3.1 Conductivity Measurement

The prepared polymer electrolyte film were characterized for ionic conductivity by using CH instrument workstation (model 604D, Austin, Texas, USA). The ionic conductivity was measured using two stainless steel electrode and using the formula

$$\sigma = 1/R_b . l/A$$

where **σ** is ionic conductivity, **Rb** is bulk resistance, **l** is the thickness of the film and **A** is the area of a film covered by the electrode. Complex spectroscopy [31] has been used to calculate the room temperature ionic conductivity of pristine PMMA and KOH salt doped PMMA polymer electrolyte film. The calculated values of conductivity are plotted in Figure 1. From the conductivity plot, it is clear that the conductivity initially increases on adding of KOH into PMMA polymer matrix which is due to the number of mobile charge carriers' enhancement as salt KOH composed of cation potassium K^+ and anion hydroxide OH^-. The conductivity (σ) at 30 wt.% KOH into PMMA attains maximum conductivity (**σ**) value of 5.21 x 10^{-5} and then continuously decreases after 40 wt.% to 80 wt.% KOH which can be attributed to the formation of multiple charge carriers [32-33]

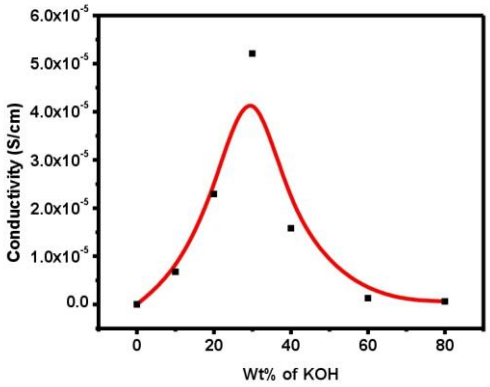


Figure 1: Ionic conductivity vs wt% of salt in pure polymer film.

3.2 Dielectric measurement

The dielectric constant measurement further established a correlation with ionic conductivity data shown in Table 1 which was recorded at three different frequencies that is 10^4, 10^5, and 10^6 Hz. At frequency range 10^4 Hz, the dielectric constant increases with increase in the salt KOH concentration and follow the same trend which we have recorded for conductivity data. At 40 wt.% KOH, the dielectric constant starts continuously decreasing up to 80 wt.% KOH which is due to the formation of multiple charge carriers. At frequency range 10^5, and 10^6 Hz, the similar trend has been seen which follows the same conductivity trend shown in Figure 1.

As it is well known that, increase in dielectric constant leads to the increase in ionic conductivity and decrease in the electronic conductivity.

3.3 Optical Measurements

Optical micrographs of the PMMA and KOH doped PMMA electrolyte films has been recorded by the use of polarized optical

microscope (POM) (Motic-model no. BA310 Pol, Carlsbad, California, USA) at 40x magnifications to see the effect of KOH salt doping on polymer films.

The optical micrograph of pure PMMA and KOH doped PMMA electrolyte films are shown in Figure 2. Figure 2 (a) is the micrograph of pure PMMA film which exhibit the dense morphology which is a interpretation of mostly crystalline nature of a electrolyte film. On the other side, the micrographs of KOH doped PMMA polymer electrolyte in Figure 2 (b) reveals the reduction in crystallinity nature of electrolyte film with a dark region which indicates the amorphous nature of a film shown in it. It is well known that, the amorphous nature of a material always be a favorable condition for a material to be an ionic conductive. The amorphous region of a film is a positive sign validate our conductivity graph.

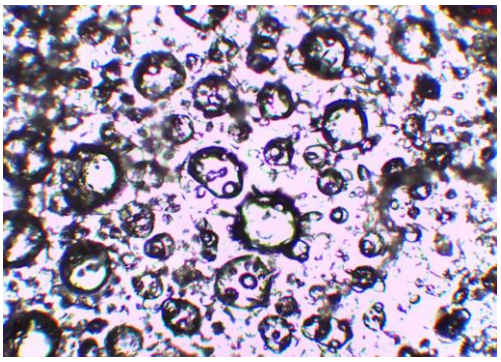
Table 1: Dielectric constant vs. wt.% of KOH at different frequencies in PMMA polymer electrolyte.

Wt% of IL	10^4 Hz	10^5 Hz	10^6 Hz
0	9.34805	8.67497	55.29351
10	115.51	4701.98	17223.44
20	851.66	8708.73	65204.72
30	4920.9	66891.97	342354.92
40	653.58	7346.84	28833.65
60	26.74	668.92	15484.21
80	13.1	196.05	8239.59

3.4 FTIR studies

The FTIR studies were performed using a CARY 630 (Agilent Technologies, USA) spectrophotometer to investigate the salt KOH-PMMA interaction. FTIR has been used for elucidation of structural information. Additionally, it shed light on intensity, position, and shape of vibrational bands followed by changes in polymer at molecular level. Figure 3 depicts the FTIR spectra of **(a)** pure PMMA, **(b)** 30 % KOH doped in PMMA, and **(c)** Pure KOH. The associated functional groups are tabulated in Table 2. It is noticed that the FTIR spectra of KOH doped PMMA contains all the peaks which is associated with pure PMMA and pure KOH with a slightly change in the intensity of the peaks, affirms the composite nature of polymer electrolyte film.

(a)



(b)

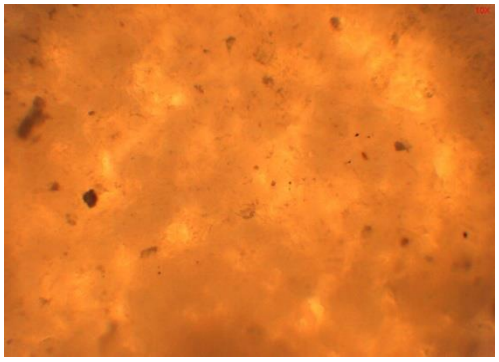


Figure 2: POM of (a) pure PMMA matrix and (b) maximum conductivity KOH doped film at magnification 10x.

Table 2: Vibrational mode in PMMA

Modes of vibration	Wave number
-CH stretching	2951
C=O stretching	1726
CH_3 stretching	1439
-OCH_3 stretching	1149
C-H stretch	2925
C=O stretch	1622
C-O stretch	1391
C-H stretch	1369

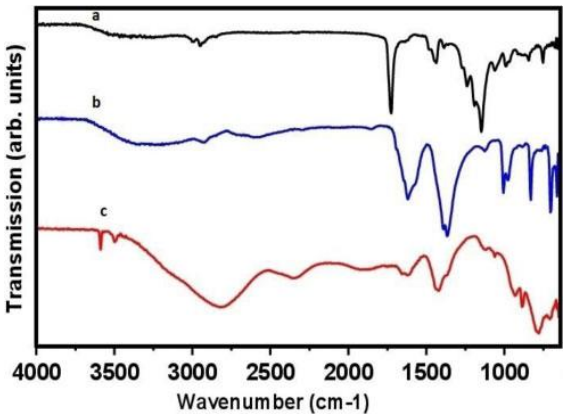


Figure 3: FTIR spectra of (a) pure PMMA, (b) 30 wt% KOH doped PMMA, and (c) pure KOH

3.5 Thermal Analysis

The thermal properties of PMMA and optimized 30 wt.% KOH doped PMMA were characterized by Differential Scanning Calorimetric (DSC). The prediction towards the glass transition temperature (T_g) for pure PMMA and KOH doped PMMA illustrated with black and red color respectively in Figure 4. The pure PMMA exhibits the glass transition temperature ($_g$-=85^{o}C) due to the tautness in the polymer chain. An ongoing enhancement in T_g is observed when potassium hydroxide is added, showing the effect in glass transition temperature (T_g=95^{o}C) which is higher than that observed in pure PMMA. The T_g of KOH doped PMMA is significantly improved than that of a pure PMMA polymer film.

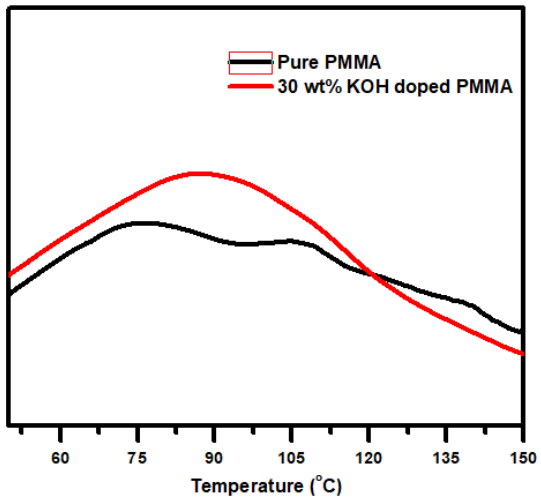


Figure 4: Deferential scanning calorimetry (DSC) curve of pure PMMA, and 30 wt% KOH doped PMMA.

4. Conclusion

This research work reports a new solid polymer electrolyte applicable in the EDLC application. Solid polymer electrolyte films of PMMA doped with KOH were prepared using solution cast technique. Complex impedance spectroscopy reveals the enhancement in ionic (σ) of PMMA þ KOH system by doping with KOH and conductivity maxima were observed at 30 wt% KOH concentrations. Dielectric data also support our conductivity data. FTIR confirms the composite nature as well as the interaction between polymer backbone and salt. Doping salt further assisted in crystallinity suppression (enhances in amorphicity) as observed in DSC. Laboratory–scale EDLC has been fabricated using maximum conducting PMMA 30%wt%KOH and r-GO-based electrodes, which shows high Csp of approximately 20.

Conflict of interest

The authors declare no conflict of interest.

References

[1] j. chem. soc. faraday trans., 1993, 89(17), 3187-3203

[2] Dzulkurnain, N.A., Ahmad, A., & Mohamed, N.S. (2015). P(MMA-EMA) Random copolymer electrolytes incorporating sodium iodide for potential application in a dye-sensitized solar cell. Polymers, 7(2), 266-280.

[3] Long, L., Wang, S., Xiao, M., & Meng, Y. (2016). Polymer electrolytes for lithium polymer batteries. Journal of Materials Chemistry A, 4, 10038-10069.

[4] Ngai, K.S., Ramesh, K., & Juan, J.C. (2016). A review of polymer electrolytes: fundamental, approaches and applications. Ionics, 22(8), 1259-1279.

[5] Arya, A., & Sharma, A.L. (2017). Polymer electrolytes for lithium ion batteries: a critical study. Ionics, 23(3), 497-540.

[6] Prabakaran, P., Manimuthu, R.P., Gurusamy, S., & Sebasthiyan, E. (2017). Plasticized polymer electrolyte membranes based on PEO/PVDF-HFP for use as an effective in lithium-ion batteries. Chinese journal of polymer science, 35(3), 407-421.

[7] Costa, L.T., Sun, B., Jeschull, F., & Brandell, D. (2015). Polymer-ionic liquid ternary systems for Li-battery electrolytes: Molecular dynamics studies of LiTFSI in a EMIm-TFSI and PEO blend. Journal of chemical physics, 143(2), 024904/1-024904/9.

[8] Polu, A.R., & Rhee, H.W. (2016). Ionic liquid doped PEO-based solid polymer electrolytes for lithium-ion polymer batteries. International journal of hydrogen energy, 1-8.

[9] Sivadevi, S., Selvasekarapandian, S., KArthikeyan, S., Sanjeeviraja, C., Nithya, H., Iwai, Y., & Kawamura, J. (2015). Proton-conducting polymer electrolyte based on PVA-PAN blend doped with ammonium thiocyanate. Ionics, 21(4), 1017-1029.

[10] Jyothi, N.K., Ratnam, K.K.V., Sundari, G.S., & Murthy, P.N. (2016). Ionic conductivity

and battery characterstic studies of a new PAN-based Na^+ ion conducting gel polymer electrolyte system. Indian journal of physics, 90(3), 289-296.

[11] He, Z., Cao, Q., Jing, B., Wang, X., & Deng, Y. (2017). Gel electrolytes based on poly (vinylidenefluoride-co-hexafluoropropylene)/thermoplastic polyurethane/poly (methyl methacrylate) with in situ SiO_2 for polymer lithium batteries. Royal society of chemistry, 7, 3240-3248.

[12] Mahant, Y.P., Kondawar, S.B., Bhute, M., & Nandanwar, D.V. (2015). Electrospun poly (vinylidene fluoride)/poly (methyl mathacrylate) composite nanofibers polymer electrolyte for batteries. Procedia materials science, 10, 595-602.

[13] Gebreyesus, M.A., Purushotham, Y., & Kumar, J.S. (2016). Preperation and characterization of lithium ion conducting polymer electrolytes based on a blend of poly(vinylidene fluoride-co-hexafluoropropylene) and poly(methylmethacrylate). Heliyon, 2(7), 1-15.

[14] Cao, L., Yang, M., Wu, D., Lyu, F., Sun, Z., Zhong, X .,… Lu, Z. (2017). Biopolymer-chitosan based supramolecular hydrogels as solid state electrolyte for electrochemical energy storage. Royal society of chemistry, 53, 1615-1618.

[15] Navaratnam, S., Ramesh, K., Ramesh, S., Sanusi, A., Basirun, W.J., & Arof, A.K. (2015). Transport mechanism studies of chitosan electrolyte systems. Electrochimica Acta, 175, 68-73.

[16] Buraidah, M. H., Teo, L.P., Au Yong, C.M., Shah, S., & Arof, A.K. (2016). Performance of polymer electrolyte based on chitosan blended with poly (ethylene oxide) for plasmonic dye-sensitized solar cell. Optical materials, 57, 202-211.

[17] Teoh, K.H., Lim, C.-S., Liew, C.-W., Ramesh, S., & Ramesh, S. (2015). Electric double-layer capacitors with corn starch-based biopolymer electrolytes incorporating silica as filler. Ionics, 21(7), 2061-2068.

[18] Shukur, M.F., Ithnin, R., & Kadir, M.F.Z. (2016). Ionic conductivity and dielectric properties of potato starch-magnesium acetate biopolymer electrolytes: the effect of glycerol and 1-butyl-3-methylimidazolium chloride. Ionics, 22(7), 1113-1123.

[19] Razalli, S.M.M., Saaid, S.I..Y.S.M., Ali, A.M.M., Hassan, O.H., & Yahya, M.Z.A. (2015). Cellulose acetate-lithium bis(trifluoromethanesulfonyl) imide solid polymer electrolyte: ATR-FTIR and ionic conductivity behavior. Functional Materials Letters, 8(3), 1540017.

[20] Chai, M.N., & Isa, M.I.N. (2016). Novel proton conducting solid bio-polymer electrolytes based on carboxymethyl cellulose doped with oleic acid and plasticized with glycerol. Scientific reports, 6, 27328.

[21] Wang, R., Mei, H., Ren, W., & Zhang, Y. (2016). Grafting modification of epoxidized natural rubber with poly (ethylene glycol) monomethylether carboxylic acid and ionic conductivity of graft polymer composite electrolytes. Royal society of chemistry advances, 6, 107021-107028.

[22] Idris, R., & Bujang, N.H. (2014). Epoxidised natural rubber based polymer electrolyte systems for electrochemical device applications. Advanced materials research, 896, 62-65.

[23] Yusoff, M., Hafiza, S.N., Sim, L.H., Chan, C.H., Aziz, S.S.S.A., Mahmud, Z.S., & Hairi, H.M. (2015). Studies on thermal and conductivity of modified natural rubber. Journal of advanced research in materials science, 12(1), 1-11.

[24] Huang H., Rempel G. L., 2013. Preparation of core-shell nanostructured PMMA-PS for prosthesis and implant material applications. Advances in Biomedical Engineering Research 1(4), 62-68.

[25] Park S.E., Chao M., Raj P.A., 2009. Mechanical properties of surface-charged Poly(Methyl Methacrylate) as denture resins. International Journal of Dentistry 2009, Article ID 841431

[26] Z. Osman, M.I. MohdGhazali, L. Othman, K.B. Md Isa, Electrochimica Acta, 2, 1-4, (2012)

[27] Hee-Tak Kim, Kyoung-Bae Kim, Sun-Wook Kim, Jung-Ki Park Electrochimica Acta, 45, 4001–4007, (2000)

[28] X.Helan Flora, M.Ulaganathan, S.Rajendran Int. J. Electrochem. Sci.,7, 7451 – 7462 (2012)

[29] Jiri Vondrak, Marie Sedlarkova, Jana Velicka, BretislavKlapste, Vtezslav Novak , Jakub Reiter, Electrochimica Acta, 46, 2047–2048, (2001)

[30] A.Manuel Stephan Electrochimica Acta., 42, 21-42, (2006)

[31] J.R. Macdonald, Impedance spectroscopy. John wiley & sons, New York, 1987.

[32] Singh R, Bhattacharya B, Rhee Hee-Woo, Singh Pramod K. Solid gellan gum polymer electrolyte for energy application. Inter J Hydrogen Energy 2015;40:9365e72.

[33] Singh R, Polu Anji R, Bhattacharya B, Rhee Hee-Woo, Varlikli Canan, Singh Pramod K. Perspectives for solid biopolymer electrolytes in dye sensitized solar cell and battery application. Renew Sustain Energy Rev 2016;65:1098e117.

[34] Xu L, Xu F, Chen F, Yang J, Zhong M. Improvement in Comprehensive Properties of Poly (Methyl Methacrylate)- Based Gel Polymer Electrolyte by a Core-Shell Poly(MethylMethacrylate)-Grafted Ordered MesoporousSilica. Journal of Nanomaterials 2011;2012:

