ORIGINAL PAPER

Effect of plasticizer on the conductivity of carboxymethyl cellulose-based solid polymer electrolyte

Shikha Gupta[1] · Pradeep K. Varshney[1]

Abstract

Lithium ion conducting solid polymer electrolyte based on carboxymethyl cellulose (CMC) complexed with lithium tetrafluoroborate was prepared by using solution cast technique. Ionic conductivity was measured using ac impedance analyzer and observed as 8.2×10^{-6} S cm^{-1} at room temperature. For further enhancement in the conductivity, plasticizer was introduced and it reached up to 3.7×10^{-3} S cm^{-1} at room temperature. Structural characterization was performed by using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscope technique. XRD results show the amorphous nature of the electrolyte film. FTIR spectroscopic analysis confirmed the complexation of the salt and plasticizer with the polymer matrix. Differential scanning calorimetry was used to determine the glass transition and melting temperatures of pure CMC and CMC-based polymer electrolyte film.

Introduction

Polymer electrolytes (PEs) have attracted the attention of the researchers from the last four decades because of their unique properties like electrode–electrolyte interaction, ease in salt doping, fabrication, versatile in shape, and high ionic conductivity [1]. These polymer electrolytes have been extensively used in variety of electrochemical devices [2]. The study was first started with high molecular weight polyethylene oxide (PEO) with Li salts and then followed by other polymers like poly acrylonitrile (PAN), poly methyl methacrylate (PMMA), polyvinylidene fluoride (PVDF), etc. [3–8]. These polymer electrolytes are different because of their unique electrical properties. However, one of the major

---

✉ Shikha Gupta
    shikha641@gmail.com

[1] Chemistry Department, Faculty of Engineering and Technology, Manav Rachna International Institute of Research and Studies, Faridabad, India

drawbacks with these synthetic polymer electrolytes is their disposal, storage and long-term degradation. Due to these limitations, researchers are focusing their interest in natural polymers called bio-polymers. Bio-polymers consist of mono-meric units which are covalently bonded, establishing chain-like molecules [22]. They also form hydrogels which minimize the extracellular matrix (ECM) and enhance tissue growth [9]. The use of bio-polymer reduces the environmental issues and also takes into account the low production cost due to the great variety and low prices of raw materials. Among such green polymers like starch, proteins, cellulose and their derivatives are best candidate due to their abundance in environment [9].

In bio-polymers, cellulose and its derivatives have received much attention. They are used in various industrial sectors like food, textiles, paper, adhesives, paints, pharmaceuticals and cosmetics. They also show ability to form good transparent film with high mechanical strength so they are also used for electro-chemical applications like batteries, fuel cells, super capacitors, display devices, sensors, etc. [10–14]. However, they have low ionic conductivity as they are crys-talline in nature which limits the application of these polymer electrolytes. Cel-lulose is one of the earth's most extensive natural organic chemical; therefore, it is thoroughly important as a renewable resource [4].

Cellulose has many derivatives in which carboxymethyl cellulose (CMC) is also one. It is a natural anionic polysaccharide, consisting of β-linked glucopyra-nose residues having partial hydroxyl groups substituted with carboxymethyl ($-CH_2COO-$) groups which can dissolve in water to form viscous solution and is widely used as a binder in li ion batteries [15–18]. Along with these, they have outstanding film forming properties as they can form a transparent film having extortionate mechanical strength [2], brittle and stiffer in nature which features a high degree of brittleness. So normally, CMC is not that much impressive in field of conductivity but can be outstandingly increase by doping, plasticizing or other techniques [3].

In this article, we present the results of SPE obtained by the plasticization of CMC with glycerol and addition of $LiBF_4$ as a dopant. From the results, we found that the effect of glycerol as a plasticizer on the ionic conductivity is much more important than the effect obtained by varying the salt concentration. Lithium salts are being used as charge carriers in the polymer electrolytes because of Lewis acid behavior which can interact with electron donor centers. The smaller size of Li^+ could contribute to ion dissociation resultant from coulombic interaction forces between the two oppositely charged ions [18]. With the commercialization of graph-ite electrodes, the $LiPF_6$ and $LiBF_4$ became the most popular salts. In both of them the later one shows the better performance of the electrolytes at high (50–80 °C) and low temperature (− 20 °C), but it also shows moderate ionic conductivity in the resulting electrolytes [19–22].

In view of the aforesaid aspects, we report the ionic conductivity of the lithium-doped CMC-based solid polymer electrolytes (SPEs). SPEs having highest conduc-tivity were chosen for X-ray diffraction (XRD) to study the crystalline/amorphous character, vibrational spectrum by FTIR and thermal analysis of polymer electrolyte by differential scanning calorimeter (DSC).

Sample preparation

All the CMC-LiBF$_4$ films were prepared using solution cast technique. In order to prepare the stock solution, 2 g of CMC sodium (high viscosity) purchased from Loba Chemie was dissolved in 100 ml of deionized water. The solution was stirred until the CMC was completely dissolved in water. Varying amount of 1 M solution of LiBF$_4$ (0.1–1 ml) (Sigma Aldrich) and various quantity of glycerol (0–20 wt%) (Merck) were added in 10 ml of CMC stock solution in different beakers. Then the mixtures were poured in different glass petri dishes and left to dry for 2 h in an oven at 50 °C to obtain thick film. Then films were peeled out and stored in desiccator for further drying.

Characterization techniques

To study the nature of the film, the X-ray diffraction (XRD) analysis was carried out by using PAN analytical. Sample (size = 10 mm) adhered onto glass slide and then placed in the sample holder of the diffractometer. Samples were scanned at 2θ ranging from 5° to 80° with X-rays of 1.5406 Å wavelength generated by a CuK$_\alpha$ source.

The thermal analyses of the sample were done using DSC in NETZCH instrument. Measurement were taken over a temperature range of 20–120 °C at heating rate of 5 °C min^{-1} under nitrogen atmosphere at flow rate of 60 ml min^{-1}.

Vibrational spectra of CMC and CMC-based electrolyte were carried by FTIR in PerkinElemer instrument at room temperature.

For the electrochemical study, the samples were characterized by electrical impedance spectroscopy (EIS). SPEs samples having thickness of 1.5 mm measured using screw gauge were cut into 1 cm × 1 cm square dimension and placed between two square stainless steel electrodes (length 1 cm) fitted with copper wires. The whole setup was hold tightly with plastic clamp. The bulk ionic conductivities (σ) of the SPEs were determined using the AC impedance spectra in the frequency range between 10^1 and 10^6 Hz with an applied voltage of 10 mV. Negative imaginary impedance ($-Z''$) versus real impedance (Z') was calculated from the plot. The conductivity of the film was calculated by using equation:

$$\sigma = L/R_\mathrm{b}A$$

where L is the electrode separation, i.e., the gap between electrodes or the thickness of the film, A is the contact area between the electrolyte film and the electrode, and R_b (Ω) is the bulk resistance obtained from the Nyquist plot at the intersection of the imaginary impedance on the real impedance axis.

Results and discussion

Table 1 shows the variation in conductivity with the addition of lithium salt solution for the CMC-based electrolyte. The conductivity followed the typical trend of polymer–salt complexes. It increased and attained a maximum at 1 ml of 1 M lithium salt solution. The increase in conductivity depends upon the number of charge carriers,

Table 1 Ion conductivity of CMC-based electrolyte with various content of 1 M Li salt solution at 298 K

1 M Li salt solution (ml)	Conductivity (S cm^{-1})
0.1	4.2×10^{-7}
0.5	5.6×10^{-7}
1.0	8.2×10^{-6}
1.5	7.7×10^{-6}

i.e., free ions and ion pairs. But beyond optimum level the number of charge carriers increased, and they become too close to each other which produced the hindrance in the conduction pathway and enabled them to recombine into neutral ion pairs, because of its conductivity decreased.

Table 2 reveals the variation in conductivity with the addition of glycerol as plasticizer. Conductivity increased from 8.2×10^{-6} S cm^{-1} to 3.7×10^{-3} S cm^{-1} at 20 wt% of glycerol at room temperature with good mechanical strength. The increase in conductivity due to plasticizer may be due to the amorphous nature of the film as compared to CMC with Li salt solution. The increase in conductivity was also attributed to the dissociation of ionic dopant and thereby produces free Li^{+} ions which can easily migrate through the plasticizer-rich phase. The effect of the plasticizer on the mobility and conductivity was because of change in properties like viscosity, dielectric constant, polymer plasticizer interaction, and ion plasticizer coordination [23–25].

Plasticizer reduced the T_{g} of the polymer matrix which helps in soften the polymer backbone and increased the flexibility which enhanced the segmental motion of the polymer chain. The high dielectric constant of glycerol allows the great dissolution of the salt which increases the number of charge carriers, promoting the ion hopping mechanism [24].

The temperature dependence conductivity of CMC electrolyte with salt and plasticizer is depicted in Fig. 1. The ionic conductivity increased linearly with inverse temperature, which obeys Arrhenius behavior. This linear behavior showed that there is no phase transition in the polymer matrix. Activation energy, EA, was calculated by using equation;

$$\sigma = \sigma_{o} \exp\left(-E_{A}/kT\right)$$

where σ_{o} is the pre-exponential factor, E_{A} is the activation energy, k is the Boltzmann constant, and T is absolute temperature. Based on the calculations, SPEs

Table 2 Ionic conductivity of CMC-based electrolyte with different weights of glycerol as plasticizer at 298 K

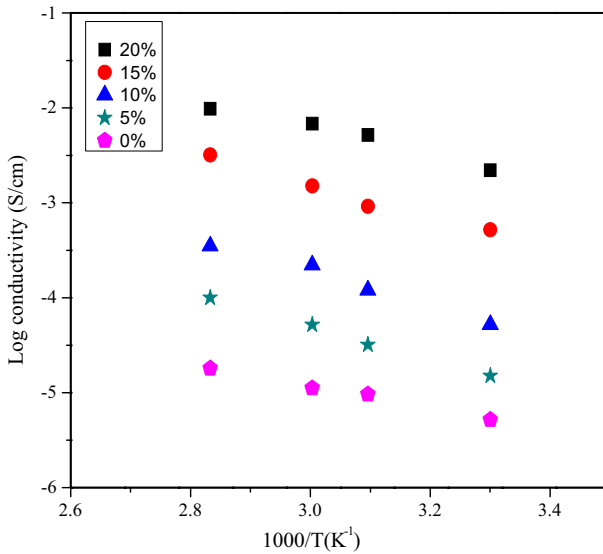| Plasticizer (wt%)	Conductivity (S cm^{-1})
0	8.2×10^{-6}
5	1.5×10^{-5}
10	5.2×10^{-5}
15	7.6×10^{-4}
20	3.7×10^{-3}

Fig. 1 Temperature dependence conductivity of CMC-based polymer electrolyte at different weight percentages of plasticizer

showed the activation energy in the range of 0.38 eV–0.21 eV. The low value of activation energy was due to the completely amorphous nature of polymer electrolyte. The ionic conductivity values of the CMC-based polymer electrolyte with plasticizer were calculated at different temperatures and were found to increase with increase in temperature, i.e., from 3.7×10^{-3} S cm^{-1} to 2.2×10^{-2} S cm^{-1}. The values of the ion conductivity obtained are summarized in Table 3. Figure 2 reveals the Nyquist plot for the CMC-based polymer film electrolyte with 20 wt% of glycerol as plasticizer at different temperatures. The semicircles in figure were observed at high-frequency region and a spike in the low-frequency region. The bulk resistance (R_b) was calculated from the intercept of the semicircle with the real impedance axis of the Nyquist plot as a function of temperature.

Electrochemical potential window measurement represents the potential stability range of polymer electrolyte materials and decides the working voltage of any electrochemical device. In the present study, the electrochemical stability of polymer electrolyte has been measured using linear sweep voltammetry techniques,

Table 3 Variation in ionic conductivity of CMC doped with Li$^+$ salt and glycerol at different temperatures

| Temperature (K)	Conductivity (S cm^{-1})
298	3.7×10^{-3}
318	5.2×10^{-3}
338	7.8×10^{-3}
355	2.2×10^{-2}

Fig. 2 Nyquist plot of CMC-based electrolyte at different temperatures
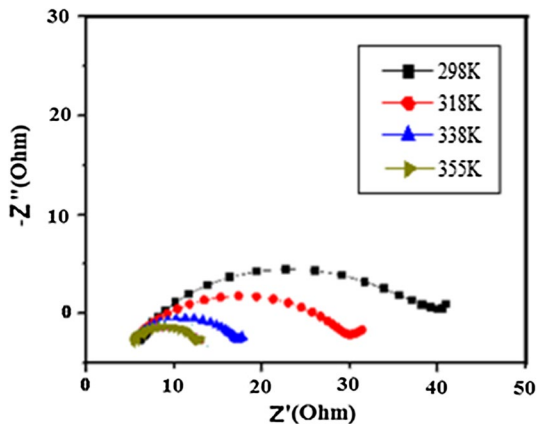
by sandwiching the solid polymer electrolytes in between two stainless steel electrodes. Figure 3 shows the I–V characteristics of the optimized polymer electrolyte at a scan rate of 0.05 mV s^{-1}. The general pattern reveled a gradual increase in current values with increasing voltage up to certain values of potential and after that, abrupt increase in current value was observed which basically represented a potential window or working voltage of polymer electrolytes. In the present studies working voltage was found to be ∼ 1.75 V.

X-ray diffraction was used to examine the amorphosity of polymer electrolytes, and high conductivity was obtained in amorphous polymers. The diffraction pattern of the CMC and SPE doped with lithium salt and plasticizer at room temperature is shown in Fig. 4. One broad peak was observed for plasticizer and salt free polymer at Bragg angle of $2\theta = 20°$. It revealed the amorphous behavior of the polymer. With the addition of plasticizer, it again showed amorphous nature the peak shifts at Bragg angle of $2\theta = 21°$. The change in shape depicted higher

Fig. 3 Electrochemical potential window for CMC-based electrolyte at scan rate of 0.05 mV s^{-1}
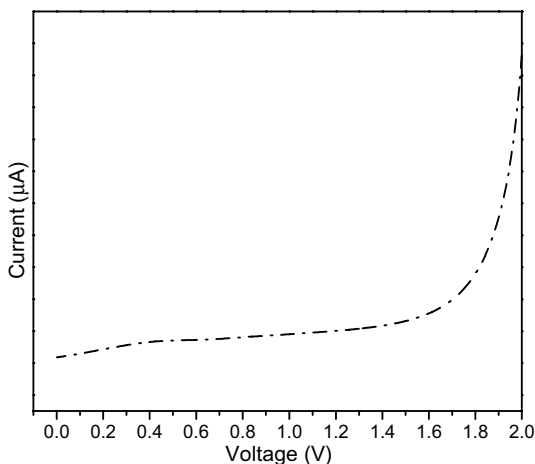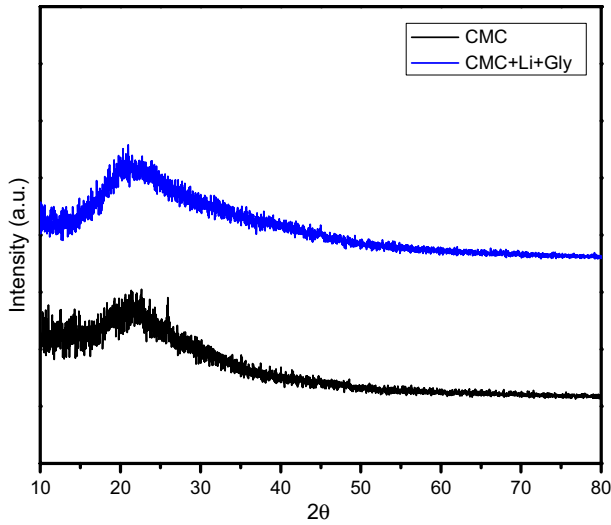
Fig. 4 X-Ray diffraction pattern of CMC film and CMC-based electrolyte film

amorphous nature of the electrolyte. Thus, it enhanced the ionic conductivity of the polymer electrolyte.

Figure 5 attributes the FTIR spectra of CMC film, CMC doped with Li salt solution film and CMC with lithium solution and plasticizer-based polymer electrolyte film. The band at 3275 cm^{-1} was due to O–H stretching bonding in CMC.
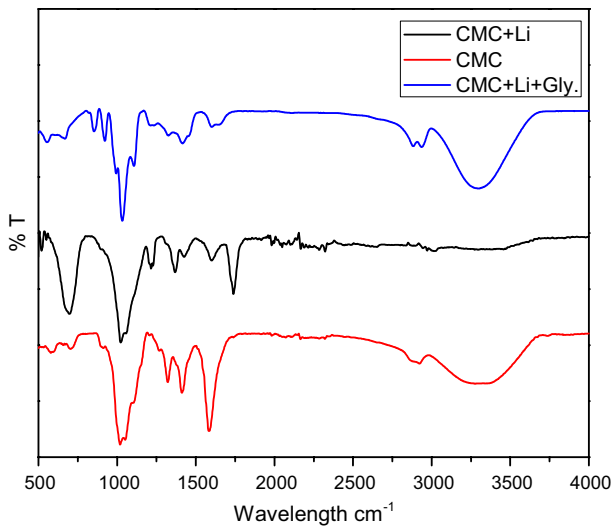

Fig. 5 FTIR spectra of CMC, CMC with Li solution and CMC with lithium solution and plasticizer-based electrolyte film

The C–H uneven stretching vibration was shown at 2922 cm^{-1} which was due to methyl group and methylene group [26, 27]. The asymmetrical COO– stretching was found at 1582 cm^{-1} [28, 29]. O–H stretching in-plane and symmetrical C–H stretching was found at peaks 1411 cm^{-1} and 1322 cm^{-1}. The C–O stretching was observed at 1018 cm^{-1} [30]. In CMC doped with Li, the O–H stretching bonding is absent and the band at 770 showing B-O stretching peak. This conforms the mixing of Li to CMC. The expansion of plasticizer builds the spectra space taking after the area of the O–H extending vibration at 3294 cm^{-1}. This demonstrated the deliquescent conduct of plasticizer and inferable from the hydrogen retreats designed by the hydroxyl gathering of each CMC and glycerol structures [31]. The sharp band around 2936 cm^{-1} was dispensed to C–H extending in uneven and reciprocal, severally. The band at 1601 cm^{-1} confirmed the presence of COO– bonding of the carboxyl group. The presence of glycerol additionally showed changes within the band region between 800 and 1200 cm^{-1} that was giving data concerning the alcoholic (C–O) stretching bands and also the uneven and isobilateral (C–O–C) stretching vibrations band. The band at 1032 cm^{-1} was due to stretching vibration of C–O in C–O–H bonds [32].

Figure 6 reveals the T_g of CMC and CMC-based polymer electrolyte. Peaks were observed at 87 °C and at 54 °C, respectively, for CMC film and CMC-based electrolyte film. T_g was decreased by incorporating glycerol due to its plasticizing impact. The plasticizing impact tends to weaken the dipole–dipole interactions; thus, it interrupted the transient cross-link bonds among polymer matrix and ordered arrangement of polymer backbone. Along these lines, it relaxed the polymer lattice and produced the exceptionally adaptable polymer chain and raising the segmental quality that winded up in higher ionic conductivity.
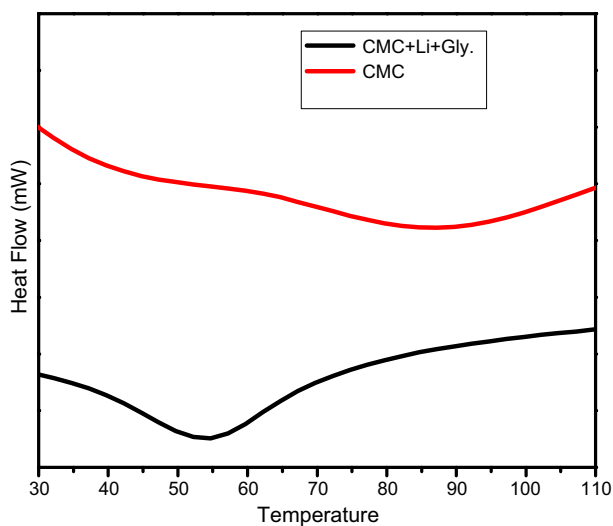

Fig. 6 The T_g of CMC and CMC-based polymer electrolyte

Conclusion

The lithium salt-doped carboxymethyl cellulose (CMC)-based polymer electrolyte with glycerol as plasticizer was successfully synthesized by solution casting technique. The investigation of complexation between polymer, salt and plasticizer was confirmed by FTIR spectra. The temperature dependence ionic conductivity was also checked and found to obey Arrhenius behavior. The ionic conductivity increased and reached up to 3.7×10^{-3} S cm^{-1} upon addition of glycerol as plasticizer. The working potential range of the synthesized polymer electrolyte was found near 1.75 V. DSC results illustrated decrease in thermal stability with the addition of plasticizer. Higher amorphous nature of electrolyte film was confirmed by XRD analysis. Lithium ion conducting solid polymer electrolyte based on carboxymethyl cellulose (CMC) complexed with lithium tetrafluoroborate could be used in an electrochemical devices.

References

1. Chandra S, Chandra A (1994) Solid state ionics: materials aspect. In: Proceedings of national academy of sciences India section, vol 64, pp 141–181
2. Selvasekarapandian S, Baskaran R, Hema M (2005) Complex AC impedance, transference number and vibrational spectroscopy studies of proton conducting PVAc–NH4SCN polymer electrolytes. Physica B 357(3–4):412–419
3. Fenton DE, Parker JM, Wright PV (1973) Complexes of alkali metal ions with poly(ethylene oxide). Polymer 14:589
4. Wright PV (1975) Electrical conductivity in ionic complexes of poly (ethylene oxide). Polym Int 7:319–327
5. Armand MB, Chabagno JM, Duclot MJ (1978) Poly-ethers as solid electrolytes. In: Proceedings of the second international meeting on solid electrolytes, 20
6. Agnihotry SA, Pradeep P, Sekhon SS (1999) PMMA based gel electrolyte for EC smart windows. Electrochim Acta 44(18):3121–3126
7. Bushkova OV, Animitsa IE, Lirova BI, Zhukovsky VM (1997) Lithium conducting solid polymer electrolytes based on polyacrylonitrile copolymers: ion solvation and transport properties. Ionics 3(5–6):396–404
8. Song JY, Wang YY, Wan CC (1999) Review of gel-type polymer electrolytes for lithium-ion batteries. J Power Sources 77(2):183–197
9. Varshney PK, Gupta S (2011) Natural polymer-based electrolytes for electrochemical devices: a review. Ionics 17(6):479–483
10. Jabbour L, Bongiovanni R, Chaussy D, Gerbaldi C, Beneventi D (2013) Cellulose-based Li-ion batteries: a review. Cellulose 20(4):1523–1545
11. Zhu H, Fang Z, Preston C, Li Y, Hu L (2014) Transparent paper: fabrications, properties, and device applications. Energy Environ Sci 7(1):269–287

12. Nyholm L, Nyström G, Mihranyan A, Strømme M (2011) Toward flexible polymer and paper-based energy storage devices. Adv Mater 23(33):3751–3769

13. Gwon H, Hong J, Kim H, Seo DH, Jeon S, Kang K (2014) Recent progress on flexible lithium rechargeable batteries. Energy Environ Sci 7(2):538–551

14. Zhou G, Li F, Cheng HM (2014) Progress in flexible lithium batteries and future prospects. Energy Environ Sci 7(4):1307–1338

15. Lestriez B, Bahri S, Sandu I, Roué L, Guyomard D (2007) On the binding mechanism of CMC in Si negative electrodes for Li-ion batteries. Electrochem Commun 9(12):2801–2806

16. Seïd KA, Badot JC, Dubrunfaut O, Levasseur S, Guyomard D, Lestriez B (2012) Influence of the carboxymethyl cellulose binder on the multiscale electronic transport in carbon–LiFePO$_4$ nanocomposites. J Mater Chem 22(45):24057–24066

17. Ibrahim SM, El Salmawi KM (2013) Preparation and properties of carboxymethyl cellulose (CMC)/sodium alginate (SA) blends induced by gamma irradiation. J Polym Environ 21(2):520–527

18. Spirk S (2018) Polysaccharides in batteries. In: Polysaccharides as battery components. Springer Briefs in Molecular Science. Springer, Cham

19. Rani MSA, Rudhziah S, Ahmad A, Mohamed NS (2014) Biopolymer electrolyte based on derivatives of cellulose from kenaf bast fiber. Polymers 6(9):2371–2385

20. Zhu YS, Xiao SY, Li MX, Chang Z, Wang FX, Gao J, Wu YP (2015) Natural macromolecule based carboxymethyl cellulose as a gel polymer electrolyte with adjustable porosity for lithium ion batteries. J Power Sources 288:368–375

21. Zhang S, Xu K, Jow T (2003) Low-temperature performance of Li-ion cells with a LiBF4-based electrolyte. J Solid State Electrochem 7(3):147–151

22. Fahmi EM, Ahmad A, Nazeri NNM, Hamzah H, Razali H, Rahman MYA (2012) Effect of LiBF4 salt concentration on the properties of poly (ethylene oxide)-based composite polymer electrolyte. Int J Electrochem Sci 7:5798–5804

23. Ahmad A, Rahman MYA, Low SP, Hamzah H (2011) Effect of LiBF4 salt concentration on the properties of plasticized MG49-TiO$_2$ based nanocomposite polymer electrolyte. ISRN Mater Sci 2011:401280-1–401280-7

24. Sekhon SS, Pradeep, Agnihotry SA (1998) In: Chowdari BVR et al (eds) Solid state ionics: science and technology. World Scientific, Singapore, pp 217–221

25. Pradhan DK, Samantaray BK, Choudhary RNP, Thakur AK (2005) Effect of plasticizer on microstructure and electrical properties of a sodium ion conducting composite polymer electrolyte. Ionics 11(1–2):95–102

26. Pradhan DK, Samantaray BK, Choudhary RNP, Thakur AK (2005) Effect of plasticizer on structure—property relationship in composite polymer electrolytes. J Power Sources 139(1–2):384–393

27. Ahmad NH, Isa MIN (2015) Structural and ionic conductivity studies of CMC based polymerelectrolyte doped with NH4Cl. In: Advanced materials research. Trans Tech Publications, vol 1107, pp 247–252

28. Shuhaimi NEA, Teo LP, Majid SR, Arof AK (2010) Transport studies of NH4NO3 doped methyl cellulose electrolyte. Synth Met 160(9–10):1040–1044

29. Coates J (2000) Interpretation of infrared spectra, a practical approach. In: Encyclopedia of analytical chemistry 10815

30. Pushpamalar V, Langford SJ, Ahmad M, Lim YY (2006) Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. Carbohyd Polym 64(2):312–318

31. Samsudin AS, Khairul WM, Isa MIN (2012) Characterization on the potential of carboxy methylcellulose for application as proton conducting biopolymer electrolytes. J Non-Cryst Solids 358(8):1104–1112

32. Silvertein RM, Webster FX, Kiemle DJ (2005) Spectrometric identification of organic compound, 7th edn. Wiley, Hoboken, p 74

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.