

## **Ionic transport study of hybrid gel polymer electrolyte based on PMMA-PLA incorporated with ionic liquid**

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### **ABSTRACT**

Hybrid gel polymer electrolytes (HGPEs) based on polymethyl methacrylate (PMMA)-polylactic acid (PLA) doped with LiTFSI and incorporated with 1-butyl-3-methylimidazolium chloride (BmimCl) were successfully prepared. The complexes of the HGPEs with different BmimCl contents were characterized via Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analysis. Based on the impedance spectroscopy analysis, the HGPEs with the composition of 80% PMMA:20% PLA:20 wt.% LiTFSI:15 wt.% BmimCl possessed the highest room-temperature ionic conductivity of  $1.63 \times 10^{-3} \text{ S cm}^{-1}$ . The Arof-Noor (A-N) method was applied to investigate its transport properties, and it was found that the diffusion coefficient,  $D$ , ionic mobility,  $\mu$ , and number density of ions,  $n$ , were the main contributors of ionic conductivity improvement. Meanwhile, the highest conducting electrolyte lithium ion transference number was 0.67. Linear sweep voltammetry (LSV) analysis showed that the electrochemical stability window of the HGPE was 3.4 V vs Li/Li<sup>+</sup>. The findings suggest that the HGPE system incorporated with this ionic liquid could be a promising candidate for use as an electrolyte in flexible lithium-ion batteries.

### **KEYWORDS**

Hybrid polymer; Ionic liquid; Lithium transference number; Potential stability

## REFERENCES

1. Nayak PK, Yang L, Brehm W, Adelhelm P (2018) From lithium-ion to sodium-ion batteries: advantages, challenges, and surprises. *Angew Chem Int Ed* 57(1):102–120
2. Baskoro F, Wong HQ, Yen H-J (2019) Strategic structural design of a gel polymer electrolyte toward a high efficiency lithium-ion battery. *ACS Appl Energy* 2(6):3937–3971
3. Xu P, Chen H, Zhou X, Xiang H (2021) Gel polymer electrolyte based on PVDF-HFP matrix composited with rGO-PEG-NH for high-performance lithium ion battery. *J Membr Sci* 617:118660
4. Wang J, Wang C, Wang W, Li W, Lou J (2022) Carboxymethylated nanocellulose-based gel polymer electrolyte with a high lithium ion transfer number for flexible lithium-ion batteries application. *Chem Eng J* 428:132604
5. Zhang P, Li R, Huang J, Liu B, Zhou M, Wen B, Xia Y, Okada S (2021) Flexible poly (vinylidene fluoride-cohexafluoropropylene)-based gel polymer electrolyte for Highperformance lithium-ion batteries. *RSC Adv* 11(20):11943–11951
6. Chen D, Lou Z, Jiang K, Shen G (2018) Device configurations and future prospects of flexible/stretchable lithium-ion batteries. *Adv Funct Mater* 28(51):1805596
7. Liu M, Jin B, Zhang Q, Zhan X, Chen F (2018) High-performance solid polymer electrolytes for lithium ion batteries based on sulfobetaine zwitterion and poly (ethyleneoxide) modified polysiloxane. *J Alloys Compd* 742:619–628
8. Fenton D (1973) Complexes of alkali metal ions with poly (ethylene oxide). *Polym* 14:589
9. Mazuki NF, Fuzlin AF, Saadiah MA, Samsudin AS (2019) An investigation on the abnormal trend of the conductivity properties of CMC/PVA-doped NH<sub>4</sub>Cl-based solid biopolymer electrolyte system. *Ionics* 25(6):2657–2667
10. Gu Y, Yang L, Luo S, Zhao E, Saito N (2022) A non-flammable, flexible and UV-cured gel polymer electrolyte with crosslinked polymer network for dendrite-suppressing lithium metal batteries. *Ionics* 28:3743–3759
11. Tu J, Wu K, Jiang J, Wu M, Hu Q, Xu G, Lou P, Zhang W (2021) A novel ceramic/polyurethane composite solid polymer electrolyte for high lithium batteries. *Ionics* 27(2):569–575
12. Tiwari R, Sonker E, Kumar D, Kumar K, Adhikary P, Krishnamoorthi S (2020) Preparation, characterization and electrical properties of alkali metal ions doped co-polymers based on TB. *J Mater Sci Eng, B* 262:114687
13. Borah S, Sarmah JK, Deka M (2021) Understanding uptake kinetics and ion dynamics in microporous polymer gel electrolytes reinforced with SiO<sub>2</sub> nanofibers. *J Mater Sci Eng, B* 273:115419
14. Du Z, Su Y, Qu Y, Zhao L, Jia X, Mo Y, Yu F, Du J, Chen Y (2019) A mechanically robust, biodegradable and high performance cellulose gel membrane as gel polymer electrolyte of lithium-ion battery. *Electrochim Acta* 299:19–26
15. Liang S, Yan W, Wu X, Zhang Y, Zhu Y, Wang H, Wu Y (2018) Gel polymer electrolytes for lithium ion batteries: fabrication, characterization and performance. *Solid State Ionics* 318:2–18
16. Ngai KS, Ramesh S, Ramesh K, Juan JC (2016) A review of polymer electrolytes : fundamental, approaches and applications. *Ionics* 22(8):1259–1279
17. Vickraman P, Aravindan V, Shankarasubramanian N (2007) A study on the blending effect of polyvinylidene fluoride in the ionic transport mechanism of plasticized polyvinyl chloride+ Lithium perchlorate gel polymer electrolytes. *Ionics* 13(5):355–360

18. Guo X, Li S, Chen F, Chu Y, Wang X, Wan W, Zhao L, Zhu Y (2021) Performance improvement of PVDF–HFP-based gel polymer electrolyte with the dopant of octavinyl-polyhedral oligomeric silsesquioxane. *Materials* 14(11):2701
19. Li L, Yang X, Li J, Xu Y (2018) A novel and shortcut method to prepare ionic liquid gel polymer electrolyte membranes for lithium-ion battery. *Ionics* 24(3):735–741
20. Long M-C, Wang T, Duan P-H, Gao Y, Wang X-L, Wu G, Wang Y-Z (2022) Thermotolerant and ireproof gel polymer electrolyte toward high-performance and safe lithium-ion battery. *J Energy Chem* 65:9–18
21. Pan Xr, Lian F, He Y, Peng Yf, Sun Xm, Wen Y, Guan Hy (2015) Enhanced mechanical strength and conductivity of PVFM based membrane and its supporting polymer electrolytes. *J Appl Polym Sci* 132(16):41839
22. Saxena P, Shukla P (2022) A comparative analysis of the basic properties and applications of poly (vinylidene fluoride) (PVDF) and poly (methyl methacrylate)(PMMA). *Polym Bull* 79:5635–5665
23. Kuppu SV, Jeyaraman AR, Guruviah PK, Thambusamy S (2018) Preparation and characterizations of PMMA-PVDF based polymer compositeelectrolyte materials for dye sensitized solar cell. *Curr Appl Phys* 18(6):619–625
24. Ramesh S, Liew C-W, Ramesh K (2011) Evaluation and investigation on the effect of ionic liquid onto PMMA-PVC gel polymer blend electrolytes. *J Non-Cryst Solids* 357(10):2132–2138
25. Zulkepely N, Majid S, Osman Z (2010) Effect of adding plasticizer on ionic conductivity and glass transition temperature of PMMA+lithium iodide complexes. In: *AIP Conference Proceedings*, vol1. American Institute of Physics, pp 205–208
26. Mazuki NF, Kuian MZ, Nagao Y, Samsudin AS (2022) Correlation studies between structural and ionic transport properties of lithium-ion hybrid gel polymer electrolytes based PMMA-PLA. *J Polym Environ* 30(5):1864–1879
27. Balo L, Gupta H, Singh VK, Singh RK (2017) Flexible gel polymer electrolyte based on ionic liquid EMIMTFSI for rechargeable battery application. *Electrochim Acta* 230:123–131
28. Wang Q-J, Zhang P, Wang B, Fan L-Z (2021) A novel gel polymer electrolyte based on trimethylolpropane trimethylacrylate/ionic liquid via in situ thermal polymerization for lithium ion batteries. *Electrochim Acta* 370:137706
29. Ravi M, Kim S, Ran F, Kim DS, Lee YM, Ryou M-H (2021) Hybrid gel polymer electrolyte based on 1-methyl-1-Propylpyrrolidinium Bis (Trifluoromethanesulfonyl) imide for flexible And shape-variant lithium secondary batteries. *J Membr Sci* 621:119018
30. Bai J, Lu H, Cao Y, Li X, Wang J (2017) A novel ionic liquid polymer electrolyte for quasi-solid state lithium air batteries. *JRSC advances* 7(49):30603–30609
31. Mishra K, Rai DK (2021) Studies on ionic liquid based nano composite gel polymer electrolyte and its application in sodium battery. *J Mater Sci Eng, B* 267:115098
32. Balducci A, Jeong SS, Kim GT, Passerini S, Winter M, Schmuck M, Appetecchi GB, Marcilla R, Mecerreyes D, Barsukov V (2011) Development of safe, green and high performance ionic liquids-based batteries (ILLIBATT project). *J Power Sources* 196(22):9719–9730
33. Liew C-W, Ramesh S, Arof AK (2014) A novel approach on ionic liquid-based poly (vinyl alcohol) proton conductive polymer electrolytes for fuel cell applications. *Int J Hydrogen Energy* 39(6):2917–2928

34. Azli AA, Manan NSA, Kadir MFZ (2017) The development of Li conducting polymer electrolyte based on potato starch/grapheme oxide blend. *Ionics* 23(2):411–425
35. Latii M, Ahmad A, Hassan NH, Kaddami H (2021) Carboxymethylchitin doped 1-butyl-3-methylimidazolium chloride based solid polymer electrolyte. *Mater, Today: Proceedings* 36:16 21
36. Hor AA, Yadav N, Hashmi SA (2022) High energy density carbon supercapacitor with ionic liquid-based gel polymer electrolyte: role of redox-additive potassium iodide. *J Energy Storage* 47:103608
37. Tsao C-H, Su H-M, Huang H-T, Kuo P-L, Teng H (2019) Immobilized cation functional gel polymer electrolytes with high lithium transference number for lithium ion batteries. *J Membr Sci* 572:382–389
38. Kuian MZ, Ramesh S, Arof AK (2021) PMMA-LiTFSI based gel polymer electrolyte for lithium oxygen cell application. *Opt Mater* 120:111418
39. Bruce PG, Vincent CA (1987) Steady state current low in solid binary electrolyte cells. *J Electroanal Chem Interf Electrochem* 225(1–2):1–17
40. Mazuki NF, Nagao Y, Kuian MZ, Samsudin AS (2020) The influences of PLA into PMMA on crystallinity and thermal properties enhancement-based hybrid polymer in gel properties. *Mater, Today: Proceedings* 49(8):3105–3111
41. Ghani NAA, Anuar FH, Ahmad A, Mobarak NN, Shamsudin IJ, Dzulkipli MZ, Hassan NH (2020) Incorporating 1-butyl-3-methylimidazolium chloride ionic liquid into iota carrageenan solid Biopolymer electrolyte for electrochemical devices application. *Sains Malaysiana* 49(2):305–313
42. Sim LN, Majid SR, Arof AK (2014) Effects of 1-butyl-3-methyl imidazolium trifluoromethanesulfonate ionic liquid in poly (ethyl methacrylate)/poly (vinylidene fluoride-co-hexafluoropropylene) blend based polymer electrolyte system. *Electrochim Acta* 123:190–197
43. Teoh EL, Chow WS (2018) Transparency, ultraviolet transmittance, and miscibility of poly (lactic acid)/poly (methyl methacrylate) blends. *J Elastomers Plast* 50(7):596–610
44. Mendes-Felipe C, Barbosa JC, Gonçalves R, Miranda D, Costa CM, Vilas-Vilela JL, Lanceros-Mendez S (2021) Lithium bis (trifluoromethanesulfonyl) imide blended in polyurethaneacrylate photo-curable solid polymer electrolytes for lithium-ion batteries. *J Energy Chem* 62:485–496
45. Gohel K, Kanchan DK (2019) Effect of PC: DEC plasticizers on structural and electrical properties of PVDF–HFP: PMMA based gel polymer electrolyte system. *J Mater Sci Mater Electron* 30(13):12260–12268
46. Ravi M, Song S, Wang J, Wang T, Nadimicherla R (2016) Ionic liquid incorporated biodegradable gel polymer electrolyte for lithium ion battery applications. *J Mater Sci Mater Electron* 27(2):1370–1377
47. Polu AR, Rhee H-W (2017) Ionic liquid doped PEO-based solid polymer electrolytes for lithium-ion polymer batteries. *Int J Hydro-gen Energy* 42(10):7212–7219
48. Haiza MN, Isa MIN (2017) Solid polymer electrolyte production from 2-hydroxyethyl cellulose: effect of ammonium nitrate composition on its structural properties. *Carbohydr Polym* 165:123–131
49. Vo DT, Do HN, Nguyen TT, Nguyen TTH, Okada S, Le MLP (2019) Sodium ion conducting gel polymer electrolyte using poly(vinylidene fluoride hexafluoropropylene). *J Mater Sci Eng, B* 241:27–35

50. Zainuddin NK, Saadiah MA, Abdul Majeed APP, Samsudin AS(2018) Characterization on conduction properties of carboxymethyl cellulose/kappa carrageenan blend-based polymer electrolyte system. *Int J Polym Anal Charact* 23(4):321–330
51. Arof AK, Amirudin S, Yusof SZ, Noor IM (2014) A method based on impedance spectroscopy to determine transport properties of polymer electrolytes. *PCCP* 16(5):1856–1867
52. Sikkanthar S, Karthikeyan S, Selvasekarapandian S, Arunkumar D, Nithya H, Junichi K (2016) Structural, electrical conductivity, and transport analysis of PAN–NHCl polymer electrolyte system. *Ionics* 22(7):1085–10944
53. Farah N, Ng HM, Numan A, Liew C-W, Latip NAA, Ramesh K, Ramesh S (2019) Solid polymer electrolytes based on poly (vinyl alcohol) incorporated with sodium salt and ionic liquid for electrical double layer capacitor. *J Mater Sci Eng, B* 251:114468
54. Tu Q-M, Fan L-Q, Pan F, Huang J-L, Gu Y, Lin J-M, Huang M-L, Huang Y-F, Wu J-H (2018) Design of a novel redox-active gel polymerelectrolyte with a dual-role ionic liquid for flexible supercapacitors. *Electrochim Acta* 268:562–568
55. Fuzlin AF, Misnon II, Nagao Y, Samsudin AS (2022) Study on ionic conduction of alginate bio-based polymer electrolytes by incorporating ionic liquid. *Mater Today:Proc* 51(2):1455–1459
56. Khoon LT, Fui M-LW, Hassan NH, Su'ait MS, Vedarajan R, Matsumi N, Bin Kassim M, Shyuan LK, Ahmad A (2019) In situ sol–gel preparation of ZrO in nano-composite polymer electrolyte of PVDF-HFP/MG49 for lithium-ion polymer battery. *J Sol-Gel Sci Technol* 90(3):665–6752
57. Yang P, Liu L, Li L, Hou J, Xu Y, Ren X, An M, Li N (2014) Gel polymer electrolyte based on polyvinylidene fluoride-co-hexafluoropropylene and ionic liquid for lithium ion battery. *Electrochim Acta* 115:454–460
58. Zhou T, Zhao Y, Choi JW, Coskun A (2021) Ionic liquid functionalized gel polymer electrolytes for stable lithium metal batteries. *Angew Chem Int Ed* 133(42):22973–22978
59. Li M, Liao Y, Liu Q, Xu J, Sun P, Shi H, Li W (2018) Application of the imidazolium ionic liquid based nano-particle decorated gel polymer electrolyte for high safety lithium ion battery. *Electrochim Acta* 284:188–201
60. Karuppasamy K, Reddy PA, Srinivas G, Tewari A, Sharma R, Shajan XS, Gupta D (2016) Electrochemical and cycling performances of novel nonafluorobutanesulfonate (nonaflate) ionic liquid based ternary gel polymer electrolyte membranes for rechargeable lithium ion batteries. *J Membr Sci* 514:350–357
61. Liew C-W, Ramesh S, Arof A (2015) Characterization of ionic liquid added poly (vinyl alcohol)-based proton conducting polymer electrolytes and electrochemical studies on the supercapacitors. *Int J Hydrogen Energy* 40(1):852–862
62. Tripathi M, Tripathi SK (2017) Electrical studies on ionic liquid based gel polymer electrolyte for its application in EDLCs. *Ionics* 23(10):2735–2746
63. Syairah A, Khanmirzaei MH, Saidi NM, Farhana NK, Ramesh S, Ramesh K (2019) Effect of different imidazolium-based ionic liquids on gel polymer electrolytes for dye-sensitized solar cells. *Ionics* 25(5):2427–2435
64. Zhai W, Zhu H-j, Wang L, Liu X-m, Yang H (2014) Study of PVDF-HFP/PMMA blended microporous gel polymer electrolyte incorporating ionic liquid [BMIM]BF<sub>4</sub> *Electrochim Acta* 133:623–6304 for Lithium ion batteries.