

N. Ataollahi, A. Ahmad*, T.K. Lee, A.R. Abdullah and M.Y.A. Rahman*

Preparation and characterization of PVDF-MG49-NH₄CF₃SO₃ based solid polymer electrolyte

Abstract: The ionic conductivity of ammonium-based solid polymer films of poly(vinylidene fluoride) (PVDF) blended with MG49, a graft of natural rubber and poly(methyl methacrylate), with various compositions of ammonium triflate NH₄CF₃SO₃, was investigated. As a result, 30 wt.% of NH₄CF₃SO₃-doped polymer electrolyte exhibits the highest ionic conductivity at 6.32×10⁻⁴ S/cm at room temperature. The conductivity enhancement can be attributed to the increase in the number of NH₄⁺ as charge carriers. The significance of the blend is the increase of one order in ionic conductivity as compared with pure PVDF electrolyte. The temperature dependence of conductivity of the electrolyte does not obey the Arrhenius law. However, the conductivity increases with temperature and it reached 1.56×10⁻³ S/cm at 363 K. X-ray diffraction reveals a decrease in crystallinity of the electrolyte upon the addition of NH₄CF₃SO₃ salt. This result is supported by scanning electron microscopy. Linear sweep voltammetry demonstrates that the anodic stability of the electrolyte is up to 4 V. Therefore, the electrolyte shows good compatibility with high-voltage electrode. Hence, this electrolyte system can be a prospective candidate as lithium-ion conducting electrolyte for lithium batteries.

Keywords: blend; ionic conductivity; MG49; polymer electrolyte; PVDF.

*Corresponding authors: **A. Ahmad**, School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia; and Polymer Research Center, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia, and **M.Y.A. Rahman**, Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600, Bangi, Selangor, Malaysia, Tel.: +60 389215439, Fax: +60 389215410, e-mail: azizan@ukm.my; mohd.yusri@ukm.my

N. Ataollahi and T.K. Lee: School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia; and Polymer Research Center, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
A.R. Abdullah: School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

1 Introduction

Polymer electrolyte has become an important material in ionic devices such as lithium ion battery, supercapacitor and dye-sensitized solar cell as it possesses ion transport. An early work on polymer electrolyte was carried out in the 1970s, when Fenton et al. (1) demonstrated that a non-conducting polymer, polyethylene oxide, started conducting when lithium salt was added into the polymer matrix. Following this research activity, the ion transport mechanism in polymer electrolyte was soon established and this has led to the development of a new host polymer of various types. Ever since Armand et al. (2) proposed the application of solid polymer electrolyte in lithium batteries, research and development efforts have been made throughout the world. One of the well-known techniques to improve the properties of solid polymer electrolyte is blending. This method is considered as a good strategy to hold back the crystallinity and enhance the ionic conductivity (3). Besides, it is a suitable way to control the different factors that influence the electrical and thermal properties of polymer electrolyte by changing the composition of blended polymer matrix (4–7).

The simplest way of introducing ion conduction in a polymer host is to solvate the inorganic ion to the polar groups of polymer. The polar groups in the polymer are thus known as solvating groups, which can solvate most of metal cations by establishing a coordination bond between them. Hence, identification of the suitable polymer host is important. The selection of poly(vinylidene fluoride) (PVDF) as a polymer host is due to its appealing properties such as strong electron-withdrawing function (F), high transparency, unique arrangement and high dielectric constant, which affect the dissociation of lithium salts and contribute to the increase in the concentration of charge carriers (8). The solid electrolyte system containing PVDF has been studied by Aravindan and Vickraman (9), Deka et al. (10) and Nath et al. (11). According to Michael and Prabakaran (12), the presence of carbon, hydrogen and fluorine atoms in the structure of PVDF resins produces polymers with high thermal and chemical stability and yet retains their thermoplastic nature, allowing ease

of processing for fabrication. Moreover, the existence of several crystalline phases known as α (TGTG'), β (TTTT) and γ (TTGTTTG'), which depend on chain conformations, provides support to the mechanical properties of the electrolyte.

Another polymer chosen as a polymer host is MG49, which is a graft of natural rubber and poly(methyl methacrylate) (PMMA). MG49 is a soft elastomer at ambient temperature with an elastic property that assists in the formation of a flat, thin and flexible film. Furthermore, it is able to improve the interfacial contact between electrolytes and electrodes in a battery system (13–15). PMMA imparts stiffening and hardening characteristics to rubber compounds. PMMA provides a path for ion conduction, and non-polar natural rubber gives the desired properties of lightweight and elasticity (16). Polar functional groups in the structure of PMMA exhibit high affinity for lithium ions. Furthermore, oxygen atoms belong to the carbonyl group (C=O) and ether group (C-O-C) and the structure of MMA monomer is expected to have a coordination bond with lithium salt. This coordination site acts as a stiffener. Therefore, fast ion transport can take place through a continuous conduction path, which does not affect the electrochemical stability of electrolytes (17). Despite the above properties, it is expected that, with the combination of these two polymers, the mechanical properties of polymer electrolyte will be improved. The novelty of the work is the preparation of a new electrolyte system composed of PVDF-MG49 blend doped with NH₄CF₃SO₃ salt. The objective of the work was to investigate the influence of salt concentration on the conductivity, structure and morphology of electrolytes. Electrolytes with the optimum conductivity were then chosen for conductivity dependence on temperature measurement and electrochemical stability study.

2 Experimental

2.1 Materials

A film of solid polymer electrolyte of PVDF-MG49-NH₄CF₃SO₃ was prepared by the solution casting technique. MG49 with low glass transition temperature ($T_g = -60^\circ\text{C}$) was supplied by Green HPSP (M) Sdn. Bhd, Petaling Jaya, Selangor, Malaysia. PVDF with a molecular weight of 534,000 was obtained from Sigma Aldrich and ammonium triflate (NH₄CF₃SO₃) was provided by Sigma Aldrich (St. Louis, MO, USA). All the materials were used without further purification.

2.2 Preparation of solid polymer electrolyte

MG49 (0.9 g) was dissolved in 22.5 ml of tetrahydrofuran (THF) (J.T. Baker, Phillipsburg, NJ, USA) and stirred for 24 h to obtain a complete dissolution. PVDF (2.1 g) was dissolved in 52.5 ml of THF and stirred for 24 h. These two solutions were mixed and stirred for 24 h to obtain a homogeneous solution. Various quantities of NH₄CF₃SO₃ salt (5–35 wt.%) were dissolved in 10 ml of THF and stirred for 1 h. After the salt was completely dissolved, it was added to the blend of PVDF-MG49 and stirred for the next 24 h. The polymer electrolyte solutions were then cast onto a glass Petri dish, and the solvent was allowed to evaporate slowly in a fume hood at room temperature. Preparation of the electrolyte samples was carried out in a vacuum glove box to minimize moisture due to the hygroscopic property. The samples were kept in a vacuum oven for 24 h at 40°C in order to ensure that all solvents trapped on the electrolyte films are removed.

2.3 Characterization

The ionic conductivity measurements were carried out by an electrochemical impedance system using a high-frequency resonance analyzer (HFRA; Solartron 1260, Schlumberger, UK) with an applied frequency from 10 Hz to 1 MHz at 10 mV of amplitude. The conductivity measurements were conducted at room temperature and in a temperature range of 303–363 K. The ionic conductivity (σ) was calculated by the following equation:

$$\sigma = \frac{l}{(R_b \times A)}$$

where l is the film thickness (0.02–0.03 cm) measured by a digital caliper, R_b is the bulk resistance obtained from the intercept on the real impedance axis (Z' axis) and A is the contact area of the thin film [$A = \pi r^2 = \pi (1.60 \text{ cm}/2)^2 = 2.01 \text{ cm}^2$]. The structure of the electrolyte samples was studied using an X-ray diffractometer (D-500 XRD, Siemens, Germany). The data were taken at the diffraction angle 2θ from 2° to 70° at the rate of 0.025 per second. The electrochemical stability of the electrolyte exhibiting the highest conductivity was evaluated using linear sweep voltammetry. The current-voltage of the sample was measured using two stainless steel electrode cell configuration (SS/polymer electrolyte/SS), between the potential ranges of -5 and +5 V. Scanning electron microscopy using a Philips XL 30 model at 5.00 k \times magnification was performed to study the morphology of all electrolyte samples.

3 Result and discussion

Figure 1 shows the variation in room temperature ionic conductivity of the electrolyte with the concentration of NH₄CF₃SO₃. The results show that the conductivity was 5.22×10^{-7} S/cm at 5 wt.% of salt. The conductivity enhances slowly upon the addition of charge carrier into the polymer host of PVDF-MG49 (18, 19). The peak in Figure 1 represents the maximum ionic conductivity measured at room temperature. The value obtained was 6.32×10^{-4} S/cm at 30 wt.% of salt, which was greater than the results reported in previous studies (14, 20). Further increase in the salt concentration was followed by a sharp decline in conductivity (2.76×10^{-4} S/cm). The reduction in conductivity is linked to the formation of ion pairs from NH₄⁺ and CF₃SO₃⁻ ions and to the restriction of ionic

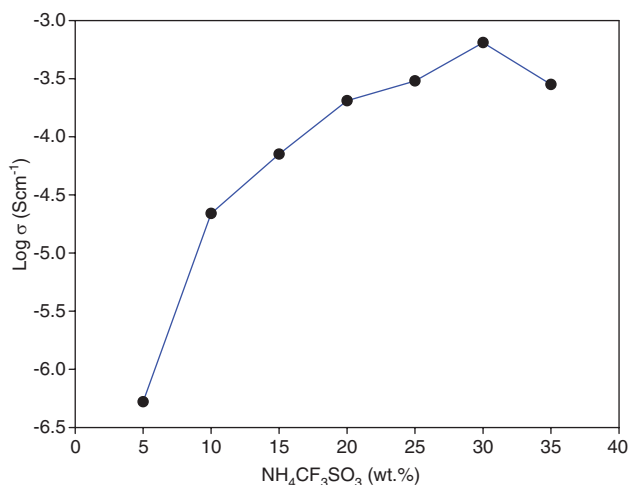


Figure 1 Conductivity vs. amount of NH₄CF₃SO₃ in PVDF-MG49 blend of polymer electrolyte films at room temperature.

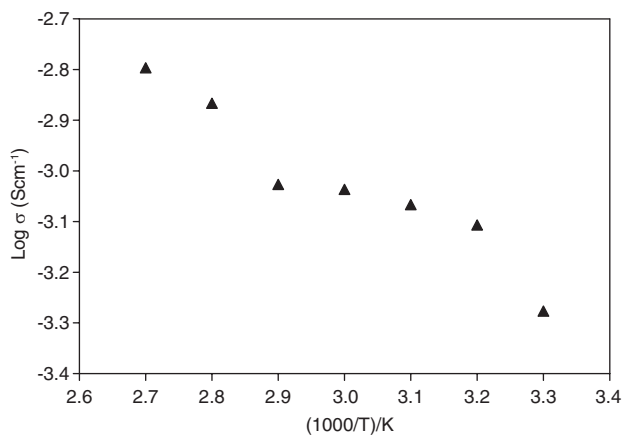


Figure 2 Arrhenius plot of PVDF-MG49-NH₄CF₃SO₃ at 30 wt.% of NH₄CF₃SO₃.

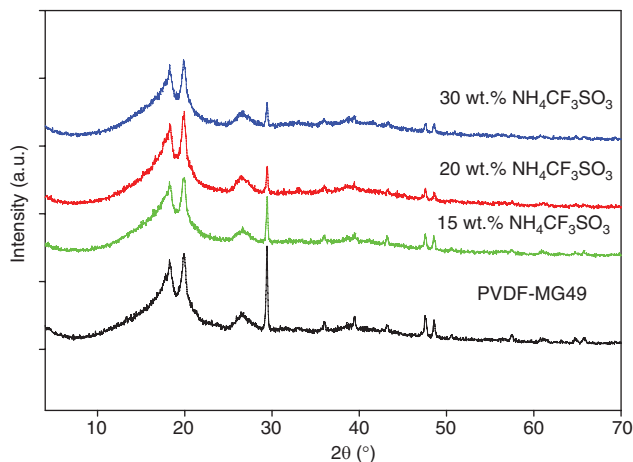


Figure 3 XRD pattern of (A) PVDF-MG49 blend and PVDF-MG49 with various concentrations of NH₄CF₃SO₃ salt.

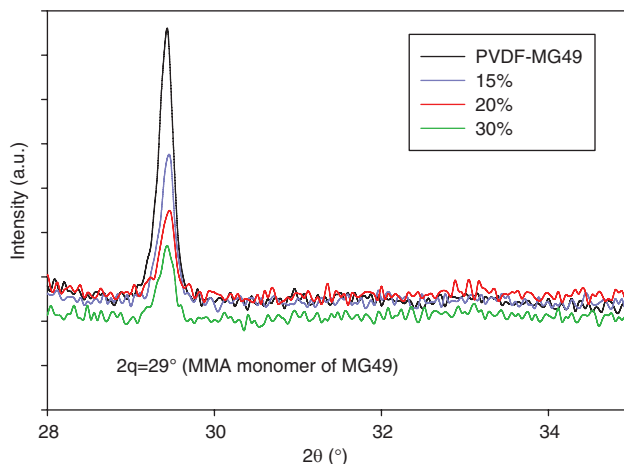


Figure 4 XRD pattern of the MMA monomer of MG49 in PVDF-MG49 blend and doped polymer electrolyte (15–30 wt.%).

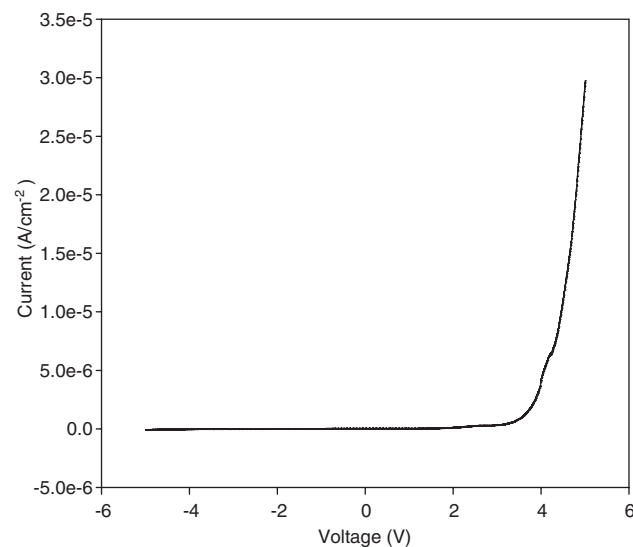


Figure 5 Linear sweep voltammogram of PVDF-MG49/LiBF₄-based polymer electrolyte at the highest ionic conductivity.

motion (21). It is believed that the high dielectric constant of PVDF assists in the dissociation of ions in the electrolyte (22). Moreover, in PVDF-MG49-NH₄CF₃SO₃ polymer electrolyte, at any instant of time, NH₄⁺ ion moves along the ether and carbonyl oxygen atoms of MG49 chains and forms a coordinated bond. This process is followed by breaking old coordination links and forming a new link, leading to ionic conductivity enhancement. According to Gray (23), salt plays an essential role in determining ionic conductivity. The large anions of salt with delocalized charge, low ion-dipole stabilization energies and low lattice energies have little tendency to form tight ion pairs. Therefore, this particular salt (NH₄CF₃SO₃) is generally

expected to promote greater dissociation, thereby providing a higher concentration of ions.

Figure 2 shows the temperature dependence of the conductivity plot for the sample with 30 wt.% of NH₄CF₃SO₃. The plot shows that the temperature enhances the ionic conductivity from 5.20×10^{-4} S/cm at 303 K to 1.56×10^{-3} S/cm at 363 K. The temperature dependence of the conductivity of this electrolyte system does not follow the Arrhenius behavior since the linear correlation factor is only 0.87. Furthermore, the conductivity mechanism of the electrolyte involves an ionic hopping motion, coupled with the relaxation/breathing and/or segmental motion of polymeric chains (24). As a result, the pre-exponential factor,

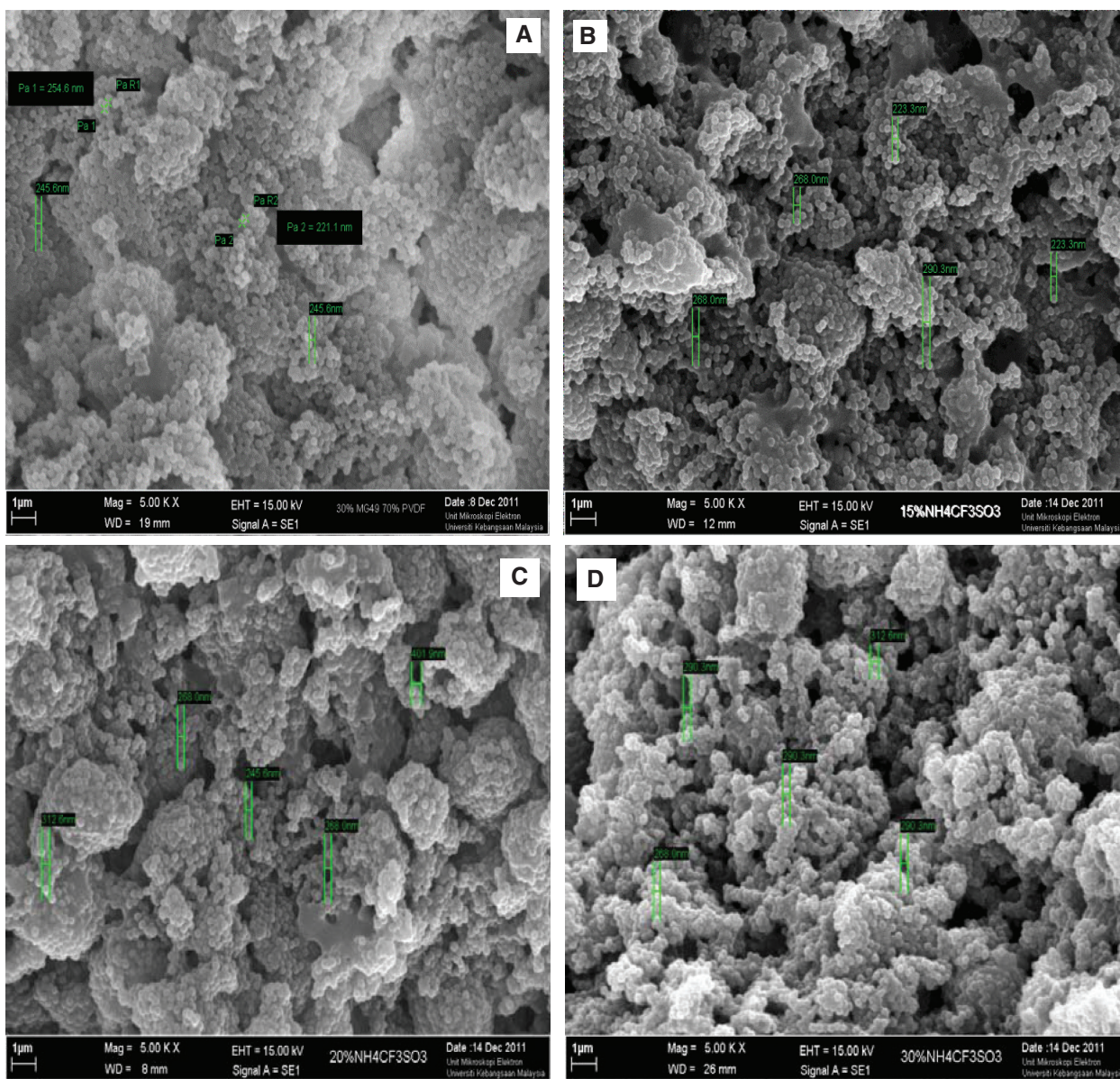


Figure 6 Scanning electron micrographs of (A) PVDF/MG49 blend, (B) 15 wt.% of NH₄CF₃SO₃, (C) 20 wt.% of NH₄CF₃SO₃ and (D) 30 wt.% of NH₄CF₃SO₃ at 5000× magnification.

σ_0 , and the activation energy, E_a , of the electrolyte cannot be estimated from the plot. The enhancement in temperature facilitates the segmental motion of the polymer chains, creating a conducting path known as free volume. Hence, the ionic conductivity was enhanced (25, 26).

Figure 3 shows the XRD patterns of the PVDF-MG49 blend and the PVDF-MG49-NH₄CF₃SO₃-based polymer electrolyte. The semi-crystalline nature of PVDF and MG49 has been confirmed by the appearance of peaks at $2\theta=18^\circ$, 20° and 26° , corresponding to the PVDF structure (11), and at $2\theta=29^\circ$ belonging to MG49 (27, 28). The change in the intensity peak of the doped samples is observed at 29.5° . The peak height decreases with the salt content. The results indicate that, upon the addition of salt, the crystallinity of the electrolyte decreases, which indicates that interaction between the constituents occurs.

It is evident from Figure 4 that the intensity of MMA peak ($2\theta=29^\circ$) decreased upon the addition of salt. In other words, the crystallinity decreased and complexation occurred in the amorphous phase of the polymer, which was complemented by the increase in the conductivity of the electrolyte.

Figure 5 shows the linear sweep voltammetry curve of the electrolyte. The anodic decomposition limit of the electrolyte is considered as the voltage at which the current flows through the cell. From the curve, an electrochemical stability of up to 4 V is observed. This finding is suitable for lithium battery applications.

Figure 6 shows the scanning electron micrographs of all electrolyte samples. The morphology of the blends PVDF-MG49 and PVDF-MG49 complexed with NH₄CF₃SO₃ is shown in Figure 6A–D, respectively. The scanning electron micrograph of the blend in Figure 6(A) indicates

the compatibility of PVDF and MG49 as a polymer matrix. Upon the addition of NH₄CF₃SO₃, a porous structure appears, which assists the absorption of active species into the electrolyte lattice; hence a higher ionic conductivity is expected.

4 Conclusions

In this work, the blend of PVDF-MG49 (70/30) complexed with NH₄CF₃SO₃ was successfully prepared via a solution casting technique. It was found that the ionic conductivity was influenced by the concentration of salt and by the maximum conductivity obtained at 6.32×10^{-4} S/cm for 30 wt.% of NH₄CF₃SO₃. The electrolyte does not obey the Arrhenius law. The crystallinity of the electrolyte decreases with NH₄CF₃SO₃ salt concentration. The electrolyte system shows sufficient electrochemical stability of up to 4 V by linear sweep voltammetry test. A porous structure appears in the electrolyte upon the addition of NH₄CF₃SO₃. The electrolyte was found to be suitable for lithium battery applications.

Acknowledgment: The authors gratefully acknowledge the School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia for allowing this research to be carried out. This work was funded by UKM under grant no. UKM-DLP-2012-021.

Received December 8, 2013; accepted January 14, 2014; previously published online February 22, 2014

References

- Fenton DE, Parker JM, Wright PV. Complexes of alkali metal ions with poly(ethylene oxide). *Polymer* 1973 Nov;14(11):589.
- Armand MB, Chabagno JM, Duclot M. Second International Meeting on Solid Electrolytes, St. Andrews, Scotland, September 20–22, Extended Abstracts; 1978.
- Kim DW, Park JK, Rhee HW. Conductivity and thermal studies of solid polymer electrolytes prepared by blending poly(ethylene oxide), poly(oligo[oxyethylene]oxysebacoyl) and lithium perchlorate. *Solid State Ionics* 1996 Jan;83(1–2):49–56.
- Tsutsumi N, Davis GT, Deroggi AS. Measurement of the internal electric field in a ferroelectric copolymer of vinylidene fluoride and trifluoroethylene using electrochromic dyes. *Macromolecules* 1991 Nov;24(24):6392–8.
- Scrosati B. Applications of electroactive polymers. London: Chapman & Hall; 1993.
- Macro GD, Lanza M, Pierceccini M. Influence of poly(ethylene glycol)methacrylate on the morphology and conductivity of poly(ethylene oxide)-sodium thiocyanate complexes. *Solid State Ionics* 1996 Aug;89(1–2):117–25.
- Ulaganathan M, Rajendran S. Effect of different salts on PVAc/PVdF-co-HFP based polymer blend electrolytes. *J Appl Poly Sci* 2010;118:646–51.
- Rajendran S, Kannan R, Mahendran O. [An electrochemical investigation on PMMA/PVdF blend-based polymer electrolytes](#). *Mater Lett*. 2001 June;49(3–4):172–9.
- Aravindan V, Vickraman P. Effect of aging on the ionic conductivity of polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) membrane impregnated with different lithium salts. *Indian J Phys*. 2012 May;86(5):341–4.
- Deka M, Nath AK, Kumar A. Ionic conduction and phase separation studies in PEO-P(VdF-HFP)-LiClO₄-dedoped

- polyaniline nanofiber composite polymer electrolytes — I. Indian J Phys. 2010 Oct;84(10):1299–305.
11. Nath AK, Deka M, Kumar A. Ionic conduction and phase separation studies in P(VdF-HFP)-LiClO₄-dedoped polyaniline nanofiber composite polymer electrolytes — II: Effect of incorporation of PC and DEC. Indian J Phys. 2010 Oct;84(10):1307–13.
 12. Michael MS, Prabakaran SRS. Rechargeable lithium battery employing a new ambient temperature hybrid polymer electrolyte based on PVK+PVdF-HFP (copolymer). J Power Sources 2004 Oct;136(2):408–15.
 13. Idris R, Glasse MD, Latham RJ, Linford RG, Schlindwein WS. [Polymer electrolytes based on modified natural rubber for use in rechargeable lithium batteries.](#) J Power Sources 2001 Mar;94(2):206–11.
 14. Su'ait MS, Ahmad A, Rahman MY. Ionic conductivity studies of 49% poly(methyl methacrylate)-grafted natural rubber-based solid polymer electrolytes. Ionics 2009 Aug;15(4):497–500.
 15. Low SP, Ahmad A, Rahman MY. Effect of ethylene carbonate plasticizer and TiO₂ nanoparticles on 49% poly(methyl methacrylate) grafted natural rubber-based polymer electrolyte. Ionics 2010 Dec;16(9):821–6.
 16. Yoshizawa M, Marwanta E, Ohno H. [Preparation and characteristics of natural rubber/poly\(ethylene oxide\) salt hybrid mixtures as novel polymer electrolytes.](#) Polymer 2000 Dec;41(26):9049–53.
 17. Rajendran S, Uma T, Mahalingam T. [Characterisation of plasticized PMMA based solid polymer electrolytes.](#) Ionics 1999;5(3–4):232–5.
 18. Ramya CS, Selvasekarapandian S, Savitha T, Hirankumar G, Baskaran R, Bhuvanawari MS, Angelo PC. Conductivity and thermal behavior of proton conducting polymer electrolyte based on poly (*N*-vinyl pyrrolidone). Eur Polym J. 2006 Oct;42(10):2672–7.
 19. Feng W, Ting F, Ying B, Chuan W, Lin Y, Zengguo F. Preparation and characterization of solid polymer electrolytes based on PHEMO and PVDF-HFP. Solid State Ionics 2009 May;180(9–10):677–80.
 20. Rajendran S, Mahendran O, Kannan R. Characterisation of [(1-x) PMMA-xPVdF] polymer blend electrolyte with Li⁺ ion. Fuel 2002 May;81(8):1077–81.
 21. Ahn JH, Wang GX, Liu HK, Dou SX. [Nanoparticle-dispersed PEO polymer electrolytes for Li batteries.](#) J Power Sources 2003 June;119(121):422–6.
 22. Song JY, Wang YY, Wan CC. Review of gel-type polymer electrolytes for lithium-ion batteries. J Power Sources 1999 Feb;77(2):183–97.
 23. Gray FM. Polymer electrolytes. Cambridge: Royal Society of Chemistry; 1997.
 24. Agrawal RC, Pandey GP. Solid polymer electrolytes: materials designing and all-solid-state battery applications: an overview. J Phys D: Appl Phys. 2008;41(22):223001.
 25. Jayathilaka PA, Dissanayake MA, Albinsson I, Mellander BE. Effect of nano-porous Al₂O₃ on thermal, dielectric and transport properties of the (PEO)₉LiTFSI polymer electrolyte system. Electrochim Acta 2002 Aug;47(20):3257–68.
 26. Ramesh S, Yahaya AH, Arof AK. [Dielectric behaviour of PVC-based polymer electrolytes.](#) Solid State Ionics 2002 Dec;152(153):291–4.
 27. Ataollahi N, Ahmad A, Hamzah H, Rahman MY, Mohamed NS. Preparation and characterization of PVDF-HFP/MG49 based polymer blend electrolyte. Int J Electrochem Sci 2012;7: 6693–703.
 28. Low SP, Ahmad A, Rahman MY. Nanocomposite solid polymeric electrolyte of 49% poly(methyl methacrylate)-grafted natural rubber-titanium dioxide-lithium tetrafluoroborate (MG49-TiO₂-LiBF₄). J Solid State Electrochem. 2011 Dec;15(11–12):2611–8.