

Computational Studies on PVDF-HFP/Li-salt Composite Electrolyte for Lithium-ion Batteries

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Abstract

Density Functional Theory (DFT) is very useful method to study the geometrical, electronic, and other important properties of molecules. Parameters and required data of Poly(vinylidene fluoride-co-hexachloropropylene) (PVDF-HFP), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and polymer electrolyte (PVDF-HFP + LiTFSI) are calculated with the B3LYP functional and 6-31+G(d,p) and 6-31++G(d,p) basis sets using Gaussian03. The optimized geometry, total energy, ionization potential, electron affinity, energy gap, and electronegativity were calculated. In result, the energy gap decreases while electron affinity increases of polymer electrolyte. Mulliken Charge distribution analysis done. IR studies shows the dominating nature of PVDF-HFP.

Keywords: DFT, HOMO-LUMO, Ionization Potential, Electron Affinity, Bandgap

INTRODUCTION

The demand of lithium-ion batteries increase continuously day by day because of portable devices and electric vehicles. However, the safety of lithium-ion battery is very important because many accident reported due to it [1]. To upgrade lithium-ion battery safety, we need to develop its components: cathode, anode, separator and electrolyte [2]. There are several type of electrolyte like liquid electrolyte solid electrolyte. However, in case of liquid electrolyte, it react with lithium metal, in result Li dendrites generate which give internal short circuits, causing battery explosion. To solve these problems solid polymer electrolytes (SPEs) are used. Recently, poly(vinylidene fluoride) (PVDF) polymer and it's copolymer poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP) are widely

used for electrolyte in lithium-ion batteries [3]. PVDF and its copolymer PVDF-HFP stick out because of its properties, involving excellent thermal and mechanical properties, high polarity and excellent chemical stability. PVDF-HFP is a superb polymer for solid polymer electrolytes (SPEs) because of its lower crystallinity, due to this reason ionic conductivity improved. It have also superb mechanical properties, good dielectric constant (~8.4), higher solubility, stronger mechanical properties, greater free volume (which play important role to synthesis better electrolytes for energy storage devices), and higher hydrophobicity (because hexafluoropropylene groups increase the fluorine content) [4]. Literately, lithium salt, LiTFSI is broadly used in solid polymer electrolyte growth, because of its better electrochemical properties and better chemical and thermal stability [5, 6]. The composition of PVDF-HFP and LiTFSI signify a porosity morphology. In

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addition, when we increase the LiTFSI amount then ionic conductivity of composites increases [2]. The advancement of solid polymer electrolyte symbolized move forward the next population of safe and high energy density solid-state lithium-ion batteries [7]. By the computation of PVDF-HFP and LiTFSI composition, the result show a difference between energy gap of PVDF-HFP and composite polymer electrolyte, also some properties like chemical hardness, chemical softness, electronegativity these all are varies which show in this paper. The present paper give quantum chemical explanation of SPEs based on lithium PVDF-HFP/LiTFSI for rechargeable Li-ion batteries.

COMPUTATIONAL DETAILS

Density Functional Theory related calculations were done using Gaussian03 program [8]. All the Calculations were done in the gas phase model with Gaussian-type basis sets [7, 9]. Density functional theory calculations using B3LYP functional and 6-31++G(d,p) and 6-31+G(d,p) basis set has been performed to investigate the geometrical, and electronic properties. For a close systems and using Koopman's theorem, ionization potential $I_p = -E_{\text{HOMO}}$ and electron affinity $E_a = -E_{\text{LUMO}}$ [10–12]. With the help of ionization potential and electron affinity, we can calculate the some thermochemistry of molecules like Electronegativity, Chemical potential, Chemical hardness [13–15].

RESULTS AND DISCUSSIONS

Geometrical Analysis

Geometrical Analysis of PVDF-HFP, LiTFSI and Polymer Electrolyte were done in gas phase using Gaussian03. Physical parameters like Bond length (in Å), Bond angle (in degree) and Dihedral angle (in degree) [16–18]. All the molecules are optimized using density functional theory and appropriate method B3LYP with 631+G(d,p) and 631++G(d,p) basis sets [19]. In geometrical parameters of PVDF-HFP the bond length in Å(angstrom) between C-F, C-H, C-C, are 1.3, 1.1, 1.5 respectively, bond angles between $C_H-C_F-C_H$, $C_F-C_H-C_F$, are 115.8 (degree), 115.6 (degree) respectively and dihedral angle between carbon atom plane is 165.5 (degree). The geometrical parameters of LiTFSI and polymer electrolytes listed in Tables 1 and 2 respectively. Optimized structure of these shown in Figures 1–3 respectively. Furthermore, thermochemistry like heat capacity, electronic energy, dipole moment, polarizability, pressure, gibb's free energy, thermal correction to energy, zero point energy, etc are given in Table 3. If force of attraction is strong between two atom that signifies bond length small. Bond angle is an angle between two adjacent bonds.

Table 1. Geometrical parameters of LiTFSI.

Structural parameters		Name of molecule
		<i>Li-TFSI</i>
Bond length (Å)	dC4-F15	1.35
	dO8-S3	1.46
	dN1-Li	1.943
Bond angle (degree)	∠S3-N1-S2	127.53
	∠F15-C4-F13	108.84
	∠O8-S3-O9	122.53
	∠O6-S2-O7	119.94
	∠S2-O6-Li16	94.74
Dihedral angle (degree)	S3-N1-S2-O6	-173.54
	O9-S3-N1-S2	-26.16
	O8-S3-N1-S2	-162.64
	O7-S2-Ni-S3	-41.38

Interaction Energies

The interaction energy [5–9], for the given polymer electrolyte (PVDF-HFP/LiTFSI) are calculated by given equation:

$$\Delta E = E - (E_1 + E_2) \quad (1)$$

Where, ΔE is interaction energy for the given polymer electrolyte, E is energy for the given polymer electrolyte (PVDF-HFP/LiTFSI), E_1 is energy of PVDF-HFP, and E_2 is energy of Lithium salt LiTFSI. Moreover, using optimized data we get energies required, which are shown in Table 3.

Table 2. Physico-chemical properties of PVDF-HFP, LiTFSI and Polymer Electrolyte.

Properties	PVDF-HFP	Li-TFSI	Polymer Electrolyte	Units
Heat Capacity (C_v)	44.021	52.062	95.415	cal/mol-kelvin
Entropy (S)	106.599	120.982	183.409	cal/mol-kelvin
Electronic Energy	27,013.41	49919.52	76913.8253	eV
RMS Gradient Norm	0.35875	1.19311	0.05192	eV/Bohr
Imaginary Frequency	0	4	4	Hz
Dipole Moment	3.727533	4.282345	7.701199	Debye
Polarizability (α)	66.563740	124.854000	160.510333	a.u.
Pressure	1.00	1.00	1.00	atm
Thermal Correction to Energy	2.9718	1.6817	4.9460	eV
Electronic Energy	27,013.41	49919.52	76913.8253	eV
Zero-point Energy Correction	2.6487	1.2868	4.2273	eV
Gibb's free energy	1.6193	--	2.6004	eV
Point group symmetry	C ₁	C ₁	C ₁	--

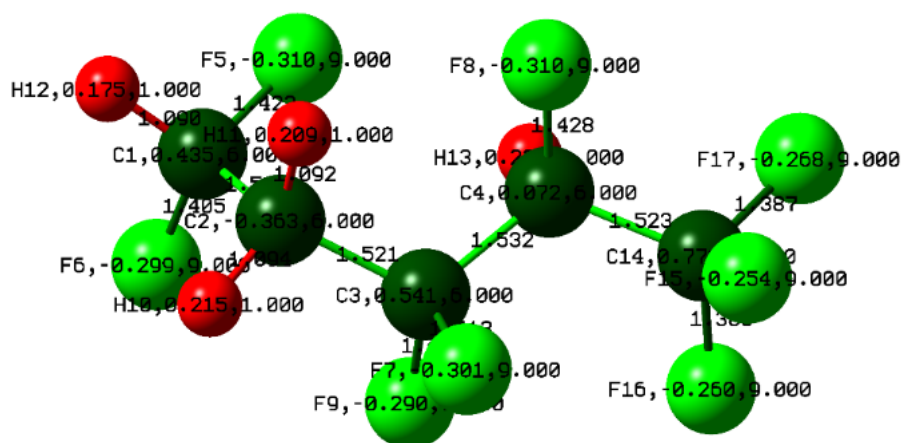


Figure 1. Optimized structure of PVDF-HFP.

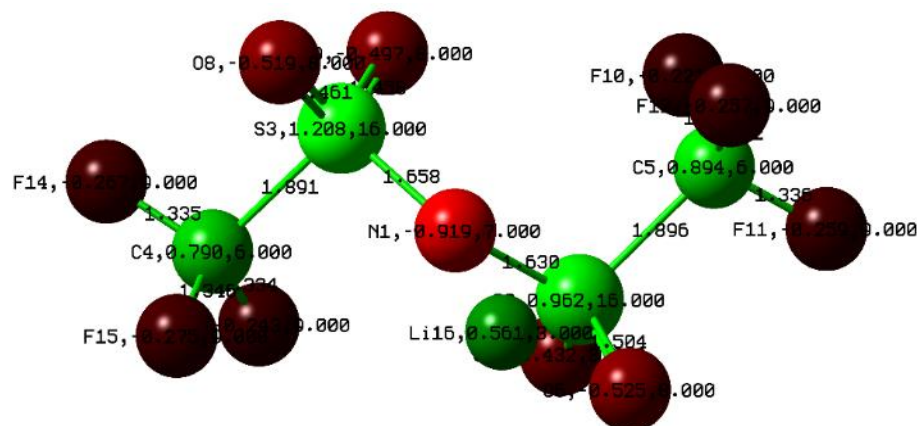


Figure 2. Optimized structure of LiTFSI.

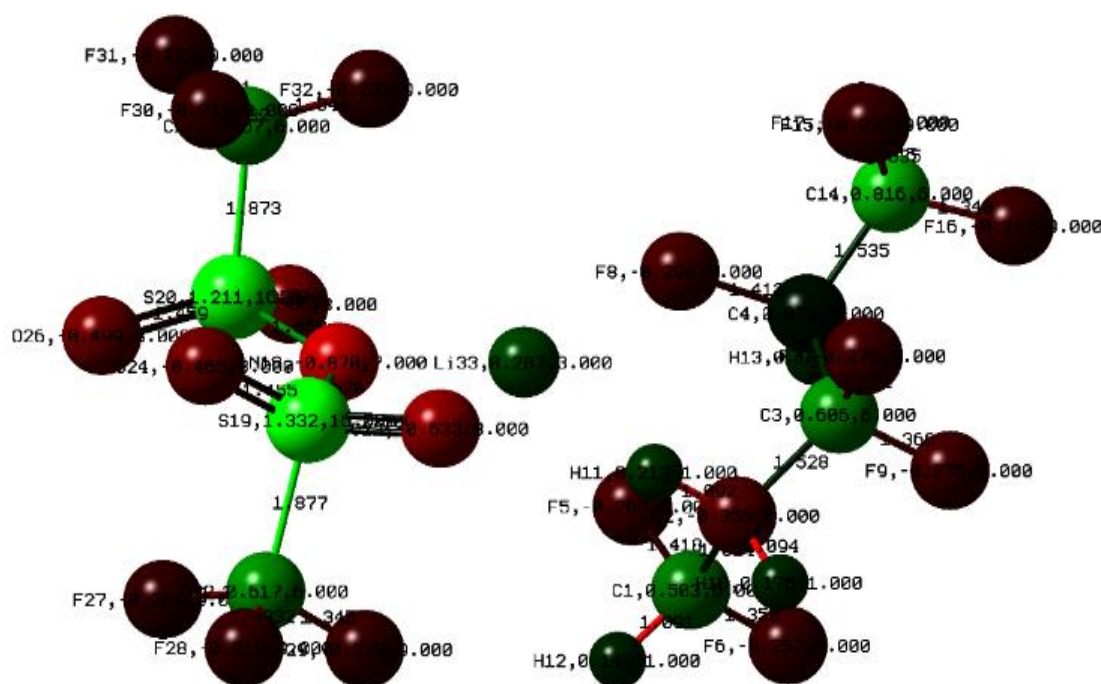


Figure 3. Optimized structure of Polymer electrolyte.

Table 3. Interaction energy.

Molecules	Energy (eV)
PVDF-HFP	-27,013.41
LiTFSI	-49919.52
Polymer electrolyte	-76913.8253

Hence, Interaction Energy (ΔE) will be 19.11 eV, which shows the stronger bond within the isolated molecules of polymer electrolyte.

Mulliken Charge Analysis

Mulliken charge produced by the mulliken population analysis which provide information of atomic charge which calculated by computational chemistry. Two types of charge distribution analysis are exist for the system. First, Mulliken Charge distribution Analysis (MCA) and Second, Hirshfeld Charge distribution Analysis (HCA) [11–13]. MCA is based on linear combination of atomic orbital molecular orbital theory. The Mulliken Charge distribution of PVDF-HFP, polymer electrolyte is given in Figures 4, 5 respectively.

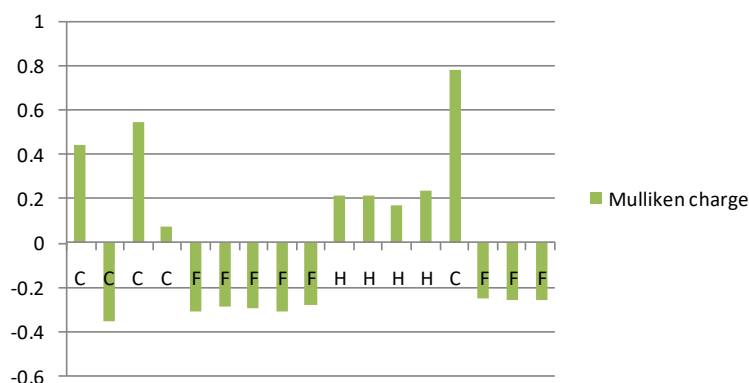


Figure 4. Mulliken charge distribution of PVDF-HFP.

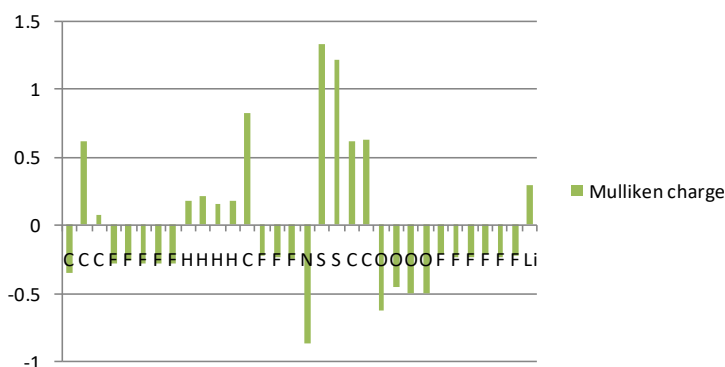


Figure 5. Mulliken charge distribution of polymer electrolyte (PVDF-HFP+ LiTFSI).

Electronic and Optical Properties

Highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) in polymer electrolyte are exposed in Figures 6. The LUMO- concentrated part have higher capacity to accept the electrons and HOMO-concentrated part have higher capacity to donate the [10]. Chemical parameters are calculated using HOMO-LUMO [9]. If the energy gap between molecules are small then molecules called soft molecules and if energy gap between molecules are large then molecules called hard molecules. Here band gap of polymer electrolyte decreasing nearly 2.44ev after the addition of Lithium salt LiTFSI that means polymer electrolyte become soft and stability of electrolyte raised. Chemical hardness of electrolyte is tells us the resistivity of chemical. The chemical softness also play an important role related to conductivity of polymer electrolyte. Here the chemical hardness of the polymer electrolyte reduce and chemical softness of polymer electrolyte enhanced, which is shown in Table 4.

Table 4. Different parameters of PVDF-HFP, Litfsi and poltmer electrolye.

System	Ionization energy (Ip) (eV)	Electron affinity (Ea)(eV)	Electronega-tivity (eV)	Chemical potential (eV)	Chemical hardness (eV)	Chemical softness (eV) ⁻¹	Electroph-ility index (eV)	HOMO-LUMO energy gap (Eg) (eV)
PVDF-HFP	9.9751	0.08082	5.0279	-5.0279	4.9471	0.2021	2.5549	9.8943
LiTFSI	8.8581	1.6879	5.273	-5.273	3.5851	0.2789	3.8777	7.1702
Polymer Electrolyte	8.196	0.74177	4.469	-4.469	3.727	0.2683	2.679	7.454

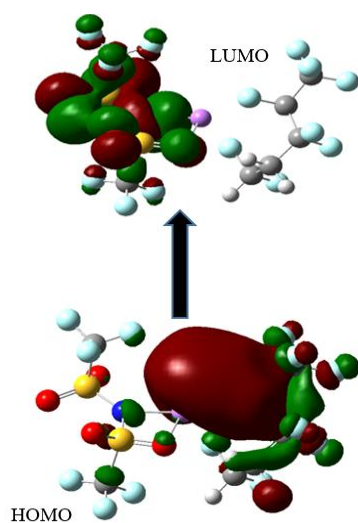


Figure 6. HOMO-LUMO state of Polymer electrolyte.

IR Studies of PVDF-HFP, LiTFSI and Polymer electrolyte

In this study, we investigated FTIR and calculated the vibrational frequencies PVDF-HFP copolymer, LiTFSI and Polymer electrolyte [6–9]. To interpret and predict the vibrational spectra quantum chemical computational methods are essential tools [13]. The IR techniques has used to investigate about molecules and functional groups. The range of IR spectra from 400 cm^{-1} to 1500 cm^{-1} has been shown. Furthermore, computational IR plot of frequencies PVDF-HFP copolymer, LiTFSI and Polymer electrolyte has given in Figures 7–9 respectively.

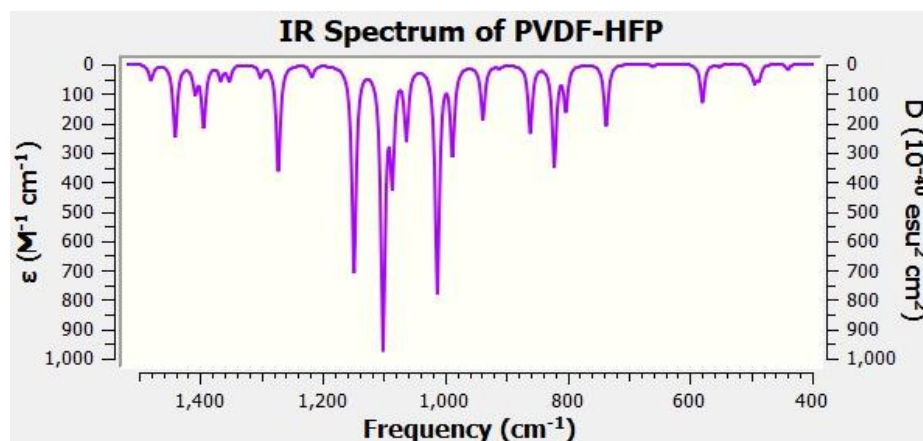


Figure 7. IR spectra of PVDF-HFP between wavenumber (cm^{-1}) and absorbance (a.u.).

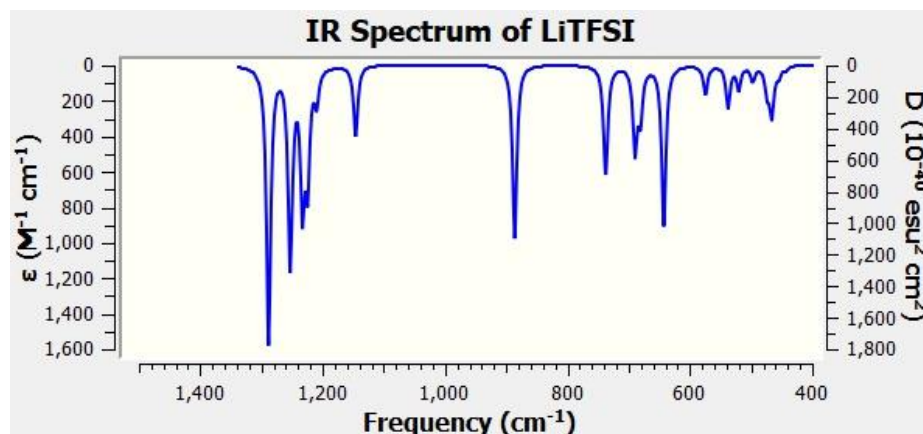


Figure 8. IR spectra of LiTFSI between wavenumber (cm^{-1}) and absorbance (a.u.).

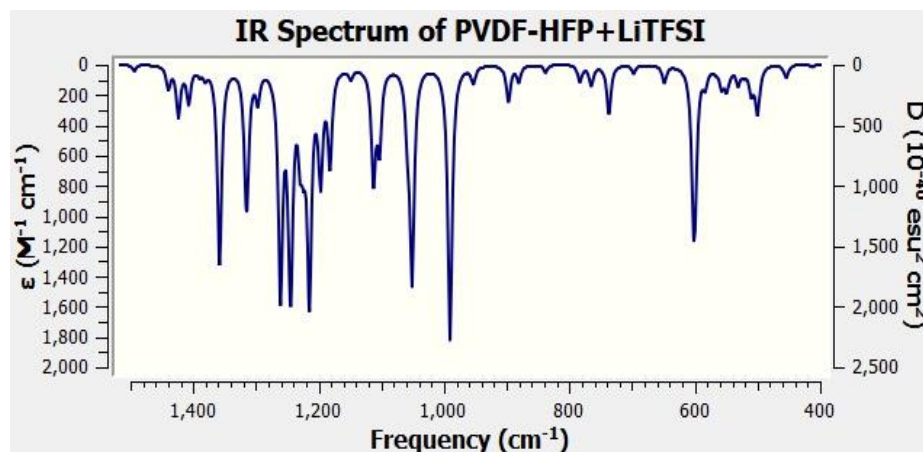


Figure 9. IR spectra of Polymer electrolyte (PVDF-HFP+LiTFSI) between wavenumber (cm^{-1}) and absorbance (a.u.).

Electrostatics Potential (ESP)

Figure 10 show the molecular electrostatic potential surface of polymer electrolyte. It is basically visualize charge regions of a molecules in three dimension. The color represent different value of electrostatics potential value at the ESP surface. Red region of the surface represent negative ESP it means their are attraction of the proton by the concentrated electron density in the molecules, blue region represent positive ESP it means there are repulsion of proton by atomic nuclei and the green region for zero ESP, i.e, the neutral portions of the surface.

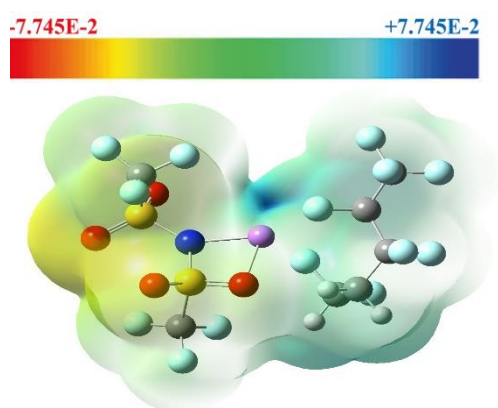


Figure 10. Electrostatic potential surface of polymer electrolyte.

CONCLUSIONS

The density functional theory studies are taken for copolymer PVDF-HFP, LiTFSI and interaction of both. The geometric analysis provide the bond length, bond angle, point group symmetry and orientation of molecules etc of individual PVDF-HFP, LiTFSI and composite polymer electrolyte. Dipole moment of PVDF-HFP, LiTFSI and Polymer electrolyte are in increasing order that support the dominating amorphous nature increases. Positive interaction energy shows the stronger bond within the isolated molecules of polymer electrolyte. Mulliken population analysis (MPA) has quantify the charge distribution within composite polymer as well as individual copolymer and salt done. The chemical reactive properties described using HOMO-LUMO theory, and the investigations provide the required data for the molecular energy gap (E_g) which show energy gap of composite polymer electrolyte decreases it means bonding become stronger and stability increased of polymer electrolyte. The chemical hardness decreases while chemical softness increases which is better for ionic conductivity. IR studies shows the dominating nature of PVDF-HFP that shows semi-crystalline nature of polymer electrolyte.

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REFERENCES

1. Chawla, N., Bharti, N., & Singh, S., "Recent advances in non-flammable electrolytes for safer lithium-ion batteries," Batteries, pp. 1-26, 2018.
2. Gonçalves, R., Miranda, D., Almeida, A. M., Silva, M. M., Meseguer-Dueñas, J. M., Ribelles, J. L. G., Costa, C. M., "Solid polymer electrolytes based on lithium bis(trifluoromethanesulfonyl)imide/poly(vinylidene fluoride -co-hexafluoropropylene) for safer rechargeable lithium-ion batteries," Sustainable Materials and Technologies, 2018.
3. Tripathi, A. K., & Singh, R. K., "Lithium salt assisted enhanced performance of supercapacitor based on quasi solid-state electrolyte," Journal of Saudi Chemical Society, 2018.

4. C.M. Costa, M.M. Silva, S. Lanceros-Méndez, “Battery separators based on vinylidene fluoride (VDF) polymers and copolymers for lithium ion battery applications,” *RSC Advances*, pp. 11404-11417, 2013.
5. A.M. Elmér, P. Jannasch, “Polymer electrolyte membranes by in situ polymerization of poly(ethylene carbonate-co-ethylene oxide) macromonomers in blends with poly(vinylidene fluoride-co-hexafluoropropylene),” *Journal of Polymer Science Part B: Polymer Physics*, pp. 79-90, 2007.
6. P. Tuhania, and P. K. Singh., “High performance polymer,” pp. 911–917, 2018.
7. X. Wang, C. Xiao, H. Liu, Q. Huang, J. Hao, and H. Fu, “Materials (Basel),” 2018.
8. N. Asthana, M. M. Dwivedi, and K. Pandey, in *International Journal of Emerging Engineering Research and Technology*, **5**, pp. 21–27, 2017.
9. X. Wang, C. Xiao, H. Liu, Q. Huang, and H. Fu, *J. Appl. Polym. Sci.*, **135**, pp. 1–9, 2018.
10. R. Sarkar and T. K. Kundu, *J. Chem. Sci.*, **130**, 1–18, (2018).
11. H. R. I. Vlfv, R. Ri, and D. Duphw, pp. 66–69, 2013.
12. S. P. Jakriya, A. M. Syed, S. K. Pillai, and D. B. Rahim, *Mater. Express*, pp. 77–84, 2018.
13. C. G. Zhan, J. A. Nichols, and D. A. Dixon, *J. Phys. Chem. A*, pp. 4184–4195, 2003.
14. W. Wang and H. Fan, “Ferroelectrics,” pp. 41–44, 2010.
15. S. Pal and T. K. Kundu, *ISRN Phys. Chem.*, pp. 1–16, 2013.
16. R. Mejri, J. Dias, and S. B. Hentati, *Eur. Polym. J.*, pp. 445–451, 2016.
17. R. Sachdeva, no. Icaet, pp. 13–15, 2016.
18. R. Mathammal, N. Jayamani, and N. Geetha, *J. Spectrosc.*, pp. 1, 2013.
19. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, (2004).