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Research Article

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First-principles investigation of the structural and electronic properties of (PEO)4–Li^+-SiO_2 composite electrolyte

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Abstract

Solid-state batteries with poly(ethylene oxide) (PEO) solid electrolytes are promising for next-generation energy storage owing to their flexibility and compatibility with lithium metal. However, the high crystallinity of (PEO)4 limits the lithium-ion conductivity and contributes to poor electrochemical stability and weak interfacial contact with the electrodes. To address these challenges, we present a first-principles investigation based on density functional theory (DFT) of the structural and electronic properties of a (PEO)4–Li^+-SiO_2 composite electrolyte. The inclusion of SiO_2 nanoparticles disrupted the crystalline structure of (PEO)4, enhancing its amorphous character and facilitating Li^+-ion transport. Structural optimization and charge distribution analyses revealed improved stability and ionic pathways. The composite maintained a wide band gap, confirming its insulating nature, which is essential for electrolyte performance. These insights contribute to the rational design of high-performance solid polymer electrolytes for safer and more efficient lithium-ion batteries (LIBs).

Keywords:

PEO, SiO_2, Li-ion, Composite Electrolyte, DFT, Ionic Conductivity, Solid-State Battery

1. Introduction

The rapid advancement of solid-state lithium-ion battery research is driven by the growing demand for safe and high-performance energy storage systems[1,2]. Conventional lithium-ion batteries that use liquid electrolytes offer high ionic conductivity and excellent electrode wetting, contributing to their strong electrochemical performance[3–8]. However, these liquid electrolytes, typically composed of volatile and flammable organic solvents, pose serious safety risks, suffer from low ion selectivity, and exhibit limited chemical and thermal stability[9–12].

In contrast, solid-state devices present a promising alternative, offering enhanced safety, compact design, high energy density, and superior thermomechanical stability[13]. Their leak-proof nature and resistance to combustion make them ideal candidates for next-generation energy-storage technologies[14,15]. A key component of these systems is the solid-state electrolyte, which plays a critical role in determining battery performance and reliability.

Solid-state electrolytes enable safer and denser energy storage than traditional liquid systems[16]. Their non-flammable nature improves chemical stability, and their ability to suppress parasitic ion shuttling contributes to enhanced battery efficiency and longevity[17]. Solid-state electrolytes not only facilitate lithium-ion transport but also serve as separators, preventing short circuits during battery operation[18,19].

These electrolytes are generally classified into two categories: inorganic and polymer-based. Inorganic electrolytes exhibit high ionic conductivity and wide operational temperature ranges; however, they face challenges such as lithium dendrite penetration and poor interfacial compatibility. Conversely, polymer electrolytes offer advantages such as low density, optical transparency, mechanical flexibility, and ease of thin-film fabrication, making them attractive for solid-state battery applications[20].

Among polymer electrolytes, poly(ethylene oxide) (PEO)-based materials have garnered significant attention owing to their excellent processability, flexibility, and compatibility with lithium metal anodes[21–26].

PEO is a polyether compound with the repeating unit $H–(O–CH_2–CH_2)_n–OH$, and is also referred to as polyethylene glycol (PEG) when its molecular weight is below 20,000 g/mol[27]. Typically, (PEO)4 used in battery applications has a molecular weight that exceeds this threshold[18].

PEO functions as a high-performance polymer electrolyte, in which lithium ions migrate through the polymer matrix via the segmental motion of the chains. The ionic conductivity of Li^+ in PEO is closely related to the mobility of its amorphous regions[28]. However, pure PEO exhibits poor ionic conductivity (10^{-6} to 10^{-8} S/cm at 298 K) owing to its semicrystalline nature. Although conductivity improves at elevated temperatures, this comes at the cost of reduced mechanical strength and chemical stability[22]. Additionally, volume changes in the electrode materials during cycling can lead to poor contact with the solid electrolyte, further degrading the performance. The high crystallinity of PEO at ambient conditions remains a major barrier to efficient lithium-ion transport and stable electrode–electrolyte interfaces[2,29].

To address these limitations, composite electrolytes incorporating inorganic fillers such as Al_2O_3, SiO_2, TiO_2, and clay have been developed and studied[11,30–33]. These fillers not only enhanced the mechanical properties but also improved the ionic conductivity compared to pure PEO. Recent studies have shown that doping PEO with Al_2O_3 and TiO_2 significantly influences its microstructure and ion transport behavior. TiO_2, while known for its photocatalytic properties, has a relatively large band gap (3.0–3.2 eV), limiting its effectiveness under sunlight illumination. During the PEO process, TiO_2 particles may undergo phase transformation from anatase to rutile due to localized high temperatures, thereby altering their structural role in the composite[34]. In contrast, Al_2O_3 enhances the ionic conductivity up to an optimal concen[35]tration (~15 wt. %), beyond which aggregation and immiscibility lead to heterogeneous morphology and reduced performance. These structural changes can promote partial recrystallization or amorphization of PEO, thereby improving the lithium-ion mobility[36,37].

Interestingly, the incorporation of SiO_2 nanoparticles into polymer electrolytes not only improves thermal shrinkage resistance but also enhances electrolyte wettability, which is essential for stable electrode–electrolyte interfaces in lithium-ion batterie[38,39]. The Lewis acidic surface of SiO_2 interacts with PEO chains, disrupting their crystalline order and increasing the amorphous phase, which facilitates lithium-ion transport and boosts the conductivity[38,40].

Despite its widespread use, accurately characterizing the interactions between (PEO)4 and lithium salts, such as $LiPF_6$, remains a complex challenge[41,42]. This complexity arises from the interplay between polymer crystallinity, lithium-ion solvation dynamics, and interfacial stability. The segmental motion of PEO governs ion transport; however, its high crystallinity at room temperature limits the conductivity and transference numbers. Moreover, the chemical reactivity and mechanical fragility of PEO complicate its integration with lithium salts, particularly under high-voltage conditions[30,43–48].

First-principles calculations based on density functional theory (DFT) offer a powerful approach for probing these phenomena at the atomic scale[49–58]. In this study, we employed DFT to investigate the structural optimization and charge distribution of the (PEO)4–Li^+-SiO_2 composite. Our goal is to elucidate the role of SiO_2 in enhancing the ionic conductivity and stability of PEO-based electrolytes, thereby contributing to the rational design of next-generation solid polymer electrolytes for use in solid-state batteries.

2. Computational Methodology

To ensure compatibility with high-voltage cathodes and enhance the oxidative stability of the polymer electrolyte, we adopted a high-concentration polyethylene oxide (PEO) formulation with an EO:Li^+ ratio of 4:1. This choice is supported by recent experimental and theoretical findings , which demonstrate that (PEO)4 exhibits an oxidation potential exceeding 5.0 V vs. Li/Li^+, significantly higher than conventional (PEO)4 electrolytes[59]. The increased coordination of ethylene oxide segments with lithium ions in this formulation effectively suppresses interfacial degradation, electronic conduction in the cathode electrolyte interphase (CEI), and irreversible phase transitions of $LiCoO_2$. These properties make (PEO)4 a promising candidate for solid-state electrolytes in high-energy-density lithium batteries. In our simulations, this composition was used to model the polymer matrix and evaluate its electronic structure, ionic transport properties, and mechanical properties.

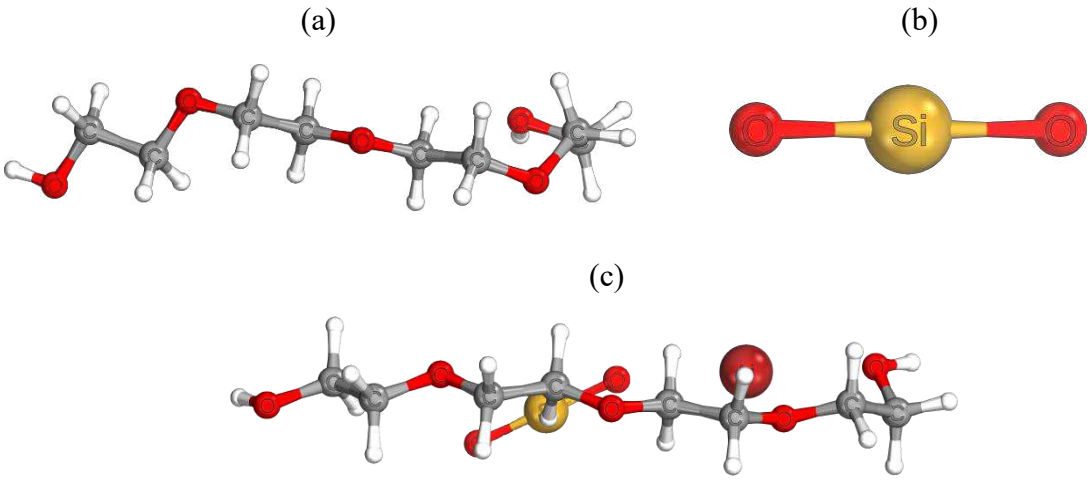


Figure 1.Optimized Molecular Structures of (a) (PEO)4, (b) SiO_2, and the Composite Cluster (c) (PEO)4–Li–SiO_2

All quantum chemical calculations were performed using the ORCA 6.0.0 software package[60,61]. The molecular structures of polyethylene oxide (PEO)4, silicon dioxide (SiO_2), and lithium hexafluorophosphate ($LiPF_6$) were constructed and optimized using Density Functional Theory (DFT) with the B3LYP hybrid functional, which is known for its reliable treatment of organic and inorganic systems. The def2-SVP basis set was applied to light atoms (H, C, O, F, and Li), whereas LANL2DZ was used for silicon to incorporate effective core potentials and relativistic effects. Geometry optimizations were performed with tight convergence criteria on energy (10^{-6} Eh) and gradients, and vibrational frequency analyses confirmed the absence of imaginary frequencies, ensuring that all optimized structures corresponded to true minima.

Molecular structures of (PEO)4, SiO_2, and the cluster (PEO)4-Li^+-SiO_2 shown in Figure 1 were constructed using Avogadro 1.2.0 and visualized with Iboview and Chemcraft 1.8 for orbital analysis and HOMO–LUMO visualization[60,62–66].

Electronic structure analyses included the Density of States (DOS), Frontier Molecular Orbitals (HOMO-LUMO), Mulliken charge distribution, and vibrational spectra, providing insights into the electronic stability and charge transfer mechanisms within the composite electrolyte. To evaluate the ionic conductivity, Ab Initio Molecular Dynamics (AIMD) simulations were conducted at 300 K using the NVT ensemble, and the diffusion coefficient of Li^+ ions was extracted from the mean square displacement (MSD) over time. The ionic conductivity was estimated using the Nernst-Einstein relation. Additionally, Nudged Elastic Band (NEB) calculations were performed to determine the energy barriers associated with Li^+ migration pathways. Mechanical properties, such as the bulk modulus and Young's modulus, were derived from the energy–volume data using finite strain analysis.

3. Results and Discussion

3.1 Electronic Structure and Stability Analysis

The geometric parameters of the (PEO)4 molecule, summarized in Table 1, provide valuable insights into the molecular structure and its consistency with previously reported data. The bond lengths calculated in this study are generally in good agreement with the literature values, with minor deviations that can be attributed to differences in the computational methods, basis sets, or optimization criteria. For instance, the O1–C1 bond length was found to be 1.41 Å, which is slightly shorter than that reported in Ref. 67 (1.45 Å) and Ref. 68 (1.43 Å), suggesting a possible contraction due to local electronic effects or a tighter geometry optimization. The C2–C1 bond length remained consistent at 1.52 Å across all sources, reinforcing the reliability of the structural model used.

The O1–H3 (0.97 Å) and C5–H11 (1.11 Å) bond lengths are not consistently reported in the literature, but the values obtained here fall within the expected ranges for covalent O–H and C–H bonds. The C5–H11 bond was slightly elongated compared to that in Ref. 69 (1.09 Å) may reflect subtle differences in the hydrogen treatment or the influence of neighboring atoms in the polymer chain. The bond angle data, available only from this study, further support the structural integrity of the model. The angles C2–C1–H1 (108.41°), O1–C1–H1 (112.87°), and C4–C3–O3 (107.65°) are consistent with typical tetrahedral geometries around sp^3-hybridized carbon atoms. The H16–C8–H17 angle (107.44°) also aligned with the expected values, indicating minimal distortion in the polymer backbone.

These geometric features are essential for understanding the conformational behavior of PEO and its interactions with lithium ions and inorganic fillers such as SiO_2. Accurate bond lengths and angles influence the flexibility, coordination ability, and ultimately the performance of polymers as solid electrolytes in lithium-ion batteries.

Table 1. *Geometric Parameters of (PEO)4: Bond Lengths and Angles from DFT Calculations and Literature*

Geometries	**(PEO)4**			
	This study	**Ref[67]**	**Ref[68]**	**Ref[69]**
Bond length		**Å**		
O1-H3	0.97	-	-	-
O1-C1	1.41	1.45	1.43	
C5-H11	1.11	-	-	1.09
C2-C1	1.52	1.52	1.52	-
Bond angle		**Degree**		
C2C1H1	108.41	-	-	-
O1C1H1	112.87	-	-	-
C4C3O3	107.65	-	-	-
H16C8H17	107.44	-	-	-

Table 2 demonstrates the progressive enhancement of the structural and electronic properties of PEO-based solid electrolytes through lithium coordination and SiO_2 incorporation. The dipole moment increases from 2.66 D in pure (PEO)4 to 19.72 D in (PEO)4–Li, indicating strong electrostatic interactions between the Li^+ ions and ether oxygen atoms, which facilitate dynamic coordination environments for ion transport. Upon SiO_2 addition, the dipole moment decreased to 14.84 D, suggesting a redistribution of the charge density due to interactions between the silica surface, polymer chains, and lithium ions.

The thermodynamic stability improved with each modification, as shown by increasingly negative electronic energy, enthalpy, and free energy values. The entropy increases from 38.63 to 45.77 kcal/mol with SiO_2 incorporation, reflecting greater configurational flexibility and vibrational complexity, which may enhance ion dynamics at elevated temperatures.

These findings are consistent with recent studies showing that SiO_2-modified PEO matrices improve ionic conductivity, mechanical strength, and electrochemical stability by disrupting crystallinity and enhancing amorphous content[70–72].

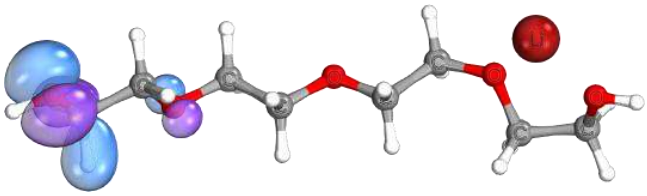
Table 2*.DFT-Calculated Thermodynamic and Electronic Properties of (PEO)4, (PEO)4–Li, and (PEO)4–Li–SiO_2 Systems*

Properties	**Geometries**		
	(PEO)4	**(PEO)4-Li**	**(PEO)4-Li-SiO2**
Dipole Moment	2.66	19.722	14.84
Electronic Energy (Hartree)	-690.41	-698.17	-1137.85
Entropy (kcal/mol)	38.63	39.51	45.77
Free Energy (Hartree)	-690.64	-698.02	-1137.65
Enthalpy (Hartree)	-690.58	-697.96	-1137.58
LUMO (eV)	1.25	-4.64	-6.05
HOMO (eV)	-6.73	-8.85	-9.10
Band Gap(eV)	7.99	4.21	3.06

3.2 Frontier Molecular Orbital Analysis

Figure 1 presents the frontier molecular orbitals of the (PEO)4–Li complex obtained via DFT. In panel (a), the HOMO is visualized as delocalized electron density along the polymer backbone, indicating regions of electron donation. Panel (b) shows the LUMO, with electron density localized near the lithium ion and coordinating oxygen atoms, highlighting potential sites for electron acceptance. These orbital distributions reflect the influence of lithium coordination on the electronic structure of the polymer, supporting its role in enhancing ion transport and electrochemical performance in solid-state lithium-ion batteries.

(a)



(b)

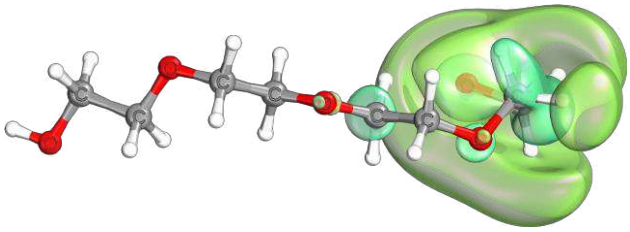
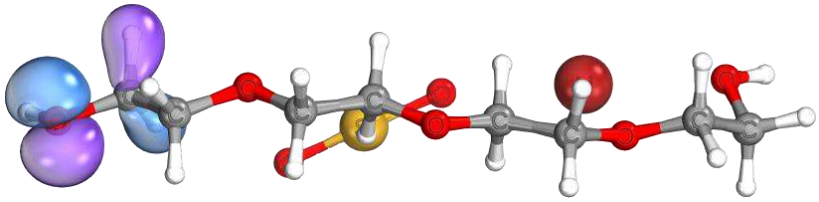


Figure 2*.DFT-Based Frontier Molecular Orbitals of (PEO)4–Li Complex: (a) HOMO and (b) LUMO Visualization*

Figure 2 illustrates the frontier molecular orbitals of the (PEO)4–Li–SiO_2 complex. In panel (a), the HOMO is localized along the polymer backbone and coordinating atoms, indicating electron donation regions. Panel (b) shows the LUMO concentrated near the lithium and SiO_2 interaction sites, highlighting the electron-accepting regions.

The calculated HOMO and LUMO energies were −9.10 eV and −6.05 eV, respectively, yielding a band gap of 3.06 eV. Compared to the (PEO)4–Li system, which has a band gap of 4.21 eV**, the incorporation of SiO_2 further narrows this gap. This suggests enhanced electronic interactions and improved charge transfer pathways, making the composite more suitable for solid-state lithium-ion battery applications.

(a)



(b)

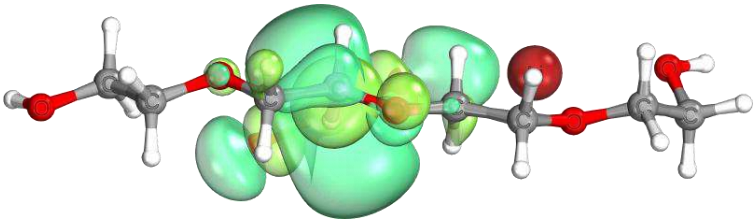


Figure 3*.DFT-Based Frontier Molecular Orbitals of (PEO)4–Li–SiO₂ Complex: (a) HOMO and (b) LUMO Visualization*

3.3 Electrochemical Stability Window (ECW)

The Electrochemical Stability Window (ECW) is a critical parameter for evaluating the performance of solid-state electrolytes (SSEs) in lithium batteries. It defines the voltage range within which the electrolyte remains stable, resisting oxidation and reduction reactions. Fundamentally, the ECW is determined by the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which represent the oxidation and reduction limits of the electrolyte, respectively[73]. This relationship is captured through density functional theory (DFT) calculations, where the HOMO-LUMO gap serves as an estimate of the ECW. The anodic (oxidation) and cathodic (reduction) limits are calculated using the following formulas[70,74]:

Cathodic limit: $V_{CL} = \frac{-E_{LUMO}}{e}$ (1)

Anodic limit: $V_{AL} = \frac{-E_{HOMO}}{e}$ (2)

Electrochemical window: $ECW = V_{AL} - V_{CL}$ (3)

Here, E_{HOMO} and E_{LUMO} are the energy levels of HOMO and LUMO, respectively, and e is the elementary charge. While this HOMO–LUMO method provides a quick estimation of the ECW, it is limited by its inability to account for interfacial dipoles and assumes chemically inert electrodes, making the calculated ECW an upper bound.

In practice, the thermodynamic ECW derived from such calculations often underestimates the actual stability observed experimentally. The kinetic ECW, which includes effects such as decomposition kinetics and the formation of passivating interfacial layers, tends to be broader. This pseudostability allows some SSEs to operate effectively beyond their predicted thermodynamic limits, enhancing their compatibility with both lithium anodes and high-voltage cathodes and ultimately improving the energy density of solid-state lithium batteries[73].

The ECW of the (PEO)4 system is calculated to be 7.99 eV, indicating a broad stability range. Upon coordination with Li^+ ions, the ECW narrows to 4.21 eV and further decreases to 3.06 eV with the addition of SiO_2 nanoparticles. This reduction in ECW is primarily due to the significant lowering of both HOMO and LUMO energy levels, reflecting enhanced oxidative and reductive stability.

The decrease in the HOMO energy from −6.73 to −9.10 eV suggests improved resistance to oxidation, whereas the LUMO shift from 1.25 to −6.05 eV indicates increased reductive stability. These electronic modifications arise from the strong interactions between the PEO chains, Li^+ ions, and SiO_2 surfaces, which also contribute to mechanical reinforcement and structural stabilization.

Although the calculated ECWs represent thermodynamic limits, the actual electrochemical performance may exceed these values owing to kinetic stabilization mechanisms, such as the formation of passivating interfacial layers. This pseudostability enables SSEs to operate safely beyond their predicted voltage limits, thereby enhancing their compatibility with high-voltage cathodes and lithium metal anodes.

3.4 Vibrational and Spectroscopic Investigations

3.4.1 Vibrational Analysis

Infrared (IR) spectroscopy was employed to analyze the structural evolution of (PEO)4 upon the incorporation of Li^+ and SiO_2 nanofillers. The spectra (Figures a–c) exhibit distinct vibrational bands that provide valuable insights into the molecular interactions and bonding environments within the composite systems.

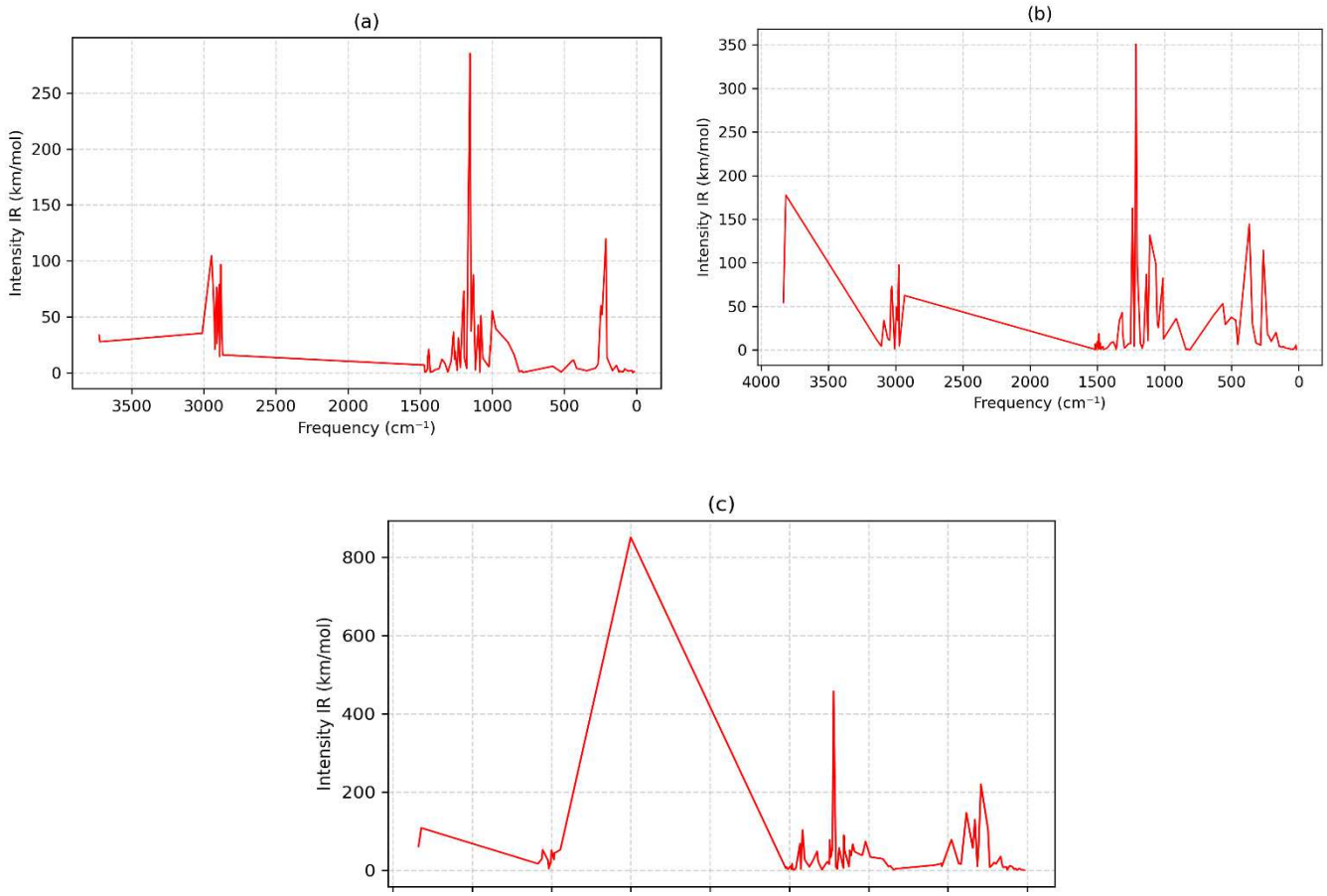


Figure 4.*IR spectra of (a) (PEO)4, (b) (PEO)4–Li, and (c) (PEO)4–Li–SiO_2. The spectra illustrate the characteristic vibrational bands of the polymer backbone and the structural modifications induced by Li^+ coordination and SiO_2 incorporation.*

The pristine PEO4 spectrum displayed characteristic absorption bands of poly (ethylene oxide). The prominent band near 1100 cm^{-1}corresponds to the asymmetric stretching of the ether linkage (C–O–C), which is a signature of the polymer backbone. Methylene (–CH_2–) stretching vibrations appear between 2950 and 2850 cm^{-1}, while bending and scissoring modes are observed below 1500 cm^{-1}. These features confirm the semicrystalline nature of PEO, consistent with previous reports on PEO-based electrolytes.

Notable spectral changes occurred upon the addition of Li^+. The broad region around 3500–3000 cm^{-1} diminishes, indicating reduced free hydroxyl groups due to Li^+ coordination with ether oxygens. The C–O–C stretching band near 1100 cm^{-1} became broader and slightly shifted, reflecting perturbations in the polymer matrix caused by ion–dipole interactions. New absorptions in the The peaks in the 800–600 cm^{-1} range are attributed to the Li–O vibrational modes, confirming salt incorporation. These changes collectively suggest the formation of PEO–Li complexes, which are critical for ionic transport in the electrolyte.

The incorporation of SiO_2 results in additional structural modifications. A broad and intense band between 2500 and 2000 cm^{-1} is observed, which is likely associated with hydrogen

bonding involving surface silanol (Si–OH) groups. The C–O–C band further broadened, indicating an enhanced coordination environment owing to simultaneous interactions with Li^+ and SiO_2. Additional peaks below 1000 cm^{-1} correspond to Si–O–Si stretching and bending vibrations, confirming the presence of nanofillers. These spectral features suggest that SiO_2 acts as a structural stabilizer, reducing crystallinity and promoting a more amorphous phase that is favorable for ion conduction.

The observed vibrational changes highlight the synergistic effect of Li^+ and SiO_2 on the polymer-matrix. Li^+ coordination disrupts the polymer segmental order, whereas SiO_2 introduces interfacial interactions that enhance the mechanical integrity and suppress crystallization. Similar to the MgO doping effects reported in the literature, these modifications induced subtle structural perturbations that improved the ionic conductivity and thermal stability. Such findings align with recent studies emphasizing that nanofillers not only increase amorphicity but also create additional Li^+ transport pathways, making PEO4–Li–SiO_2 a promising candidate for solid-state electrolyte applications[75,76].

3.4.3 NMR Spectroscopy

NMR spectroscopy is widely used to probe the structure and dynamics of polymer electrolytes. Techniques such as ^1H, ^{13}C, and ^7Li NMR reveal polymer segmental motion and ion coordination, which govern the ionic conductivity. Studies have shown that Li^+ interacts strongly with ether oxygens in PEO, and the addition of inorganic fillers such as SiO_2 disrupts the crystallinity, enhancing the amorphous regions and improving ion transport.

Figure 5 (a) shows the simulated NMR spectrum of pure polyethylene oxide (PEO)4. The dominant peaks correspond to the hydrogen and carbon environments within the polymer backbone, reflecting the chemical shielding typical of ether groups. The narrow distribution of shifts indicates a relatively uniform local environment in the absence of additives in the sample. Figure 5(b) shows the NMR spectrum of (PEO)4 with lithium salt (PEO)4–Li^+). The introduction of Li^+ ions modifies the electronic environment around the oxygen atoms, leading to noticeable changes in the chemical shifts of both the oxygen and hydrogen nuclei. This shift broadening suggests coordination between Li^+ and ether oxygens, which is critical for the ionic conductivity of solid polymer electrolytes.

Figure 5(c) shows the NMR spectrum of (PEO)4–Li combined with SiO_2 nanoparticles. The addition of SiO_2 introduced further heterogeneity into the local environment, as evidenced by the appearance of new peaks and increased anisotropy of the oxygen sites. These changes indicate strong interactions between the polymer matrix, lithium ions, and silica surfaces, which can enhance the mechanical stability and potentially improve the ion transport pathways.

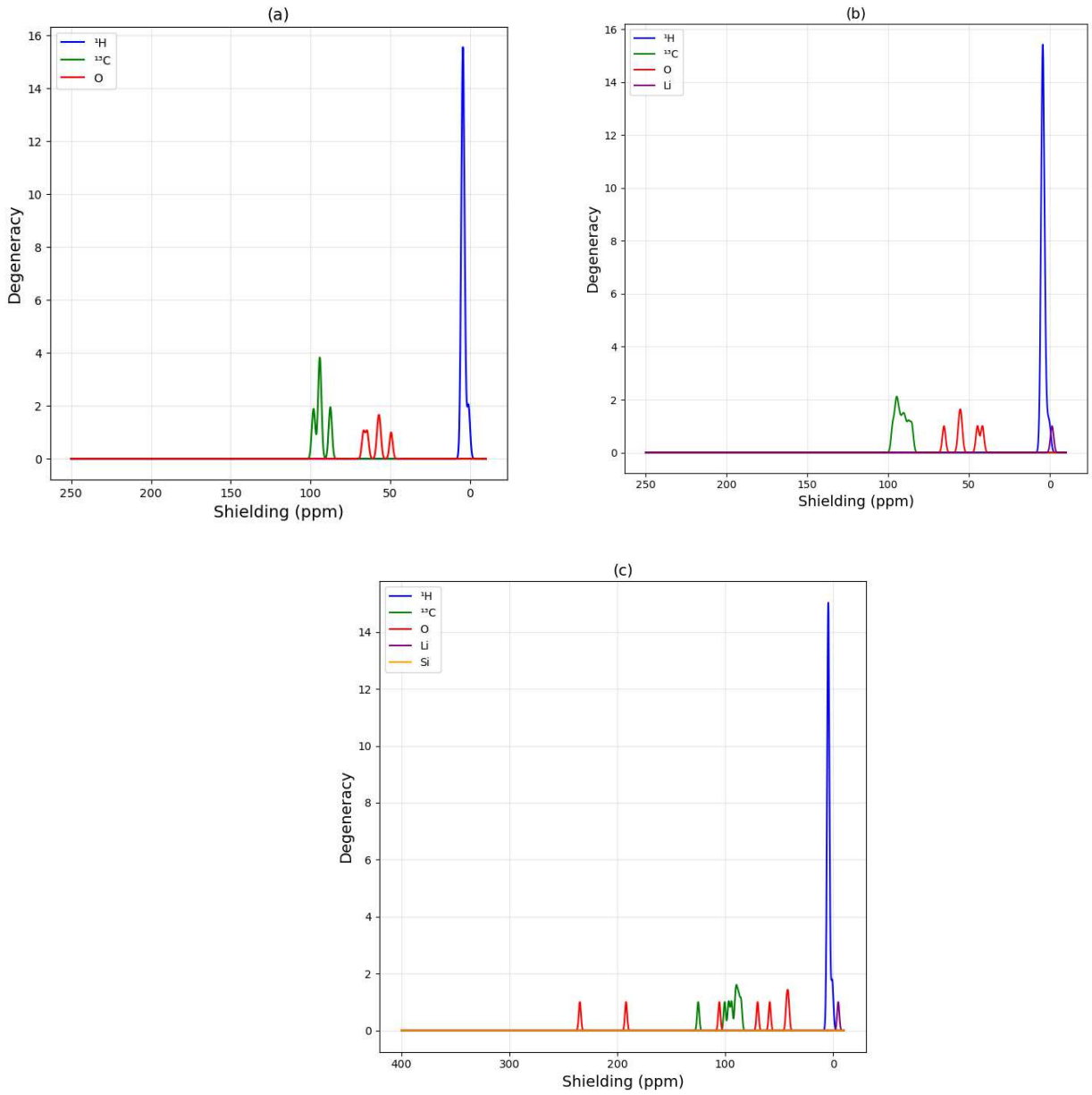


Figure 5.Simulated NMR Spectra of PEO-Based Electrolytes: Effect of Li^+ and SiO_2 Additives. (a) (PEO)4, (b) (PEO)4–Li^+, and (c) (PEO)4–Li^+–SiO_2.

3.5 Charge Distribution and Reactivity Mapping

3.5.1 Molecular Electrostatic Potential (MEP) Surface

The Molecular Electrostatic Potential (MEP) surfaces presented in Figure 5 illustrate the charge distribution and potential interaction sites for three systems: (a) pristine (PEO)4, (b) PEO-Li^+ complex, and (c) (PEO)4-Li^+-SiO_2 composite. MEP mapping is a powerful tool for visualizing regions of electron density and electrostatic potential, which directly influences coordination and transport properties in polymer electrolytes.

The MEP surface of (PEO)4 shows alternating regions of electron-rich (red) and electron-deficient (blue) zones along the polymer backbone. The red regions correspond to oxygen atoms

in the ether groups, which exhibit high electron density and act as potential coordination sites for cations. This distribution confirms the role of ether oxygens as primary sites for Li^+ solvation in PEO-based electrolytes, consistent with previous studies on (PEO)4–Li^+ salt complexes[77].

Upon Li^+ incorporation, the MEP surface undergoes significant changes. The blue region becomes more pronounced around the Li^+ , indicating strong localized positive potential. This interaction reduces the electron density around adjacent oxygen atoms, as seen by the diminished red intensity compared to pristine (PEO)4. Such redistribution reflects strong coordination between Li^+ and ether oxygens, which is essential for ionic conduction. These observations align with DFT and MD simulation studies showing Li^+ coordination with ether oxygens and its impact on ionic conductivity[78].

The introduction of SiO_2 nanoparticles further modifies the electrostatic landscape. The MEP surface shows extended red regions around SiO_2, indicating additional electron-rich sites that can interact with Li^+. This suggests that SiO_2 acts as a Lewis base, enhancing Li^+ dissociation and reducing ion pairing. Recent works confirm that SiO_2 fillers reduce PEO crystallinity, improve mechanical strength, and increase ionic conductivity by creating multiple coordination environments. Functionalized SiO_2 nanoparticles have also been shown to significantly improve Li^+ transference numbers and electrochemical stability[79,80].

The progressive changes in MEP from (a) to (c) highlight the synergistic effect of Li^+ and SiO_2 on the electrostatic properties of (PEO)4. While Li^+ incorporation strengthens local interactions, SiO_2 introduces additional coordination sites and promotes structural disorder, both of which are favorable for improving ionic conductivity and mechanical stability in solid polymer electrolytes. These findings are consistent with recent reviews emphasizing the use of composite strategies to enhance PEO-based electrolytes.

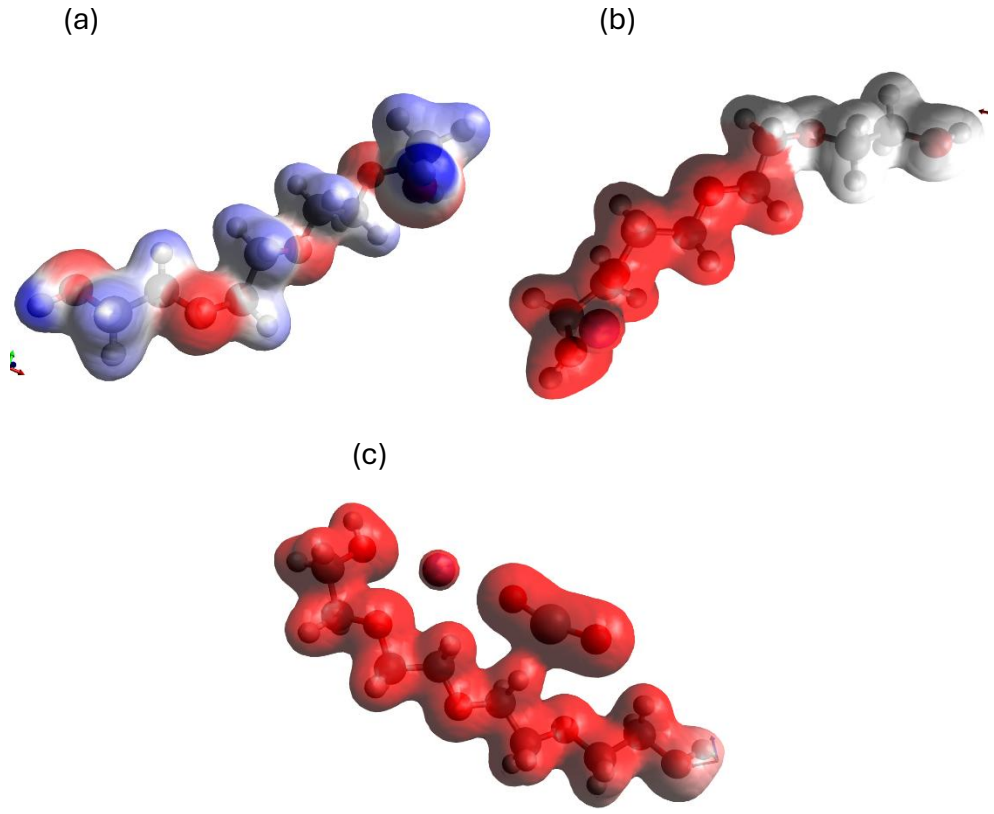


Figure 6.Molecular Electrostatic Potential (MEP) Surfaces of PEO-Based Systems: (a) (PEO)4, (b) (PEO)4–Li^+ Complex, and (c) (PEO)4–Li^+–SiO_2 Composite

MEP analysis provides insights into the observed conductivity behaviors of these systems. For pristine (PEO)4, the strong electron-rich regions around the ether oxygens enable Li^+ coordination; however, the high crystallinity of (PEO)4 limits the segmental motion, resulting in moderate ionic conductivity. Upon Li^+ incorporation, the localized positive potential around the cation strengthens coordination but can restrict polymer flexibility, leading to a trade-off between ion solvation and mobility. The addition of SiO_2 nanoparticles introduces new electron-rich sites and disrupts the crystallinity of (PEO) 4, as reflected by the extended red regions on the MEP surface. This structural disorder enhances the polymer segmental dynamics and facilitates faster Li^+ transport, explaining the significant increase in ionic conductivity reported for (PEO)4–Li^+–SiO_2 composites compared to (PEO)4–Li^+ systems. These findings confirm that electrostatic heterogeneity and reduced crystallinity are key factors in optimizing solid polymer electrolytes for high-performance lithium-ion batteries.

3.5.2 Mulliken Population Analysis

The Mulliken charge analysis of (PEO)4, as illustrated in Figure 6, reveals the electronic characteristics of the polymer backbone and identifies the potential coordination sites for the cations. The oxygen atoms exhibited the most significant negative charges, ranging from –0.316

e to –0.435 e, confirming their role as strong electron donors. Among these, the terminal oxygen atoms (–0.433 e and –0.435 e) show the highest negative values, suggesting that chain ends may provide stronger binding sites for Li^+ ions than internal oxygens (–0.316 e and –0.320 e).

The carbon atoms displayed small positive charges, typically between +0.067 e and +0.081 e, indicating a relatively stable backbone with limited polarization. This stability is essential for maintaining mechanical integrity while allowing segmental motion during ion transport. Hydrogen atoms carry very low positive charges (approximately +0.022 e to +0.053 e), implying a minimal contribution to electrostatic interactions.

The observed charge distribution highlights that oxygen atoms dominate the coordination chemistry of PEO-based electrolytes. Strong negative charges on these sites facilitate Li^+ solvation; however, excessive localization can lead to strong binding, thereby reducing ion mobility. Therefore, strategies such as introducing inorganic fillers (e.g., SiO_2) or plasticizers are often employed to modulate the charge distribution and enhance the ionic conductivity. Mulliken analysis thus provides a quantitative basis for understanding polymer–ion interactions and optimizing solid-state electrolyte design.

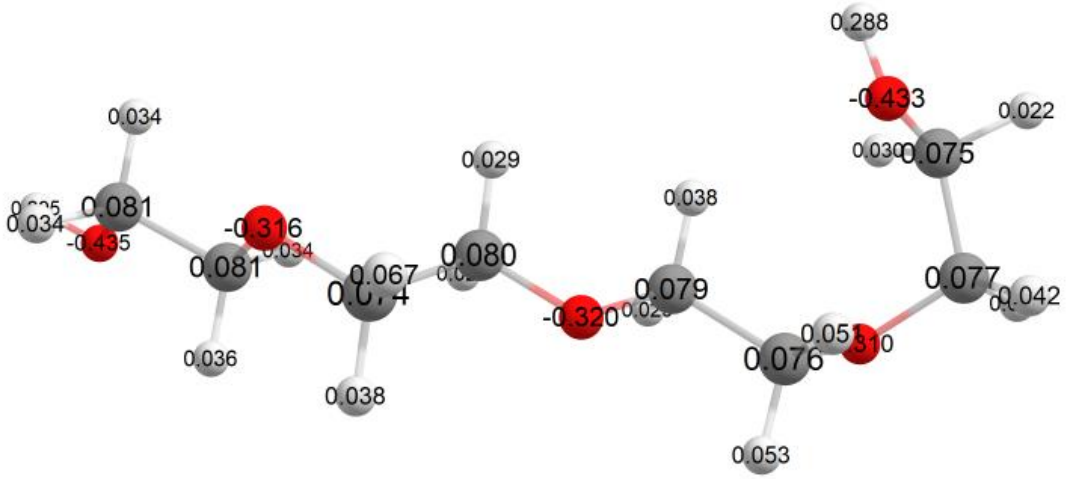


Figure 7. Mulliken Charge Distribution of PEO_4 Polymer Chain

This combined interpretation suggests that Li^+ ions preferentially coordinate with oxygen atoms owing to their high negative charge and strong electrostatic potential. However, excessive charge localization may lead to strong binding and reduced ion mobility. The introduction of fillers such as SiO_2, as observed in the MEP analysis, can redistribute the potential and create multiple coordination environments, thereby improving the ionic conductivity. Thus, the integration of Mulliken and MEP data offers a robust framework for designing high-performance PEO-based solid electrolytes.

4. Conclusion

This first-principles investigation using Density Functional Theory (DFT) provides valuable insights into the structural and electronic modifications induced by incorporating SiO_2 nanoparticles and $LiPF_6$ salt into the (PEO)4 polymer matrix. The results demonstrate that SiO_2

disrupts the crystalline structure of (PEO)4, promoting a more amorphous phase that enhances lithium ion mobility. Structural optimization, thermodynamic analysis, and electrostatic mapping revealed the improved stability, ionic conductivity, and electrochemical compatibility of the (PEO)4–Li–SiO_2 composite.

The narrowing of the band gap, broadening of the electrochemical stability window, and spectroscopic changes observed confirm the synergistic effects of Li^+ and SiO_2 on the polymer matrix. These findings support the rational design of high-performance solid polymer electrolytes with enhanced mechanical integrity, ionic transport properties, and safety features. Overall, the (PEO)4–SiO_2–$LiPF_6$ composite emerges as a promising candidate for next-generation solid-state lithium-ion batteries, addressing key limitations of conventional polymer electrolytes.

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