



Anisotropically tuning interfacial thermal conductance between graphite and poly(ethylene oxide) by lithium-ion intercalation: A molecular dynamics study

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ABSTRACT

Understanding interfacial thermal transport between lithiated two-dimensional materials and polymers can provide useful guidelines to design thermally tunable and conductive composites for efficient thermal management of energy systems. In this work, molecular dynamics simulations are conducted to investigate the effect of lithium (Li)-ion intercalation on the interfacial thermal transport between graphite and poly(ethylene oxide) (PEO). Results show that Li-ion intercalation anisotropically affects the enhancement of the interfacial thermal conductance (ITC) between graphite and PEO. The cross-plane ITC monotonically increases with increasing degree of lithiation, while a significant enhancement of the in-plane ITC is only observed when the graphite host is fully lithiated. The anisotropic effect can be attributed to the intercalation-induced strong Lennard-Jones interactions between the two contacting materials. This work may open up new opportunities to design thermally conductive polymeric composites and thermally controllable interfaces through ion intercalation of 2D materials.

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1. Introduction

Polymeric composites with superior thermal properties have been widely used for thermal management in electronics and energy storage/conversion systems because of the growing risks of thermal-related issues (e.g., thermal runaway, overheating) in these devices [1,2]. Because of the high thermal conductivity of graphite, the thermal conductivity of polymeric composites can be significantly improved by using graphite as a filler material [3]. Although extensive research has been conducted to design thermally conductive graphite/polymer composites, the thermal conductivity of such composites is still far below expectation [4]. These unsatisfactory results can be partially attributed to the high interfacial thermal resistance (or Kapitza resistance) between the graphite fillers and the polymer matrix [5,6]. Therefore, it is of great importance to understand the thermal transport across graphite/polymer interfaces for designing thermally conductive polymeric composites.

To date, many approaches have been reported to control the thermal transport in bulk materials and the thermal transport across interfaces, including hybridization [7], electric-field modulation [8], structure poling [9], covalent bonding [10,11], inter-

face modification [12], interlayer rotation [13], and functionalization [14–16]. Among them, many approaches can effectively increase interfacial thermal conductance (ITC). However, tuning the thermal transport between two contacting materials dynamically and reversibly seems rather challenging for the thermal management of energy systems. Recent experimental studies have shown that the thermal conductivity of 2D materials (e.g., MoS₂, black phosphorus) can be electrochemically tuned by Li-ion intercalation [17,18]. For instance, Zhu et al. measured the thermal conductivity of MoS₂ using time-domain thermoreflectance and showed that the thermal anisotropy ratio in bulk MoS₂ crystals can be electrochemically tuned from 52 to 110 by changing the concentration of intercalated Li ions [17]. The thermal transport properties of lithiated graphite have also been studied by MD simulations [19–21]. The electrochemical intercalation of Li ions into graphite is reversible and controllable, which follows the redox reaction: $x\text{Li}^+ + x\text{e}^- + \text{C}_6 \leftrightarrow \text{Li}_x\text{C}_6$, where C₆ represents the graphite host, and the lithiation degree x ranges from 0 to 1 depending on the charge/discharge state [22,23]. Such an electrochemical intercalation strategy may also be applicable to tune the interfacial thermal transport between 2D materials and polymers. Although previous MD studies have shown that the thermal transport across graphite/Al and graphite/Cu interfaces varies with the degree of lithiation [20,21], how the ion intercalation affects the ITC be-

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Table 1

The lithiation degree, number of intercalated Li ions, and atomic charge of the carbon atoms in Li_xC_6 . A constant charge of $+0.882e$ is assigned to intercalated Li ions, and the atomic charge of carbon atoms in Li_xC_6 is determined accordingly to keep the charge neutrality of simulation systems. The charge densities (σ , calculation details are given in the supplementary materials) on the Li_xC_6 basal and edge planes are calculated based on the atomic charge of each carbon atom in Li_xC_6 .

Li_xC_6	Graphite	LiC_{18}	LiC_{12}	LiC_{10}	LiC_8	LiC_6
Lithiation degree	$x = 0$	$x = 1/3$	$x = 0.5$	$x = 0.6$	$x = 0.75$	$x = 1$
Number of Li ions	0	320	480	576	720	960
Charge (e/carbon)	0	-0.049	-0.0735	-0.0882	-0.11025	-0.147
σ_{basal} (e/nm ²)	0	-0.367	-0.55	-0.66	-0.825	-1.1
σ_{edge} (e/nm ²)	0	-0.092	-0.143	-0.172	-0.216	-0.283

tween graphite and polymers remains unknown and deserves further study.

It is known that the intercalated Li ions between adjacent atomic layers can change the interlayer interactions, structures, and atomic charges of the graphite host during the lithiation process [23,24]. These intercalation-induced changes are expected to influence the interactions between graphite basal/edge planes and polymer matrix differently because of the layered structure of graphite, resulting in anisotropic thermal transport across the graphite/polymer interfaces. Although the significance of cross-plane ITCs in graphite-based polymeric composites has been highlighted in prior work [25,26], few studies have focused on their in-plane ITCs [11]. In some cases, the in-plane ITC across the graphite/polymer interface is critical for the overall thermal performance of the composites, particularly when edge-enriched materials (e.g., graphitic petals) [27] are involved. Therefore, understanding the effect of Li-ion intercalation on the cross-plane and in-plane interfacial thermal transport between graphite and polymer is desired.

In this work, we perform non-equilibrium molecular dynamics (NEMD) simulations to study the thermal transport across Li_xC_6 /PEO interfaces with different degrees of lithiation. We found that the cross-plane ITC between Li_xC_6 and PEO monotonically increases with increasing lithiation degrees, while the in-plane ITC between Li_xC_6 and PEO can only be significantly enhanced when the graphite host is fully lithiated. To understand the underlying mechanisms of such anisotropic ITC enhancements, we investigate the density distribution of PEO, the radial distribution function (RDF) between the two contacting materials, and the vibrational density of state (VDOS) of Li_xC_6 and PEO to evaluate the atomic interactions and vibrational coupling between Li_xC_6 and PEO at the interface. In addition, we decompose ITC into the contributions from graphite-PEO and Li-PEO interactions, as well as Coulombic and Lennard-Jones (LJ) interactions to evaluate the effect of intercalated Li ions on the thermal transport across Li_xC_6 /PEO interfaces. The results may provide new insights to the design of thermally conductive polymeric composites and tunable interfaces for more efficient thermal management. The mechanisms revealed in this work may also be applicable to other 2D materials and may provide a better understanding of the thermal transport in polymer-based solid-state lithium-ion batteries.

2. Simulation methods

The simulation system consists of 30 $\text{P}(\text{EO})_{50}$ chains and Li_xC_6 with an in-plane size of $\sim 43 \times 45 \text{ \AA}^2$, which is sufficiently large to include most of the important phonon modes contributing to the interfacial thermal transport and thus can exclude the size effect [11]. The Li_xC_6 ($0 \leq x \leq 1$) contains 8 monolayer graphene sheets (720 carbon atoms in each layer) and a corresponding amount of intercalated Li ions (Table 1). The lithiation degree x is varied from 0 (pristine graphite) to 1 (fully lithiated graphite, LiC_6) to represent

Table 2

12-6 Lennard-Jones parameters for Li_xC_6 .

Interactions	ϵ (kcal/mol)	σ (Å)
C-C	0.107496	3.35
Li-Li	0.025156	2.1835
C-Li	0.052003	2.76675

different lithiation states of the graphite host (Table 1). In the initial construction of Li_xC_6 , the interlayer spacing is kept at 7 Å, and the Li ions are uniformly placed on the middle plane between two neighboring graphene sheets (Fig. S1). As shown in Fig. 1, the PEO molecules are placed in contact with the Li_xC_6 basal plane (defined as the ‘cross-plane’ configuration, Fig. 1a and b) or edge (defined as the ‘in-plane’ configuration, Fig. 1c and d) to calculate the cross-plane and in-plane ITC values between Li_xC_6 and PEO, respectively. The force-field parameters of Li_xC_6 including atomic charges (Table 1) and 12-6 LJ constants (Table 2) are adopted from prior work [19]. In addition, the interactions between the carbon atoms in Li_xC_6 are described by the Tersoff potential. The all-atom optimized potentials for liquid simulation (OPLS-AA) force field, which has been validated in our prior work [14], is employed to model the PEO matrix. The Lorentz-Berthelot mixing rules ($\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$; $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, where ϵ and σ are the energy and distance constants, respectively) are used to determine the 12-6 LJ parameters for all the intermolecular non-bonding interactions. The long-range Coulombic interaction is evaluated by the particle-particle-mesh (PPPM) algorithm with an accuracy of 1×10^{-4} [28]. Periodic boundary conditions are used in all directions during the relaxation process. A cutoff distance of 10 Å is used for all the non-bonding interactions, including LJ and electrostatic forces. The timestep is set to be 0.25 fs for all simulations because of the light hydrogen atoms [11]. All the molecular structures of Li_xC_6 /PEO are visualized by the Open Visualization Tool (OVITO) software [29].

All simulations are conducted using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [30]. The interfacial thermal transport between Li_xC_6 and PEO is evaluated using the NEMD simulation method at 300 K and 1 atm. The simulation system is first relaxed in the isothermal-isobaric (NPT) ensemble at 10 K for 1 ns to stabilize the structure of Li_xC_6 . The resultant system is annealed to 600 K with a heating rate of 50 K/ns in the NPT ensemble and kept at 600 K for 18 ns to further equilibrate the molecular structures. The system is then quenched to 300 K and equilibrated in the NPT ensemble for 3 ns to converge the density. A final 4 ns of relaxation in the canonical ensemble (NVT) at 300 K is performed before the 4 ns of microcanonical ensemble (NVE) NEMD production simulation. For the Li_xC_6 /PEO interface with the in-plane configuration, a few intercalated Li ions are observed to diffuse into the PEO matrix near the Li_xC_6 /PEO interface (Fig. S2) during the NPT (600 K) annealing process when the graphite host is not fully lithiated.

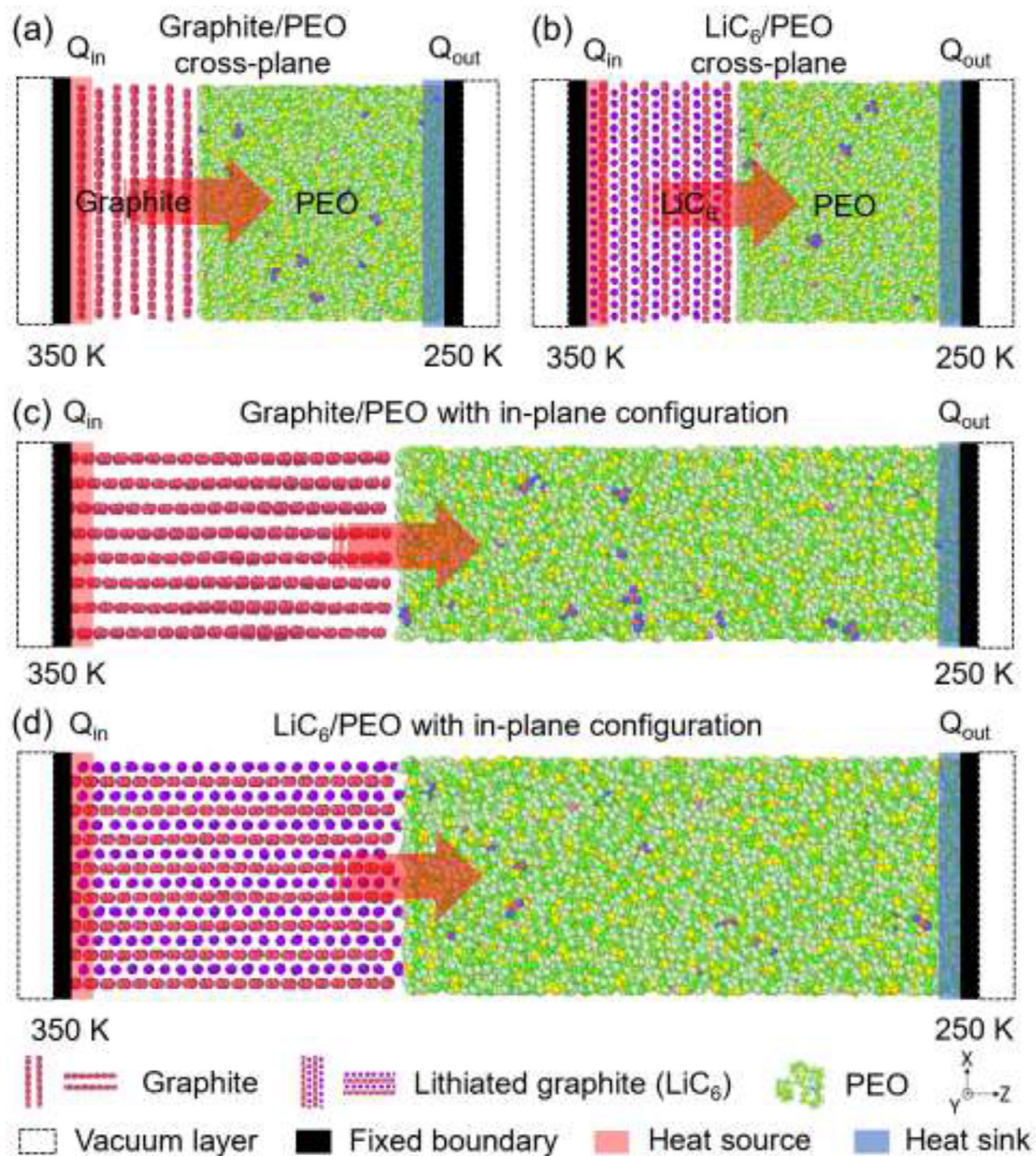


Fig. 1. Simulation setup of the representative $\text{Li}_x\text{C}_6/\text{PEO}$ systems with different interface configurations to calculate the cross-plane and in-plane ITCs: (a) Graphite/PEO system with the cross-plane configuration, (b) LiC_6/PEO system with the cross-plane configuration, (c) Graphite/PEO system with the in-plane configuration, and (d) LiC_6/PEO system with the in-plane configuration. The red arrow shows the heat flow from Li_xC_6 to PEO. ITCs are calculated via NEMD simulations: heat source (red) and heat sink (blue) are maintained at 350 K and 250 K using Langevin thermostats, respectively. The two boundaries (black) in the z -direction are fixed by 3 Å. Two 5 Å-thick vacuum layers (areas with black dashed lines) next to these two fixed layers are added to prevent heat leakage between the heat source and heat sink.

These diffusing Li ions are excluded during the NEMD production simulations to avoid their influence on the analysis of thermal transport mechanisms across $\text{Li}_x\text{C}_6/\text{PEO}$ interfaces.

In the NEMD simulations, the heat source and heat sink are maintained at 350 K and 250 K using Langevin thermostat, respectively. The two boundaries in the z -direction are stabilized by two 3 Å-thick fixed layers. Two 5 Å-thick vacuum layers next to these two fixed layers are added to prevent possible heat leakage between the heat source and heat sink [31]. A slab size of 2 Å, which is less than the width of the interfaces, is used to calculate the temperature profiles in all simulations. ITCs with standard deviations are calculated using the last 2 ns of the production period divided into five time blocks. A relatively large temperature differ-

ence of 100 K between the two thermostats is adopted to improve the signal to noise ratio for calculating the ITC values because the values calculated with a smaller temperature difference of 50 K are within the error bar of the case with a relatively large temperature difference. Fig. 1 shows the representative equilibrated structures of $\text{Li}_x\text{C}_6/\text{PEO}$ (e.g., graphite/PEO, LiC_6/PEO) systems with the cross-plane and in-plane configurations. The corresponding steady-state temperature profiles and energy tallies of these simulation systems are shown in Fig. S3 and S4. After the NEMD simulations reach steady state, ITCs can be calculated from $G = J/\Delta T$, where G is the ITC, J is the heat flux, and ΔT is the temperature drop across a single $\text{Li}_x\text{C}_6/\text{PEO}$ interface calculated by fitting the temperature profiles at the hot side and cold side (Fig. S3 and S4).

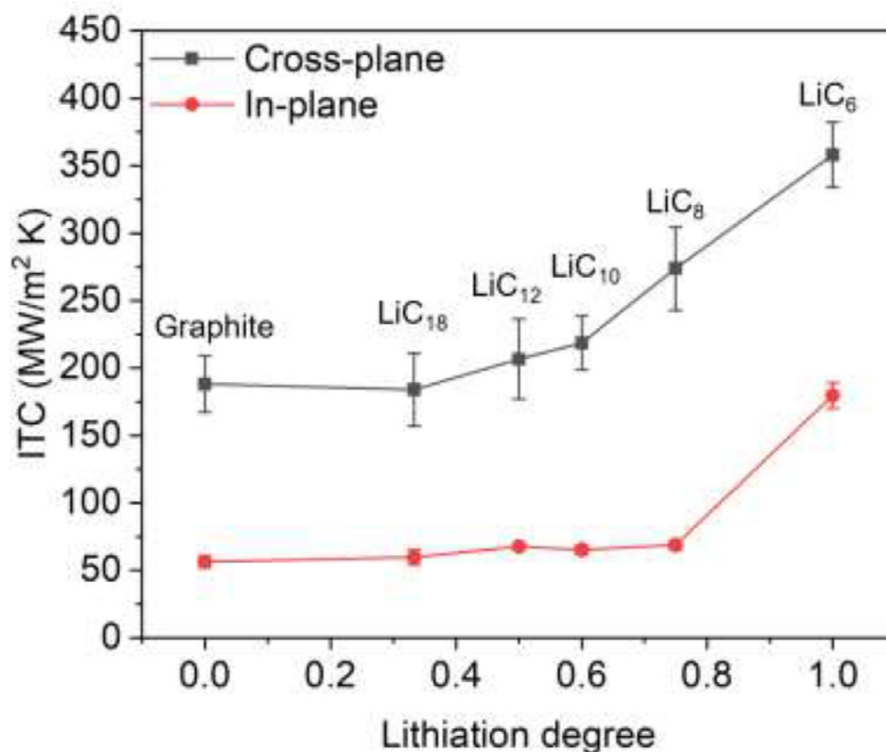


Fig. 2. Cross-plane and in-plane ITCs across the Li_xC_6 /PEO interfaces as a function of lithiation degree x ranging from 0 to 1.

3. Results and discussion

3.1. Lithiation-controlled ITC between Li_xC_6 and PEO

Fig. 2 shows the cross-plane and in-plane ITCs across the Li_xC_6 /PEO interfaces when the lithiation degree varies from 0 (pristine graphite) to 1 (LiC_6 , fully lithiated graphite). The calculated cross-plane and in-plane ITC values across a single graphite/PEO interface are $188 \pm 21 \text{ MW/m}^2 \text{ K}$ and $56 \pm 4 \text{ MW/m}^2 \text{ K}$, respectively. These values are comparable to those of the graphene/polymer interfaces, in which the cross-plane and in-plane ITCs across two graphene/polymer interfaces fall into the range of $61 - 71 \text{ MW/m}^2 \text{ K}$ (equivalent to $122 - 142 \text{ MW/m}^2 \text{ K}$ for a single interface) and $30 - 32 \text{ MW/m}^2 \text{ K}$ (equivalent to $60 - 64 \text{ MW/m}^2 \text{ K}$ for a single interface), respectively [11]. Moreover, the cross-plane ITC across the Li_xC_6 /PEO interface increases monotonically with an increasing degree of lithiation (Fig. 2). For instance, the cross-plane ITC across the LiC_6 /PEO interface is $358 \pm 24 \text{ MW/m}^2 \text{ K}$, corresponding to an enhancement of 190% compared with that of the graphite/PEO interface. Comparatively, the in-plane ITC across the Li_xC_6 /PEO interface (Fig. 2) only increases slightly from $56 \pm 4 \text{ MW/m}^2 \text{ K}$ to $69 \pm 4 \text{ MW/m}^2 \text{ K}$ when the lithiation degree x rises from 0 (graphite) to 0.75 (LiC_8). A significantly higher in-plane ITC ($180 \pm 9 \text{ MW/m}^2 \text{ K}$) is observed when the graphite host is fully lithiated ($x = 1$, LiC_6), much higher than those ($56 - 69 \text{ MW/m}^2 \text{ K}$) across other Li_xC_6 /PEO interfaces with the in-plane configuration when $x \leq 0.75$. Note that the diffusing Li ions have negligible contributions to the interfacial thermal transport between Li_xC_6 and PEO with the in-plane configuration. For instance, the ITCs of the LiC_8 /PEO interface with an in-plane configuration with and without the diffusing Li ions are $71 \pm 2 \text{ MW/m}^2 \text{ K}$ and $69 \pm 4 \text{ MW/m}^2 \text{ K}$, respectively. Therefore, these diffusing Li ions (Fig. S2) can be reasonably excluded during the NEMD production simulations.

3.2. The density distribution of PEO

When Li ions are intercalated into the graphite host, ionic carbon-lithium bonds will be formed, leading to negatively charged carbon atoms [24]. The electron charges on each carbon atom as a function of lithiation degree are summarized in Table 1. These negatively charged carbon atoms can enhance the Coulombic interactions between Li_xC_6 and PEO, thus affecting the density distribution of the polymer. Fig. 3 shows the peak densities of PEO near the interfaces in the Li_xC_6 /PEO systems. The peak densities of PEO near the Li_xC_6 basal plane (cross-plane configuration) or edge plane (in-plane configuration) are generally following a growing trend as the lithiation degree increases. Moreover, the densities of PEO near the Li_xC_6 basal plane are significantly higher than those near the Li_xC_6 edge plane with the same lithiation degree, which may be attributed to the higher charge density on the Li_xC_6 basal plane compared with that of the Li_xC_6 edge plane (Table 1). For instance, the peak densities of PEO near the graphite basal and edge planes are 2.1 and 1.48 g/cm^3 , respectively. When the graphite host is fully lithiated (LiC_6 , $x = 1$), the peak densities of PEO near the LiC_6 basal and edge planes increase to 2.68 and 1.75 g/cm^3 , respectively. Such an observation correlates well with the ITC values shown in Fig. 2, suggesting that the PEO densities at the Li_xC_6 /PEO interfaces are the key to the enhancement of interfacial thermal transport. Because of the stronger Coulombic interactions between Li_xC_6 and PEO as the lithiation degree increases, more PEO molecules are attracted by Li_xC_6 closer to its basal plane or edge plane, leading to enhanced cross-plane or in-plane thermal transport across the Li_xC_6 /PEO interfaces.

3.3. Radial distribution function (RDF) analysis

Fig. 4 shows the interatomic distances between Li_xC_6 and PEO chains near the interfaces with the cross-plane and in-plane con-

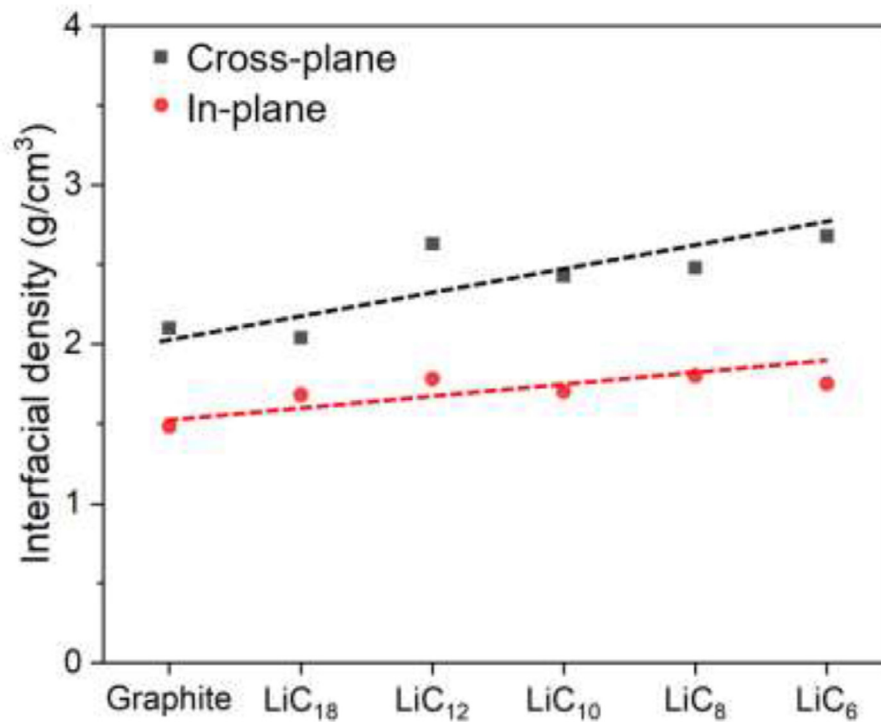


Fig. 3. The peak density of the PEO molecules near $\text{Li}_x\text{C}_6/\text{PEO}$ interfaces with different degrees of lithiation.

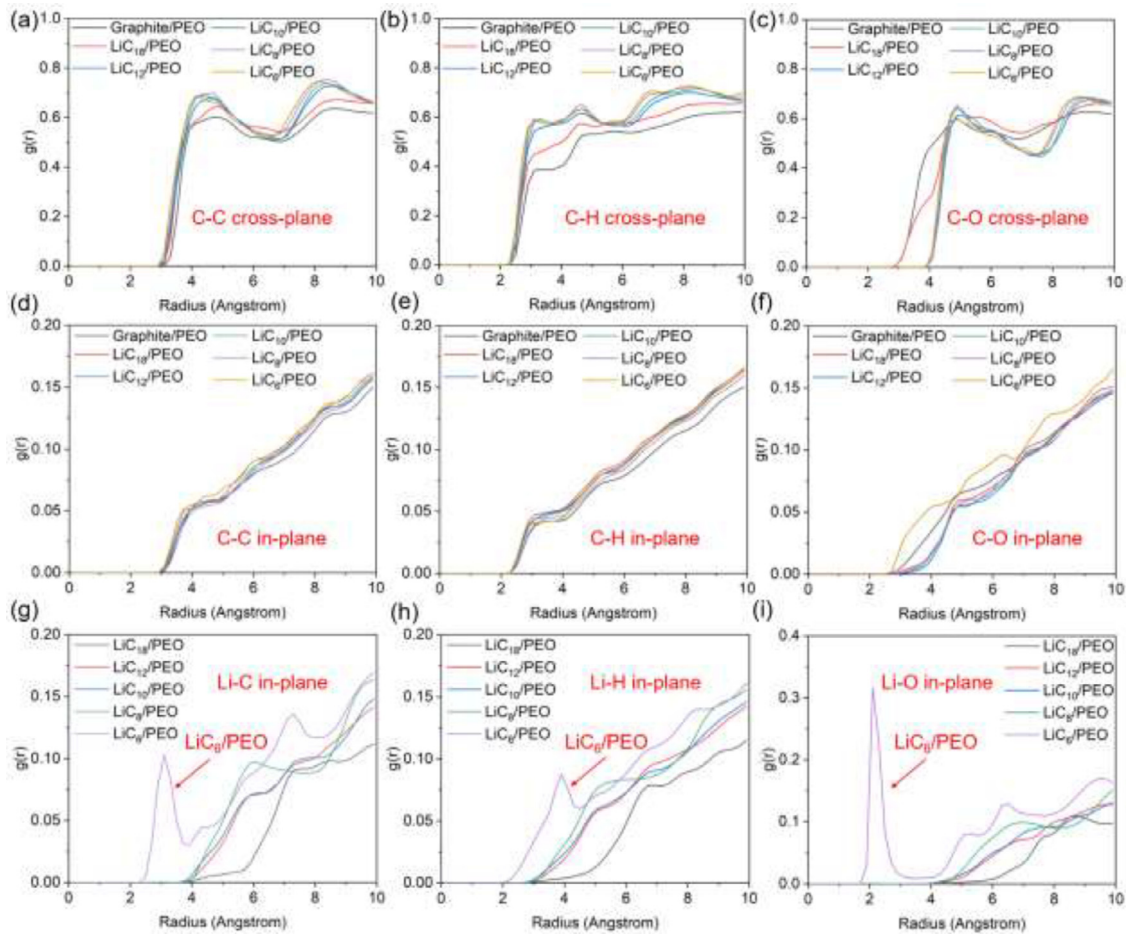


Fig. 4. RDFs of the carbon atoms in Li_xC_6 with respect to the (a) carbon atoms, (b) hydrogen atoms, and (c) oxygen atoms in PEO molecules in $\text{Li}_x\text{C}_6/\text{PEO}$ systems with the cross-plane configuration. RDFs of the carbon atoms in Li_xC_6 with respect to the (d) carbon atoms, (e) hydrogen atoms, and (f) oxygen atoms in PEO molecules in $\text{Li}_x\text{C}_6/\text{PEO}$ systems with the in-plane configuration. RDFs of the intercalated Li ions in Li_xC_6 with respect to the (g) carbon atoms, (h) hydrogen atoms, and (i) oxygen atoms in PEO molecules in $\text{Li}_x\text{C}_6/\text{PEO}$ systems with the in-plane configuration.

figurations. The interatomic distance is characterized by RDF calculated as $g(r) = n(r)/(4\pi r^2 \rho \Delta r)$, where $n(r)$ is the number of atoms in a shell of thickness Δr at a distance r from the reference atom in Li_xC_6 , and ρ is the average atom number density of PEO molecules. To calculate the interatomic distances between Li_xC_6 and PEO, the oxygen (O), carbon (C), or hydrogen (H) atoms are used to represent PEO, and the Li or C atoms are selected to represent Li_xC_6 . As shown in Fig. 4, the atomic interactions between Li_xC_6 and PEO differ substantially in the two interfacial configurations. In Li_xC_6 /PEO systems with the cross-plane configuration, the interatomic distances (indicated by the first peak position of the RDF) between the carbon atoms in Li_xC_6 and the carbon atoms (C-C, Fig. 4a), hydrogen atoms (C-H, Fig. 4b), and oxygen atoms (C-O, Fig. 4c) in PEO molecules are calculated to be 4 Å, 3 Å, and 5 Å, respectively. The C-C and C-H RDFs shift to the left with higher magnitudes (i.e., higher $g(r)$ values) as the lithiation degree increases, indicating that more hydrogen and carbon atoms in the PEO molecules are attracted by the Li_xC_6 basal plane closer to the interfaces. Such an RDF shift-up phenomenon correlates well with the higher negative charge values of graphite carbon atoms and higher PEO densities at the interfaces as the lithiation degree increases. The more negatively charged carbon atoms lead to a stronger electrostatic attractive force of Li_xC_6 to PEO molecules and attract these polymer molecules closer to the Li_xC_6 basal plane, thus increasing the polymer density near the interfaces (Fig. 3a) and providing more pathways for phonon transport. Considering the van der Waals force (F_{IJ}) modeled by 12-6 LJ potential: $F_{IJ} = -24\varepsilon[2(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$, where ε is the energy constant, σ is the distance constant, and r is the interatomic distance, a shorter interatomic distance can result in a stronger van der Waals force, thus leading to significantly enhanced cross-plane thermal transport across the Li_xC_6 /PEO interfaces particularly at high lithiation degrees (e.g., LiC_8 and LiC_6), which coincides with the ITC results shown in Fig. 2.

In Li_xC_6 /PEO systems with the in-plane configuration, the first peak positions of the C-C (Fig. 4d), C-H (Fig. 4e), and C-O (Fig. 4f) RDFs between graphite and PEO are located at 4 Å, 3 Å, and 5 Å, respectively, almost the same as those of the RDFs in Li_xC_6 /PEO systems with the cross-plane configuration. However, the magnitudes of the RDFs in Li_xC_6 /PEO systems with the in-plane configuration are much lower than those in Li_xC_6 /PEO systems with the cross-plane configuration, agreeing well with the density profiles of PEO near the interfaces (Fig. 3a). Furthermore, the RDFs of the C-C (Fig. 4d) and C-H (Fig. 4e) exhibit no significant variations with the lithiation degree in Li_xC_6 /PEO systems with the in-plane configuration. A noticeable variation is observed for the C-O RDF (Fig. 4f) in the in-plane model when the graphite host is fully lithiated. The results indicate that the oxygen atoms in PEO molecules are attracted closer to LiC_6 edges. To understand such a variation of the C-O RDF in Li_xC_6 /PEO systems with the in-plane configuration, RDFs of the intercalated Li ions in Li_xC_6 with respect to the carbon atoms (Li-C, Fig. 4g), hydrogen atoms (Li-H, Fig. 4h), and oxygen atoms (Li-O, Fig. 4i) in PEO molecules are calculated. As shown in Fig. 4i, the first peak position of the Li-O RDF in the LiC_6 /PEO system with the in-plane configuration is significantly decreased to 2.1 Å, which is consistent with the reported Li-O distance between lithium salts and polymer electrolytes (e.g., PEO) in lithium-ion batteries [32,33]. Shorter atomic distances between Li-O atoms lead to stronger interactions between them. It can thus be concluded that the shorter interatomic C-O distance in the LiC_6 /PEO system with the in-plane configuration (Fig. 4f) is induced by the strong Li-O interactions at the interface. Notably, such strong Li-O interactions are only observed in the LiC_6 /PEO system with the in-plane configuration. Therefore, the PEO molecules are attracted closer to the LiC_6 edge plane because of the strong Li-O interactions, which can significantly

enhance the in-plane thermal transport between LiC_6 and PEO.

Furthermore, the VDOS of Li_xC_6 and PEO are analyzed (see details in SI) to quantify the cross-plane and in-plane vibrational coupling effects between the two contacting materials, which can play an important role in interfacial thermal transport [34,35]. The VDOS of Li_xC_6 (Fig. S5) in the cross-plane and in-plane systems are decomposed to the cross-plane and in-plane vibrational modes, respectively. Although the shift of VDOS is observed in Li_xC_6 induced by Li-ion intercalation (Fig. S6), the VDOS overlap areas (Table S1) between the cross-plane modes of Li_xC_6 (Fig. S5a) and PEO (Fig. S7a) in the cross-plane systems remain similar in the frequency range from 0 to 60 THz when lithiation degree varies. The same phenomenon is observed for the VDOS overlap areas between the in-plane modes of Li_xC_6 (Fig. S5b) and PEO (Fig. S7b) in the in-plane systems. These results imply that the vibrational coupling may exert a minor influence on the thermal transport across Li_xC_6 /PEO interfaces. Thus, the enhanced ITC may be mainly attributed to the stronger interactions between Li_xC_6 and PEO induced by Li-ion intercalation, which is different from the phenomena observed in graphite/Al and graphite/Cu systems [20,21].

3.4. Decomposition of ITC

To further understand the underlying mechanisms dictating the interfacial thermal transport between Li_xC_6 and PEO, the cross-plane and in-plane ITCs are decomposed into the contributions from graphite-PEO and Li-PEO interactions, as well as LJ and Coulombic interactions (see details in SI), following the methods described in our prior work [14]. As shown in Fig. 5a and b, the cross-plane ITC is mainly contributed by LJ interactions between the graphite host and PEO, while the contributions of Li-PEO and Coulombic interactions to the cross-plane interfacial thermal transport are negligible. Notably, the intercalated Li ions do not directly contribute to the cross-plane interfacial thermal transport across Li_xC_6 /PEO interfaces because of the long interatomic distance between the intercalated Li ions and PEO molecules, which is consistent with the result reported in prior work (e.g., Li_xC_6 /Al interface) [20]. These findings suggest that the enhanced long-range Coulombic interactions induced by Li-ion intercalation will attract more PEO molecules closer to the basal planes of Li_xC_6 , but it is the short-range LJ interactions that dominate and increase the cross-plane interfacial thermal transport across the Li_xC_6 /PEO interfaces. Such a phenomenon of enhanced thermal transport has been widely observed in other materials in the presence of strong Coulombic interactions [14,16,36].

The LJ interactions between graphite host and PEO molecules also dominate the in-plane thermal transport across the Li_xC_6 /PEO interfaces (Fig. 5c and d) when the graphite host is not fully lithiated. However, the contribution (99.5 MW/m² K) of Li-PEO interactions to the in-plane ITC significantly increases and is comparable to that (80.2 MW/m² K) of graphite-PEO interactions in LiC_6 /PEO system with the in-plane configuration. Such an observation correlates well with the Li-O RDF in the LiC_6 /PEO system with the in-plane configuration (Fig. 4g-i). Fig. 5e and f show the representative cases of Li_xC_6 /PEO interfaces with the in-plane configuration when the graphite host is not fully lithiated (e.g., LiC_8 /PEO, $x = 0.75$) and fully lithiated (LiC_6 /PEO, $x = 1$), respectively. The intercalated Li ions in LiC_8 /PEO systems with the in-plane configuration are well confined in the LJ gap of the graphite host. Thus, the Li-PEO contributions to the in-plane thermal transport across the LiC_8 /PEO interface are negligible because of the long interatomic distance. However, the densely intercalated Li ions near graphite edges are partially attracted by the PEO molecules in LiC_6 /PEO systems with the in-plane configuration, forming an intermediate Li-ion layer at the interface (Fig. 5f). These Li ions are confined by

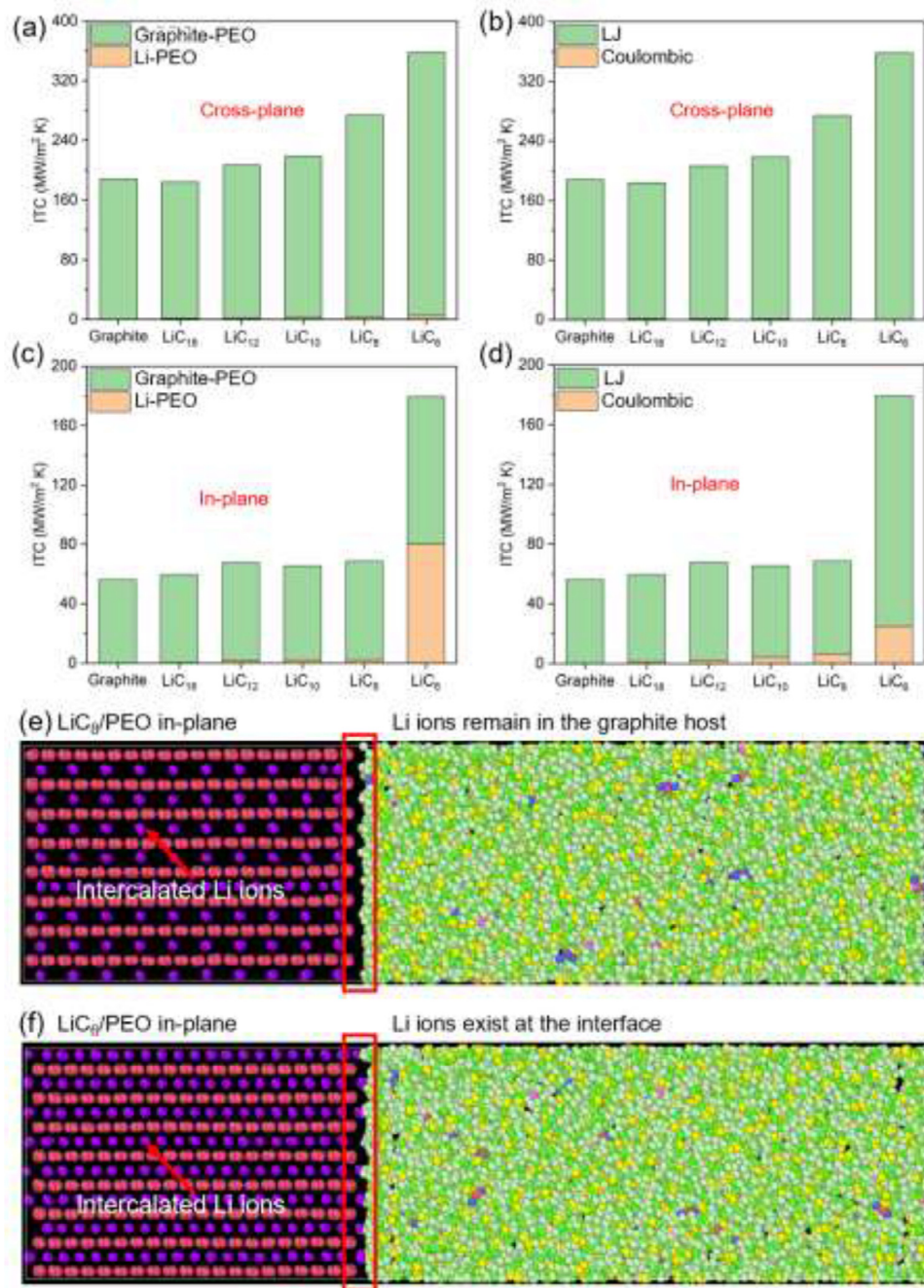


Fig. 5. Decomposition of ITC into different contributions from: (a) graphite-PEO and Li-PEO interactions in the cross-plane systems, (b) LJ and Coulombic interactions in the cross-plane systems, (c) graphite-PEO and Li-PEO interactions in the in-plane systems, and (d) LJ and Coulombic interactions in the in-plane systems. The molecular structures of (e) LiC₆/PEO interface with the in-plane configuration showing the intercalated Li ions are well confined by the graphite host and (f) LiC₆/PEO interface with the in-plane configuration showing the intermediated Li-ion layer at the interface.

the graphite host and cannot diffuse into the PEO matrix. More importantly, this intermediate Li-ion layer leads to short interatomic distances between LiC₆ and PEO in the in-plane system (Fig. 4d-i). Therefore, the contribution from Li-PEO interaction becomes significant, leading to enhanced in-plane thermal transport across the LiC₆/PEO interface.

4. Conclusions

In summary, we have calculated the cross-plane and in-plane ITCs between Li_xC₆ and PEO with different degrees of lithiation. Results show that the interfacial thermal transport between

graphite and PEO in the two directions can be effectively enhanced and controlled by lithiation. The intercalation-induced anisotropic effect on the interfacial thermal conductance between graphite and PEO originates from the layered structure of the graphite host. In the cross-plane case, the intercalated Li ions are well-confined in the graphite host and are isolated from the PEO matrix. While in the in-plane case, an intermediated Li-ion layer between Li_xC₆ and PEO can be formed when the graphite host is fully lithiated since the densely intercalated Li ions near the graphite edge are partially attracted by the PEO molecules. We further reveal that the enhanced interfacial thermal transport between Li_xC₆ and PEO is mainly contributed by the stronger LJ interactions rather

than Coulombic interactions. When Li ions are intercalated into the graphite host, the strong Coulombic interactions between Li_xC_6 and PEO can attract the polymer molecules closer to the basal plane or edge plane of the intercalated graphite host, thus allowing the LJ forces at the interfaces to achieve more efficient thermal transport. The results of this work may provide a novel approach to design controllable 2D material/polymer interfaces and thermally conductive polymeric composites.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Siyu Tian: Investigation, Methodology, Software, Writing – original draft. **Zhihao Xu:** Investigation, Validation, Software. **Shiwen Wu:** Software, Visualization. **Tengfei Luo:** Funding acquisition, Supervision, Writing – review & editing. **Guoping Xiong:** Funding acquisition, Supervision, Writing – review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.ijheatmasstransfer.2022.123134](https://doi.org/10.1016/j.ijheatmasstransfer.2022.123134).

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