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PERSPECTIVE

Thermal transport in lithium-ion battery: A micro perspective for thermal management

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In recent years, lithium ion (Li-ion) batteries have served as significant power sources in portable electronic devices and electric vehicles because of their high energy density and rate capability. There are growing concerns towards the safety of Li-ion batteries, in which thermal conductivities of anodes, cathodes, electrolytes and separator play key roles for determining the thermal energy transport in Li-ion battery. In this review, we summarize the state-of-the-art studies on the thermal conductivities of commonly used anodes, cathodes, electrolytes and separator in Li-ion batteries, including both theoretical and experimental reports. First, the thermal conductivities of anodes and cathodes are discussed, and the effects of delithiation degree and temperature of materials are also discussed. Then, we review the thermal conductivities of commonly used electrolytes, especially on solid electrolytes. Finally, the basic concept of interfacial thermal conductance and simulation methods are presented, as well as the interfacial thermal conductance between separator and cathodes. This perspective review would provide atomic perspective knowledge to understand thermal transport in Li-ion battery, which will be beneficial to the thermal management and temperature control in electrochemical energy storage devices.

Keywords lithium ion batteries, thermal management, phonon transport, interfacial thermal transport, amorphous materials

1 Introduction

Lithium-ion batteries have important applications in portable electronic devices and electric vehicles because of their advantages, such as high safety performance, high energy density and long service life [1–4]. However, the heat generated inside the battery increases rapidly with the decrease of package volume and the increase of energy density. The heat mainly originates from the exothermic electrochemical reaction and the Joule heat generated by the current in the process of charging and discharging. If the internal heat transfer performance of the battery is weak, then the heat dissipation efficiency is low, which may lead to local heating, followed by thermal stress. This will seriously affect the cyclability of the battery, and even lead to the thermal runaway of the battery [5]. In addition, the increase of the internal temperature of the battery is bound to affect the electrochemical reaction efficiency and the transport properties of carriers, thus affecting the performance stability. Therefore, an in-depth understanding of the micro-mechanism of heat transport in lithium-ion batteries plays a vital role in improving heat dissipation, safety and stability [6–8].

Lithium-ion batteries are usually composed of anodes, cathodes, electrolytes and separators. Electrolytes are used to provide lithium ion transport channels, and the role of the separator is to allow lithium ions to pass through but not electrons to pass through. Anode and cathode materials are usually made of intercalation compounds. During charging, lithium-ion is deintercalated from the cathode material and inserted into the negative material through electrolyte, and the negative material is in a lithium-rich state. During discharge, lithium-ion is removed from the negative material and then embedded into the cathode material through the electrolyte, and the cathode material is in a lithium-rich state. At the same time, electrons with the same amount of electricity as lithium ions are transmitted in the external circuit in

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order to maintain charge balance, thus forming a current. The thermal management of lithium-ion batteries strongly depends on the thermal conductivities of electrode materials, electrolytes and the interfacial thermal resistance between electrodes and electrolytes. Therefore, an in-depth understanding of the micro-mechanism of heat transport in lithium-ion batteries from the material level plays an important role in improving heat dissipation and safety.

This paper is organized as follows. First, the thermal conductivities of electrode materials, including anode materials and cathode materials, are reviewed. Next, we briefly introduce the thermal conductivities of solid electrolytes. Then, the interfacial heat transport in lithium-ion batteries is discussed. Finally, we present conclusions and provide an outlook.

2 Thermal conductivities of electrode materials

Improving the thermal conductivities of electrode materials is an important way to improve the internal thermal transport performance of lithium-ion batteries. The conventional design of electrodes in commercial lithium-ion batteries is a mixture of electrochemically active materials, carbon black conductive agents and polymer adhesives, and coated on metal foil collectors [9]. Among them, carbon black occupies a large volume fraction in the conventional cathode electrode structure, which is used to ensure excellent conductivity between active material particles and metal foil collectors. However, carbon black is a poor thermal conductor, and its thermal conductivity is only 0.1 to 1 W/mK at room temperature, which has become the main reason for the low overall heat dissipation performance of traditional cathode electrodes [9, 10]. In order to solve this problem, Maleki *et al.* [10] systematically studied the effects of graphite particle size, carbon black content, external temperature and compression pressure on the thermal conductivities of battery anode materials. The results show that the thermal conductivities of anode materials increases with the increase of compression pressure and graphite particle size, and decreases with the increase of carbon black content and temperature. Therefore, the anode material with the best thermal conductivity can be achieved by using low content carbon black, high compression pressure and large size graphite particles as far as possible.

In addition, graphene and carbon nanotubes have attracted wide attention in academia and industry because of their ultra-high intrinsic thermal conductivity [11–14]. The results indicate that the thermal conductivity of single-walled carbon nanotubes is between 1750 and 5800 W/mK, and the thermal conductivity of multi-walled carbon nanotubes can be as high as 3000 W/mK [15, 16]. And the carbon nanotubes which meet a certain chirality have metal properties and show good electrical conductivity. Based on this, Koo *et al.* [17] used multi-walled carbon nanotubes as matrix materials to encapsulate electrochemical active materials to make anode materials for lithium-ion batteries. The measurement results show that the in-plane and vertical plane thermal conductivity of carbon nanotube reinforced electrode is 141 W/mK and 3.6 W/mK, which is two orders of magnitude higher than that of traditional carbon black-based electrode. Recently, Lee *et al.* [18] assembled carbon nanotubes and lithium cobaltate particles into a composite electrode with an in-plane thermal conductivity of 205.8 W/mK, which is about three orders of magnitude higher than that of conventional laminated electrodes. Compared with conventional laminated electrodes, this electrode not only has similar capacity but also shows better rate performance and stability. This study provides an idea for the manufacture of electrodes without polymer binders and metal collectors. In 2013, Goli *et al.* [19] significantly improved thermal management of lithium-ion batteries by using hybrid phase change material with graphene fillers, as shown in Fig. 1. Phase transition materials can store latent heat

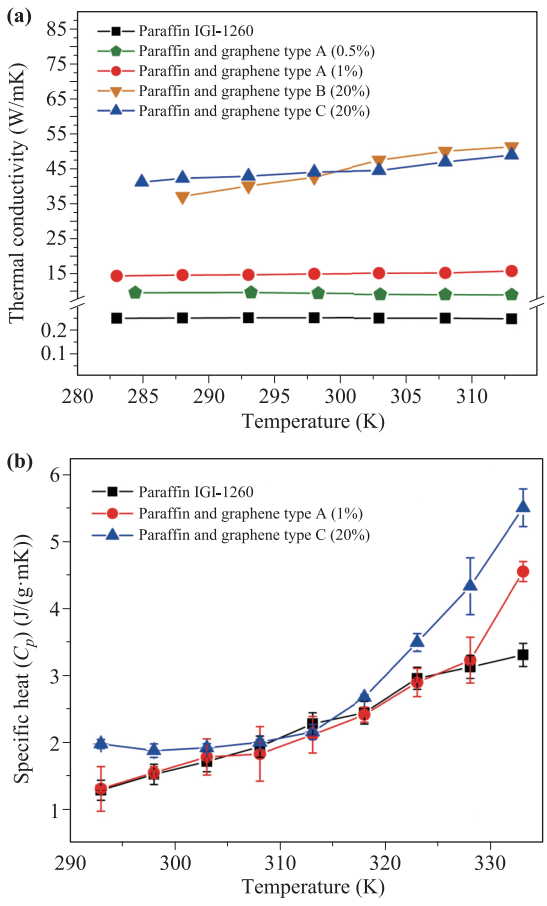

Fig. 1 **(a)** Thermal conductivity of the graphene-paraffin composites as a function of temperature. Here the percentage of graphene increases from 0 to 20%. **(b)** Specific heat of the graphene-paraffin composites and pure paraffin. For details, please refer to Ref. [19].

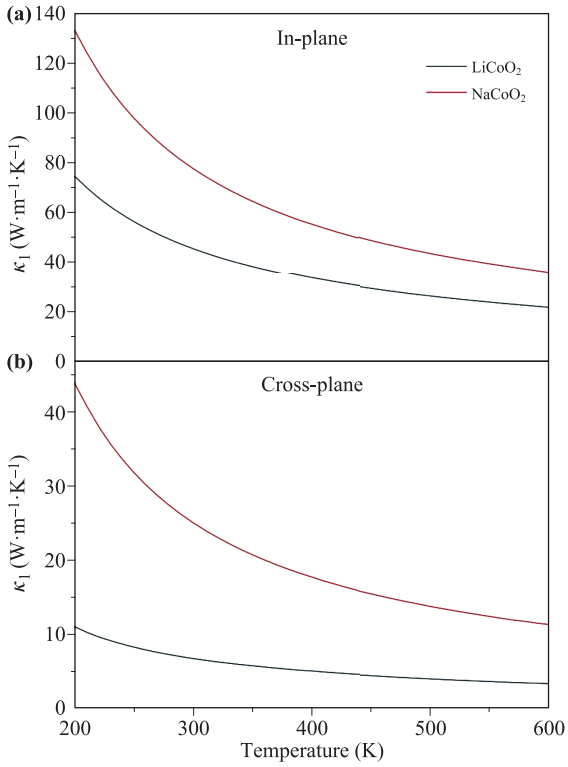

Fig. 2 Lattice thermal conductivities of $LiCoO_2$ and $NaCoO_2$ as the function of temperature. For details, please refer to Ref. [21].

through phase transformation thereby inhibiting the increase of temperature inside batteries. Moreover, due to the incorporation of graphene to the hydrocarbon-based phase change material, the thermal conductivity increases by two orders of magnitude while maintaining latent heat storage capacity, thus greatly improved the stability of lithium-ion batteries.

Previous optimization of electrode materials mainly focused on the specific energy, cycle life, and power, as well as the ionic and electronic transport, with relatively little attention devoted to thermal transport properties. Lithium cobalt oxide ($LiCoO_2$) is a commonly used cathode material for lithium-ion batteries. In 2019, He *et al.* [20] studied the lattice thermal transport of monocrystalline and polycrystalline ($LiCoO_2$), using molecular dynamics methods and thermal resistance models. The results show that the thermal conductivity of ($LiCoO_2$) single crystal reaches the order of 100 W/mK, with strong orientation dependence, temperature dependence and size effect. However, the polycrystalline $LiCoO_2$ exhibits isotropy and low thermal conductivity due to the phonon-grain scattering, the thermal resistance of the grain boundaries, and the specific size dependence of the thermal conductivity of the polycrystalline. In 2020, Mattila *et al.* [21] compared the lattice thermal conductivity of $NaCoO_2$ and $LiCoO_2$, using first-principles calculation combined with linearized Boltzmann transport theory. They found that at room temperature, the in-plane thermal conductivity and cross-plane thermal conductivity of $LiCoO_2$ are $\kappa_x = 46$ W/mK, $\kappa_z = 6.6$ W/mK, and the in-plane thermal conductivity and cross-plane thermal conductivity of $NaCoO_2$ are $\kappa_x = 78$ W/mK, $\kappa_z = 25$ W/mK, respectively, as shown in Fig. 2. The $NaCoO_2$ has higher phonon thermal conductivity because of its higher phonon lifetime.

In 2020, Yang *et al.* [22] systematically studied the heat transport properties of $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, and its alloy structure $Li(Ni_xMn_yCo_z)O_2$ $(x+y+z=1)$ through first-principles calculations, as shown in Fig. 3. The $LiCoO_2$ has the highest lattice thermal conductivity and exhibits remarkable anisotropy properties. At room temperature, the thermal conductivity of $LiCoO_2$, $LiNiO_2$, $LiMnO_2$ is 45.9 W/mK, 8.9 W/mK and 6.0 W/mK, respectively. They also found that the lattice distortion of $LiNiO_2$, $LiMnO_2$ greatly shortens the phonon lifetime, which causes their thermal conductivities to be lower than

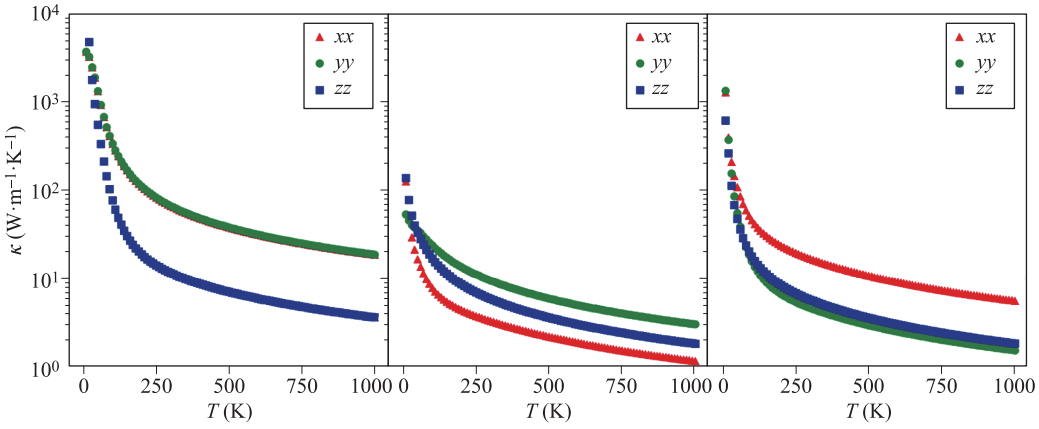

Fig. 3 Thermal conductivities of (left) $LiCoO_2$, (center) $LiNiO_2$ and (right) $LiMnO_2$ as a function of temperature. For details, please refer to Ref. [22].

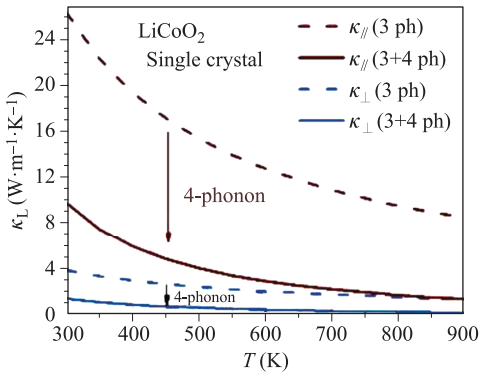

Fig. 4 Lattice thermal conductivities of $LiCoO_2$ and Li_xNbO_2 predicted by first principles. For details, please refer to Ref. [23].

that of $LiCoO_2$, and explains why the alloy structure $Li(Ni_xMn_yCo_z)O_2$ has lower thermal conductivity when the contents of Ni, Mn are dominant. Their research provides a new strategy for battery thermal management and electrode design.

At present, most of the calculations of thermal conductivities of electrode materials in lithium batteries consider only three-order lattice anharmonicity, whereas four-order lattice anharmonicity is rarely considered. In 2020, Feng *et al.* [23] employed first-principle calculation including high-order lattice anharmonicity and predicted the thermal conductivities in lithium intercalation materials, as shown in Fig. 4. They found the thermal conductivity of Li_xTMO_2 materials are significantly lower than previous predictions. The theoretical upper limit of lattice thermal conductivity of $LiCoO_2$ is 6 W/mK, which is much lower than the prior theoretical predictions. They also studied the effect of lithium removal on thermal conductivity of Li_xTMO_2. They found that thermal conductivity decreased significantly with decreasing lithium-ion concentration. The in-plane thermal conductivity of $Li_{0.33}CoO_2$ decreases to 6.5 W/mK, and the cross-plane thermal conductivity decreases to 0.41 W/mK. Their research provided theoretical guidance for designing high energy density batteries and controllable lithium-ion batteries.

In the process of repeated charge and discharge of the lithium-ion battery, lithium-ion is de-intercalated and embedded back and forth between the two electrodes, and the content of lithium-ion in the electrode will have a significant effect on the thermal conductivity of the electrode. Therefore, the study of the effect of different lithium content on the thermal transport properties of electrode materials is very important for the internal thermal management of the battery. In 2014, Cho *et al.* [24] measured the effect of different lithium content on the thermal conductivity of lithium cobaltate electrodes by Time-domain thermoreflectance (TDTR). They found that with the lithium removal of $Li_{1.0}CoO_2$ to $Li_{0.6}CoO_2$, the elastic modulus decreased from 325 GPa to 225 GPa, resulting in a decrease in thermal conductivity from 5.4 W/mK to 3.7 W/mK, and with the lithium-ion cycle, the process is reversible. Their research provides insight for dynam-

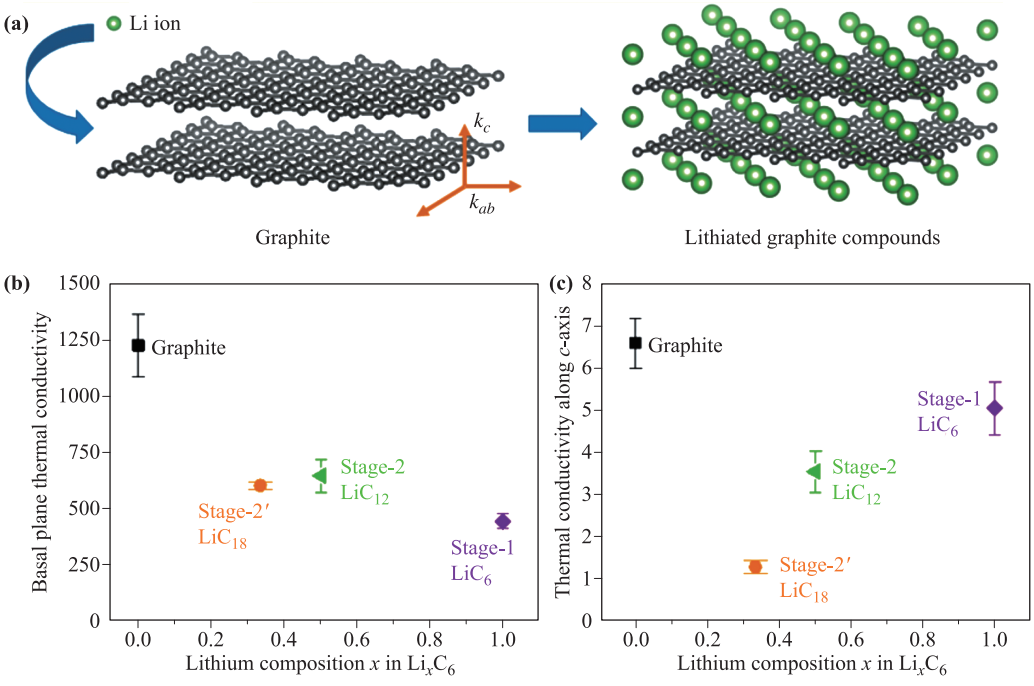

Fig. 5 **(a)** Schematic of the graphite and lithiated graphite compounds. The **(b)** basal plane thermal conductivity and **(c)** thermal conductivity along *c*-axis of Li_xC_6 with different lithium composition. For details, please refer to Ref. [25].

ically controlling the thermal conductivities of electrode materials for lithium-ion batteries.

In 2016, Qian *et al.* [25] studied the effect of different lithium content on the thermal conductivity of lithium-graphite intercalation compound (Li_xC_6) by molecular dynamics simulation, as shown in Fig. 5. They found that the intercalation of lithium has an anisotropic effect on the thermal conductivities of graphite electrodes: the in-plane thermal conductivity decreases monotonously from 1232 W/mK of original graphite to 444 W/mK of LiC_6, while the thermal conductivity of vertical plane decreases from 6.5 W/mK of graphite to 1.3 W/mK of LiC_{18}, and then increases to 5.0 W/mK of LiC_6 with the increase of lithium content. The underlying mechanism for this phenomenon is that the intercalation of lithium ions suppresses the phonon lifetime of lithium-graphite intercalation compounds and reduces the phonon group velocity in the plane, but it significantly increases the phonon group velocity in the vertical plane. Therefore, the thermal conductivity of lithium-graphite intercalation compounds is adjusted anisotropically.

The frequent intercalation and detachment of lithium ions from the electrode will also lead to the transformation of electrode materials from crystalline to amorphous. For example, silicon is considered as the anode material for the next generation of high energy density lithium-ion batteries because of its high theoretical capacity (4200 mAh/g) and abundant reserves. In 2000, Li *et al.* [26] found that with the intercalation of lithium-ion, the crystal structure of silicon electrode was gradually destroyed and amorphous Li–Si alloy was formed. Subsequently, Limthongkul *et al.* [27] confirmed once again that the intercalation of lithium ions can lead to the transformation of crystalline silicon into amorphous silicon. In 2004, Dahn *et al.* [28] quantitatively studied the changes of the crystal structure of silicon electrode materials during charge and discharge by in-situ and non-in-situ XRD methods. They also found that lithium-ion intercalation can lead to the amorphization of crystalline silicon. Similarly, in Lithium cobaltate electrode materials, it is also found that lithium removal will lead to the transformation of crystal structure from order to disorder [29]. Therefore, an in-depth understanding of the heat transfer operation of amorphous materials is very important for the internal thermal management of lithium-ion batteries.

However, the heat transport behavior of amorphous materials is quite different from that of crystalline materials. In an ideal crystal material, lattice vibration can be expressed by phonons with certain wave vectors and frequencies. The process of heat transport can be regarded as phonon diffusion driven by temperature gradients, and phonon are thermally resisted by scattering. This model is similar to the heat conduction of ideal gas molecules and is called the phonon gas model [30]. Later, based on this model, Debye, Peierls, Klemens, Callaway and others have developed a series of theoretical models to study the heat transport phenomenon of crystal materials, which makes the microscopic mechanism of heat transport and scattering mechanism on crystal materials more and more clear [31–34]. However, for amorphous materials, due to the lack of periodicity, the wave vector is no longer a correct quantum number, and the concept of phonon is no longer applicable, which brings a great challenge to the study of thermal transport properties of amorphous materials. As early as 1911, Einstein first studied the thermal conductivities of amorphous materials. He assumed that the heat transport process in amorphous materials is a series of random walking processes of harmonic oscillators with the same frequency and independent of each other, and thus proposed the amorphous limit model (amorphous limit model) [35]. In 1992, Cahill, Watson and Pohl [36] proposed a theoretical model (minimum thermal conductivity), describing the minimum thermal conductivities of amorphous solids based on the concept of random walk of independent oscillators proposed by Einstein, which is widely used to predict the thermal conductivities of amorphous materials. In 1993, Allen and Feldman [37] found that the normal vibration modes in amorphous materials can be divided into three types, namely propagon, diffuson and locon. The propagon is a delocalization mode with a definite wave vector in the low-frequency range, which is similar to the phonon. The diffuson is also a delocalized mode, but it does not have the characteristics of plane waves and cannot propagate heat in the crystal in the form of phonons, but heat transfers through the process of diffusion and transport. The locon is a high-frequency mode localized in space, which corresponds to the local vibration of the atom and its contribution to the heat transport is negligible. In 2018, Agne *et al.* [38] established a model called diffuser minimum thermal conductivity to describe the thermal conductivities of amorphous materials, which gives the thermal conductivity limit of the thermal transport process dominated by diffusers. At present, academia

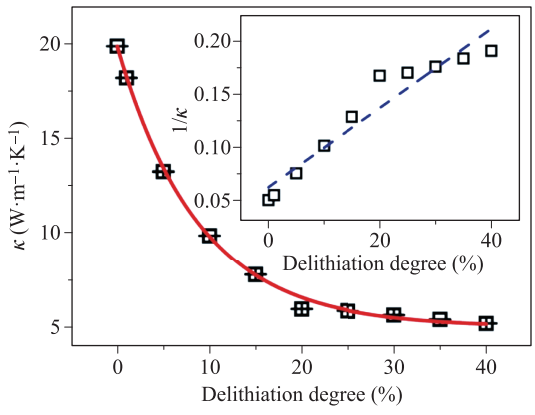

Fig. 6 Thermal conductivity of $LiCoO_2$ changes with the delithiation degree at 300 K. For details, please refer to Ref. [29].

has begun to pay attention to the effect of amorphization of electrode materials caused by charge and discharge on the thermal transport properties of lithium battery electrodes.

In 2018, Hu *et al.* [29] studied the effect of delithiation on the thermal conductivities of Lithium cobaltate electrode materials by non-equilibrium molecular dynamics method, as shown in Fig. 6. They found that in the process of lithium removal, the thermal conductivity of the electrode material decreased significantly, and the temperature dependence gradually weakened, showing an exponential behavior. Through the calculation and analysis of thermal energy transport coefficient and thermal energy density spectrum, it is found that delithiation leads to the transition of electrode materials from order to disorder, which induces the heat transport of non-propagating phonon modes. In addition, the propagating phonon modes are also strongly scattered by lithium vacancies, which lead to a significant decrease in thermal conductivity and temperature dependence.

In 2019, using picosecond time-domain thermoreflectance platform, Abdullaev *et al.* [39] experimentally measured nanoscale thermal transport properties of lithiated amorphous Si (a-Si) anode films. They found that upon electrochemical lithiation, there is 40% increase in thermal conductivity of a-Si, which may reach up to 2.2 W/mK. This large increase of thermal conductivity is attributed to the enhanced contribution to thermal conductivity from lithium ions.

He *et al.* [40] simulated the thermal conductivity of lithium cobaltate crystals and lithium cobaltate polycrystals by molecular dynamics method. The results show that compared with lithium cobaltate crystals with remarkable anisotropy, lithium cobaltate polycrystals show isotropic thermal transport characteristics and thermal conductivity decreases significantly. They also proposed a theoretical model for predicting the thermal conductivity of polycrystalline lithium cobaltate, which is consistent with the results of molecular dynamics simulation.

For a more intuitive understanding of the thermal conductivity of electrode material, we summarized the reported room temperature thermal conductivities of several common electrode materials ($LiCoO_2$, $LiMnO_2$, $LiFePO_4$, $Li(Ni_xMn_yCo_z)O_2$, $NaCoO_2$, amorphous Si and graphite), as shown in Table 1.

3 Thermal conductivity of separator and solid electrolyte

Separator is an important component of lithium-ion batteries, which allows lithium ions to pass without allowing electrons to pass through. Previous studies suggest that low thermal conductivity of the separator is one bottleneck issue for highly efficient thermal management in Li-ion batteries [41]. In 2016, Yang *et al.* [42] prepared hierarchical nano/micro-Al_2O_3/ polymer separator with thermal conductivity of 5 times higher than that of a commercial polyethylene diaphragm, and its thermal conductivity can reach 1 W/mK. Numerical simulations show that the increase in thermal conductivity is due to the addition of nanoparticles that reduce the thickness of the polymer layer on the Al_2O_3 particles. At the same time, the nano/micro-Al_2O_3/ polymer separator has better performance and safety compared with commercial polymer diaphragm, and has similar ionic conductivity.

Compared with liquid lithium-ion batteries, all-solid-state lithium-ion batteries with non-flammable solid electrolytes have attracted more attention due to their better safety and higher performance [43–46]. The structure of all-solid-state lithium-ion batteries is similar to that of liquid lithium-ion batteries, except that there is no separator, because solid electrolyte not only acts as ionic conductor, but also acts as diaphragm [47]. Gel Polymer Electrolytes (GPEs), as a solid electrolyte, has attracted wide attention because it is expected to improve the safety of the next generation of all-solid-state lithium-ion batteries. However, the low thermal conductivity seriously restricts its application. In 2017, Vishwakarma *et al.* [48] increased the thermal conductivity of Gel Polymer Electrolytes (GPE) to 2.5 times by adding BN/Al_2O_3 ceramic nano/micro particles to GPE. The measurement of ion mobility characteristics showed that the addition of BN/Al_2O_3 ceramic nano/particles had little effect on the electrochemical performance of GPE. They also found that the change in thermal conductivity measured by the experiment is completely in line with the effective medium theory. The establishment of a numerical model through effective medium theory may help the battery thermal management and electrode material optimization design.

Poly (ethylene oxide) (PEO) based materials are also alternative candidates for solid electrolytes. In 2019, Meng *et al.* [49] explored the thermal conductivity of PEO using molecular dynamics simulation. The structure and temperature dependent thermal conductivity are shown in Fig. 7. It is found that the enhancement of structural order can significantly improve the thermal conductivity of PEO. The thermal conductivity of crystalline PEO at room temperature can reach 60 W/mK, which is two orders higher than that of amorphous PEO. They also found that temperature-induced morphological changes can lead to obvious stepped negative temperature dependence of thermal conductivity in crystalline PEO.

4 Interfacial thermal transport

Due to the existence of the interface, when the phonon passes through the interface, it will be strongly scattered, resulting in interfacial thermal resistance [50], which greatly affects the internal heat transport of lithium batteries. Therefore, in-depth understanding of the interface

Table 1 The room temperature thermal conductivities of several common electrode materials ($LiCoO_2$, $LiMnO_2$, $LiFePO_4$, $Li(Ni_xMn_yCo_z)O_2$,$NaCoO_2$, amorphous Si and graphite).

Name	Thermal conductivity (W/mK)
$LiFePO_4$	$\kappa_{x,y} = 25$, $\kappa_z = 1$ (Ref. [70])
	$\kappa = 1.48$ (Ref. [71])
$Li(Ni_xMn_yCo_z)O_2$	$(x, y, z) = (0,1,0)$: $\kappa = 17.9$ (Ref. [22])
	$(x, y, z) = (6,2,2)$: $\kappa = 13.3$ (Ref. [22])
	$(x, y, z) = (8,1,1)$: $\kappa = 9.7$ (Ref. [22])
	$(x, y, z) = (0,1,0)$: $\kappa_x = 16.5$, $\kappa_y = 4.5$, $\kappa_z = 5.6$ (Ref. [22])
	$(x, y, z) = (1,0,0)$: $\kappa_x = 3.2$, $\kappa_y = 9.2$, $\kappa_z = 5.7$ (Ref. [22])
	$(x, y, z) = (0,0,1)$: $\kappa_{x,y} = 63.3$, $\kappa_z = 11.1$ (Ref. [22])
$LiCoO_2$	$\kappa = 4$ (Ref. [72])
	100% Li$\rightarrow\kappa = 5.4$ and 60% Li$\rightarrow\kappa = 3.7$ (Ref. [24])
	$\kappa = 21.25$ (Ref. [73])
	100% Li$\rightarrow\kappa = 19.8$ and 60% Li$\rightarrow\kappa = 5.2$ (Ref. [29])
	$Li_{0.33}CoO_2\rightarrow\kappa_{x,y} = 9.7$, $\kappa_z = 6.5$ (Ref. [23])
	$Li_{0.33}CoO_2\rightarrow\kappa_{x,y} = 1.4$, $\kappa_z = 0.41$ (Ref. [23])
	Monocrystal: $\kappa_x = 147.02 \pm 12.5$, $\kappa_y = 141.52 \pm 10.9$, $\kappa_z = 100.62 \pm 14.3$ (Ref. [20])
	Polycrystalline: $\kappa = 10.45$ (Ref. [20])
	Polycrystalline: $\kappa = 5.4$ (Ref. [20])
	$\kappa_{x,y} = 28$, $\kappa_z = 2.0 \pm 0.3$ (Ref. [24])
	$\kappa_{x,y} = 46$, $\kappa_z = 6.6$ (Ref. [42])
$NaCoO_2$	$\kappa_{x,y} = 78$, $\kappa_z = 25$ (Ref. [21])
Si	$\kappa = 145$ (Ref. [21])
	Amorphous-Si$\rightarrow\kappa = 1.4$ (Ref. [8])
	Lithiation amorphous-Si$\rightarrow\kappa = 2.0 \pm 0.4$ (Ref. [39])
$LiMn_2O_4$	$\kappa = 1.48$ (Ref. [39])
	$\kappa = 32$ (Ref. [72])
	$\kappa_{x,y} = 27$, $\kappa_z = 0.81$ (Ref. [74])
Graphene–SnO_2	$\kappa = 535.3$ (Ref. [75])
Graphite	$\kappa_{x,y} = 31$, $\kappa_z = 1.06 \pm 0.16$ (Ref. [76])
	$\kappa_x = 1232$ (Ref. [42])
	Fully lithiation (LiC_6), $\kappa_{x,LiC_6} = 444$ (Ref. [25])
	$\kappa_{z,graphite} = 6.5\rightarrow\kappa_{z,LiC_{18}} = 1.3\rightarrow\kappa_{z,LiC_6} = 5.0$ (Ref. [25])
	$\kappa = 5$ (Ref. [77])

heat transport and interface phonon scattering mechanism is of great significance to improve the heat dissipation of all-solid-state lithium batteries. At present, there are two main theoretical models used to study interfacial heat transport, namely, acoustic mismatch model [51] and diffusion mismatch model [52]. In the acoustic mismatch model, it is assumed that the interface is completely smooth, and the phonon is regarded as a plane wave in an elastic continuous medium. Thus, the phonon is specular reflected at the interface, and the interface thermal resistance comes from the phonon velocity difference caused by different acoustic impedance of different materials. The acoustic mismatch model is proved to be successful at very low temperatures, but it is no longer applicable at high temperatures (higher than 30 K), even if the interface is completely smooth [53]. On the other side, for the interface with defects and disorder, even at low temperature as low as 1 K, the acoustic mismatch model cannot give accurate results. For this case, the diffusion mismatch model reveals its ability to provide accurate theoretical prediction [54]. In the diffusion mismatch model, it is assumed that the interface is completely rough, the phonon diffuse reflection occurs at the interface, and the probability of the phonon entering the material on both sides of the interface is proportional to the phonon density of state in the material, but independent of the phonon incident state. The diffusion mismatch model can give consistent results with the experimental results under the condition of high temperature and completely rough interface [55]. Although the establishment of these two models provides

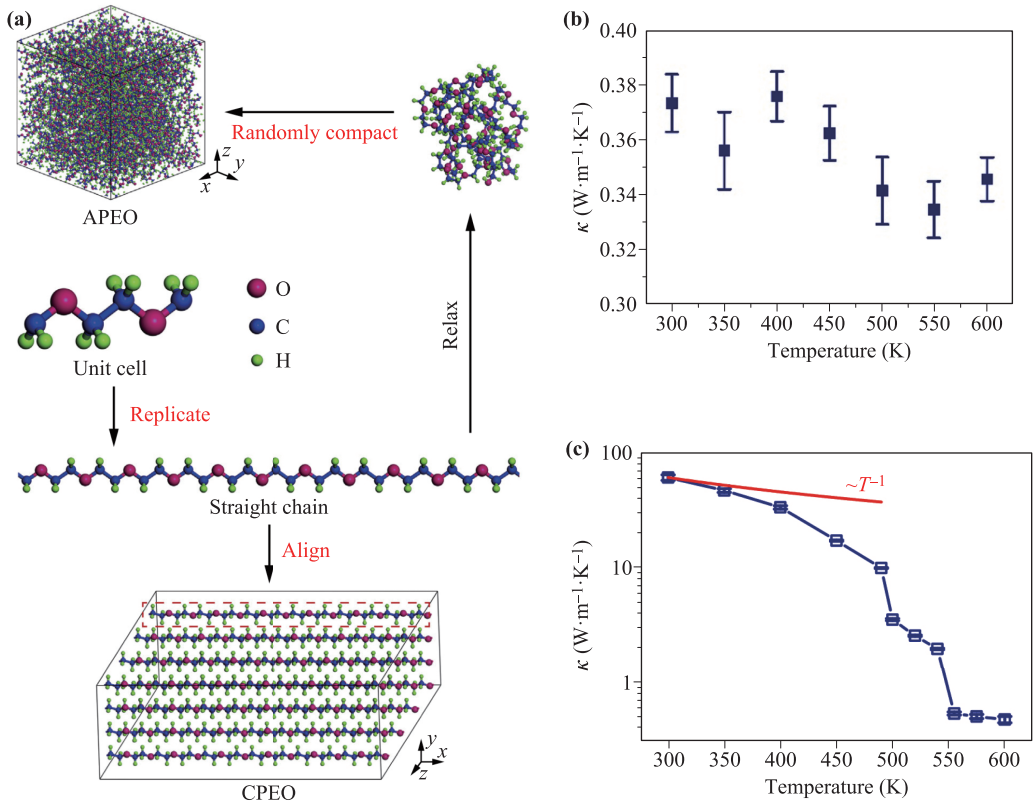

Fig. 7 **(a)** The schematic preparation procedure of crystalline PEO and amorphous PEO structures from PEO unit cell. **(b)** Thermal conductivity of amorphous PEO as a function of temperature; **(c)** thermal conductivity of crystalline PEO as a function of temperature. For details, please refer to Ref. [49].

theoretical guidance for people to understand the problem of interfacial heat transport, both models are based on the study of elastic continuum without considering the specific atomic structure at the interface. Recently, molecular dynamics method and atomic Green's function method are powerful methods to study interfacial heat transport based on atomic structure [56–66]. The molecular dynamics method can directly simulate the interfacial thermal resistance of the interfacial system on the atomic scale, without assumption of the specific scattering of phonons at the interface. Furthermore, molecular dynamics calculations can consider the effect of anharmonic terms on the thermal transport properties. It is widely used to study the thermal transport properties of the interface [62–65].

In 2020, using molecular dynamics simulation, Dhakane *et al.* [67] studied thermal transport in a pristine heterogeneous interface, and also explored the effects of bridged functional groups, include 3-Aminopropyl triethoxysilane (APTES), n-Butyl trimethoxysilane (nBTMS) and 3-Mercaptopropyl trimethoxysilane (MPTMS) molecules. It is found that molecular bridging at the interface can lead to 250% enhancement in interfacial thermal conductance for the APTES case, which agrees well with experimental measurement. These results demonstrate the key role of the cathode-separator interface in thermal management of the Li-ion cell. Furthermore, it is suggested that pronounced improvement in interfacial thermal transport can be realized by molecular bridging.

5 Summary and perspectives

In conclusion, although significant progress has been made in understanding the physical processes in Li-ion batteries, the thermal properties of anodes, cathodes, electrolytes and separators are less explored, and they play key roles for determining the safety in Li-ion battery. In this review, we summarized the state-of-the-art studies on the thermal conduction of anodes, cathodes, electrolytes and separators in commonly used Li-ion batteries. This work would provide advanced knowledge about thermal properties in Li-ion battery, and facilitate the advancement in thermal management in related applications.

There are still some scientific issues that remain unclear. For example, the research on the effect of electrode amorphization on the thermal transport properties of lithium batteries caused by charge-discharge process is far from enough, and further research is still needed to clarify these problems. The interface between electrode and electrolyte has an important influence on the internal heat transport

properties of all-solid-state lithium batteries, which still deserves further comprehensive studies.

In addition, the commonly used molecular dynamics method is based on the simulation of lattice vibration, which cannot take into account the contribution of electrons to thermal transport. Therefore it is only suitable for simulating the thermal transport behavior of non-conducting materials. However, studies have shown that in all-solid-state lithium-ion batteries, with the removal of lithium ions, lithium cobaltate will transition from semiconductors to conductors [68, 69], resulting in a conductor/non-conductor interface. In the process of heat transport at the conductor/non-conductor interface, the interaction between electrons and phonons will become very important, and the molecular dynamics method will no longer be applicable. Theoretically, the influence of electron–phonon and phonon–phonon interaction on the transport properties can be considered by using the non-equilibrium Green's function method [78–80].

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