Highly Anisotropic Thermal Transport in LiCoO$_2$

Hui Yang, $^†, \nabla$ Jia-yue Yang, $^†$ Christopher N. Savory, $^¶, ^§, \nabla$ Jonathan M. Skelton, $^||$
Benjamin J. Morgan, $^⊥, \nabla$ David O. Scanlon, $^¶, ^#, ^@, \nabla$ and Aron Walsh $^*, ^†, \triangle, \nabla$

$^†$Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, UK
$^‡$School of Energy and Power Engineering, Shandong University, Qingdao 266237, China
$^¶$University College London, Department of Chemistry, 20 Gordon Street, London WC1H 0AJ, UK
$^§$Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, UK
$^||$School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK
$^⊥$Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK
$^#$Thomas Young Centre, University College London, Gower Street, London WC1E 6BT
$^@$Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK
$\triangle$Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Korea
$\nabla$The Faraday Institution, Quad One, Harwell Science and Innovation Campus, Didcot, UK

E-mail: a.walsh@imperial.ac.uk

Abstract

LiCoO$_2$ is the prototypical cathode in lithium ion batteries. Its crystal structure consists of Li$^+$ and CoO$_2^-$ layers that alternate along the hexagonal $(0001)$ axis. It is
well established that ionic and electronic conduction are highly anisotropic; however, little is known regarding heat transport. We analyse the phonon dispersion and lifetimes of LiCoO$_2$ using anharmonic lattice dynamics based on quantum chemical force constants. Around room temperature, the thermal conductivity in the hexagonal $ab$ plane of the layered cathode is $\approx 6$ times higher than that along the $c$ axis, based on the phonon Boltzmann transport. The low thermal conductivity ($< 10 \text{ W m}^{-1} \text{K}^{-1}$) originates from a combination of short phonon lifetimes associated with anharmonic interactions between the octahedral face-sharing CoO$_6^-$ networks, as well as grain boundary scattering. The impact on heat management and thermal processes in lithium ion batteries based on layered positive electrodes is discussed.

Lithium cobalt oxide, LiCoO$_2$, has been widely used as a cathode material in lithium ion batteries (LIBs) following its discovery in 1980$^1$ and its commercialization in the 1990s. The compound offers a number of attractive features including ease of synthesis, reversible lithium insertion, and high specific energy density.$^{2,3}$ LiCoO$_2$ crystallizes in a layered structure (spacegroup R$\bar{3}$m; Figure 1a) in which CoO$_6$ and LiO$_6$ octahedra form parallel slabs. This layered structure means the material is effectively a 2D ionic and electronic conductor.$^{4,5}$

Co can be partially replaced by the transition metals Ni and Mn to form the NMC system, LiNi$_x$Mn$_y$Co$_{z}$O$_2$ ($x + y + z = 1$). The Co:Ni:Mn ratio can be tuned to optimize the mechanical and electrochemical performance, while reducing cost.$^{6,7}$ Many NMC compositions preserve the same structure type, with some local Jahn-Teller distortions depending on the combination of oxidation states present in the mixed-metal system.$^{6,8}$

One key challenge for LIBs is to improve lifetimes and safety characteristics without compromising energy and power densities.$^{9,10}$ Thermal management is an important issue and is intimately connected to chemical degradation and battery lifetime. There is a significant gap in knowledge of battery manufacturers and developers on how temperature and thermal management affects capacity/power fade, thermal runaway, and other performance changes of Li-ion cells.$^{11}$ With the advances of computational methods, many key battery
processes can be accurately described by computer simulations, including the defect chemistry and associated ionic and electronic transport.\textsuperscript{12} However, little is known regarding heat transport.

Figure 1: (a) Layered crystal structure of LiCoO\textsubscript{2} with spacegroup R\textoverline{3}m, where the stacking is along the hexagonal \(c\) axis. The image was generated using VESTA.\textsuperscript{13} (b) Calculated phonon dispersion of LiCoO\textsubscript{2} using three \(E_{xc}\) functionals within DFT. The supercell expansion used for calculating the harmonic force constants was \(3 \times 3 \times 3\).

In this Letter, we assess the vibrational and thermal transport properties of LiCoO\textsubscript{2} within many-body perturbation theory. For the harmonic phonon dispersion, we find a sensitivity with the choice of electron exchange and correlation functional \((E_{xc})\) within density functional theory (DFT). Using a hybrid \(E_{xc}\), we calculate the lifetime and heat conduction of each phonon mode, which sum to give the total lattice thermal conductivity. We predict a value of 53.6 W m\(^{-1}\) K\(^{-1}\) (hexagonal \(ab\) plane) and 8.4 W m\(^{-1}\) K\(^{-1}\) (\(c\) axis) at room temperature in the pristine LiCoO\textsubscript{2} crystal. The origin and impact of this large anisotropy is explored.

\textit{Phonon dispersion.} The harmonic phonon dispersion of LiCoO\textsubscript{2} is shown in Figure 1. The positive frequencies across the vibrational Brillouin zone confirm a dynamically stable structure. The four atoms in the primitive (rhombohedral setting) unit cell results in 12 \((3N)\) phonon modes. A group theoretic analysis within the \(D_{3d}\) point group assigns the acoustic \((A_{2u} + E_u)\) and optic branches \((A_{1g} + 2A_{2u} + 2E_u + E_g)\). From these, only the \(2A_{2u} + 2E_u\) modes are infra-red (IR) active, while the \(A_{1g} + E_g\) modes are Raman active.
The low-spin d^6 configuration of Co(III) in pristine LiCoO_2 avoids the electronic structure complexity of Co(II) and Co(IV) species. However, we still expect some sensitivity to the choice of exchange-correlation functional in DFT as the localized wavefunctions of 3d transition metals are susceptible to self-interaction errors.\textsuperscript{14}

The LDA and LDA+U functionals produce qualitatively similar phonon dispersion, in agreement with the work of Du and co-workers.\textsuperscript{8} However, the inclusion of non-local exchange with HSE06 results in a stiffening of the frequencies in the optic branch (also observed in other dielectric materials\textsuperscript{15}). A comparison with available experimental data is given in Table 1. For example, IR measurements place an \( E_u \) mode at 7.8 THz, which compares to 7.6 THz from HSE06, while LDA/LDA+U predict a value at \(~6\) THz. Care should however be taken with direct comparison with experiment as the predictions do not include finite-temperature effects; these include thermal expansion and higher-order anharmonic frequency shifts.

Table 1: Comparison of phonon frequencies for select modes at the \( \Gamma \) point in the vibrational Brillouin zone of LiCoO_2. Values are given in THz for different \( E_{XC} \) functionals (TS = Tkatchenko-Scheffler dispersion) and peaks extracted from available room-temperature experimental IR and Raman spectra.

<table>
<thead>
<tr>
<th>Method</th>
<th>( A_{1g} )</th>
<th>( E_g )</th>
<th>( A_{2u} )</th>
<th>( E_u )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>18.09</td>
<td>14.30</td>
<td>12.25</td>
<td>7.64</td>
</tr>
<tr>
<td>LDA+U</td>
<td>17.95</td>
<td>14.73</td>
<td>11.14</td>
<td>6.42</td>
</tr>
<tr>
<td>HSE06</td>
<td>19.12</td>
<td>15.52</td>
<td>12.27</td>
<td>7.53</td>
</tr>
<tr>
<td>HSE06+TS</td>
<td>19.17</td>
<td>15.62</td>
<td>12.81</td>
<td>7.56</td>
</tr>
<tr>
<td>Exp.</td>
<td>17.87\textsuperscript{a}</td>
<td>14.57\textsuperscript{a}</td>
<td>12.59\textsuperscript{b}</td>
<td>7.80\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Raman active modes\textsuperscript{16} \textsuperscript{b}IR active modes\textsuperscript{17}

**Lattice thermal conductivity.** The lattice (or vibrational) thermal conductivity of a crystalline material (\( \kappa \)) depends on the cumulative speed and lifetime of the heat-carrying phonon modes. Formally, it is determined by the tensor product of the modal heat capacity (\( C_V \)), group velocity (\( v \)), and phonon mean free path (\( v \times \tau \) phonon lifetime) summed over all modes (\( \lambda \)) and averaged over wavevectors (\( q \)):

\[
\kappa = \frac{1}{NV_0} \sum_{q,\lambda} C_{V,q,\lambda} v_{q,\lambda} \otimes v_{q,\lambda} \tau_{q,\lambda}
\]  

(1)
where \( N \) is the number of atoms and \( V_0 \) is the volume of the crystallographic unit cell. The heat capacity and group velocity can be determined from the harmonic phonon dispersion (Figure 1); however, within the harmonic approximation the lifetime is ill-defined (infinite) due to absence of phonon-phonon interactions.

We calculate the lifetime of each phonon mode within many-body perturbation theory by taking into account the leading term of three-phonon scattering events.\(^{18}\) The resulting thermal conductivity is plotted in Figure 2. The conductivity decays exponentially as temperature increases and is found to be highly anisotropic. Around room temperature, the thermal conductivity calculated in the hexagonal \( ab \) plane is 53.6 W m\(^{-1}\) K\(^{-1}\), while the value along the \( c \) axis is 8.4 W m\(^{-1}\) K\(^{-1}\). The experimentally measured thermal conductivity is as low as 4 W m\(^{-1}\) K\(^{-1}\) at 280 K,\(^{19}\) which is slightly below our calculated result along the \( c \) axis. Our predictions should result in an upper limit as in real imperfect samples, other scattering processes occur due to extended (e.g. dislocations and grain boundaries) and point (e.g. Li\(_x\)Co\(_{1-x}\) antisite) defects. The experimental value of thermal conductivity is reproduced if a threshold of 2 nm is set for the maximum phonon path length (see Figure 2).

**Origin of anisotropy.** Phonon lifetimes and mean free paths have only recently become accessible to first-principles calculations, and the majority of available data is on face-centred cubic systems.\(^{18,20,21}\) In comparison to materials with isotropic connectivity such as GaAs and CdTe,\(^{22}\) the average strength of three-phonon interactions in LiCoO\(_2\) is three orders of magnitude larger. The associated phonon lifetimes of LiCoO\(_2\) are three orders of magnitude shorter (see Figure 3). To investigate the origins of the anisotropy, we have separated the \( c \)-axis transport from the \( a/b \)-axis component in Figure 3. The modes that make the largest contributions to in-plane transport have faster group velocities and longer modal lifetimes. The mean-free path of the heat carrying modes are up to 44 nm in the \( ab \) plane and 446 nm along the \( c \) axis in the perfect crystal. However, the thermal conductivity (Equation 1) is an integral over the vibrational Brillouin zone, and the lower density of long-lived modes along the \( c \) axis results in its smaller contribution to thermal transport.
Figure 2: Calculated lattice thermal conductivity ($\kappa$) of LiCoO$_2$ along the $a$, $b$ and $c$ axes. The experimental data$^{19}$ was measured on polycrystalline samples using a steady-state technique. The black line is a simulation of a polycrystalline (poly) film of LiCoO$_2$ using a phonon-boundary scattering model which limits the mean free path typically to the average grain size. The boundary required to match the experimental room-temperature data, using the first-principles phonon lifetimes, is 2 nm.

Heat generation during the charge-discharge process of a battery can exceed 1W/cm$^3$ depending on the cycling rate. This is due to a combination of resistive heating from ion and electron transport, as well as changes in entropy.$^{23}$ Simulations of battery components so far assume isotropic thermal transport, which we have shown is not the case. The thermal stability of LiCoO$_2$ is known to be poor, which can lead to thermal runaway under high-temperature operation or overcharging.$^{24}$ We expect that the thermal conductivity of NMC compositions will be even lower than LiCoO$_2$ owing to the additional phonon-scattering due to cation disorder and spatial inhomogeneity. However, cation disorder may also provide a kinetic barrier to secondary phase formation, which can account for the improved stability of the NMC compositions. Very recent analysis has shown the impact of thermal effects on anion redox where heat dissipation contributes to voltage hysteresis upon battery cycling.$^{25}$ Investigation of the coupling between the vibrational modes of defects with bulk phonon transport is a worthwhile direction for future research.
Figure 3: Results from anharmonic lattice dynamics of LiCoO$_2$ calculated from the three-phonon scattering rates. Group velocity are in (a) and (b), modal lifetime are in (c) and (d), and phonon mean-free paths are in (e) and (f). The left and right columns are components along $c$ and $a/b$ axes, respectively. The hotter parts in the heat maps, from red (low) to yellow (high), refer to modes that make a larger contribution to thermal transport.
To conclude, the thermal conductivity in LiCoO$_2$ is highly anisotropic by a factor of 6 between the in-plane and out-of-plane heat transport. First-principles analysis of the harmonic phonon dispersion, and anharmonic phonon-phonon interactions, reveal that the anisotropy largely originates from differences in the group velocity of the heat-carrying phonon modes. We found that a hybrid electron exchange and correlation functional can describe the vibrational properties of LiCoO$_2$ and will likely be essential for the commercial NMC system, where the mixed-oxidation states of Ni, Mn and Co exhibit strong electron correlation. Our study provides a robust foundation for the understanding and description of thermal processes in battery systems.

Computational methods. The starting point for the structural relaxation was the experimentally-determined structure of LiCoO$_2$ from the work of Cava and co-workers.$^{26}$ The total energy and electronic structures calculations were performed using DFT as implemented in the Vienna Ab initio Simulation Package$^{27}$ with a plane-wave basis set (600 eV cutoff). Structural relaxation was performed with a $6 \times 6 \times 6$ $k$-point mesh, for which the total energy was converged to within 1 meV per atom. A force tolerance of 0.001 eV/Å was used for convergence of the ion positions to ensure accurate phonons.

The inter-layer interactions are weak in LiCoO$_2$ so that we employed a dispersion correction. The Tkatchenko-Scheffler approach$^{28}$ (with Hirshfeld partitioning$^{29}$) reproduces the experimental lattice parameters,$^{26}$ as well as the Li-intercalation energies.$^{30,31}$ For LDA+$U$, a representative $U$ value of 3.9 V was applied to the Co d orbitals. The hybrid HSE06$^{32}$ functional was used in both harmonic and anharmonic lattice-dynamics calculations.

The second-order (harmonic) force constants were computed using a $3 \times 3 \times 3$ supercell expansion and a finite-difference displacement step of $3 \times 10^{-2}$ Å. The third-order (anharmonic) force constants were also computed using $3 \times 3 \times 3$ expansion and a $3 \times 10^{-2}$ Å step. The lattice thermal conductivity of LiCoO$_2$ was obtained by solving the phonon Boltzmann transport equation within the relaxation-time approximation using the Phono3py package.$^{33}$

Data access statement: The associated structure files and input/output of the phonon
calculations are available in an online data repository: [link to be updated upon acceptance].

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