Atomic-Scale Study Of Thermal Transport At Lithium

In this study, the equilibrium molecular dynamics (EMD) and nonequilibrium molecular dynamics (NEMD) are employed for exploring the anisotropic thermal transport properties inside lithium cobalt oxide (LiCoO2) as a cathode material in rechargeable lithium ion batteries. Here we provide a deeper study of them in respect of thermal transport properties in three LiCoO2-based systems with different crystalline type: monocrystalline, polycrystalline and bicrystalline interface. Results indicate that the thermal conductivity in monocrystalline LiCoO2 is clear dependent on both the box size and temperature. For polycrystalline LiCoO2 generated by Voronoi tessellation method, effects of grain randomicity and box size on thermal conductivity can be negligible when the box size is two times larger than grain size, but the thermal conductivity rapidly increases with increasing grain size. Then the anisotropic thermal transport mechanism are further elaborated from the perspective of phonon mean free path (PMFP). Conclusion compared with the monocrystalline thermal conductivity shows that the obvious decrease in polycrystalline can be attributed to boundary thermal resistance and limited PMFP. Finally, NEMD is performed to study the effects of boundary tilt angle, rotation direction and grain size on boundary thermal conductance. Studies show the calculated thermal conductance is strong dependent on boundary tilt angles and varies from 7.5 to 25.3 GWm-2K-1. Further experiments are suggested to approve the simulation predictions of thermal transport properties.

I. INTRODUCTION

Lithium-ion batteries have played a central role in economic and efficient energy storage options for portable electronic device and electric vehicles today [1]. The thin film rechargeable lithium ion battery as a promising secondary battery is usually composed of the cathode, anode, current collector, electrolyte and separator [2]. LiCoO2 has been widely used for cathode material in lithium ion battery with its excellent electrochemical performances such as thigh energy density, proper power density and long cycle life time. Nevertheless, the cathode material in Li ion battery produced with LiCoO2 has awful thermal conduction properties, which may bring about thermal runaway and thermal decomposition with the gradually elevated temperature. That is why most lithium ion batteries operate in practice in a restricted temperature range of 20 °C to 55 °C, in which the generated heat is easily regulated in the process of operating. For LiCoO2 cathode material, many previous studies [4-7] mainly focus on the electrochemical and Li ion diffusion by experiments and theoretical analysis, little thermal transport properties at atomic scale was researched by molecular dynamic simulations, especially the thermal conductivity. In reality, however, the LiCoO2 electrode material are mainly composed of the textured polycrystalline structures. For polycrystalline structure, the three dimensional Voronoi tessellation approach is usually employed for simulating the microstructure with the grain random distribution.

With the development of nanotechnology, nanoscale polycrystalline materials have been intensely attracted by its obvious different characteristics compared with monocrystalline ones, such as the mechanical properties and thermal properties [8]. Therefore, to adequately describe the thermoelectric performance of one material, an accurate investigation in terms of the thermal conductivity is first required at atomic scale. As we all know, two primary methods are

usually employed for extracting the lattice thermal conductivity at atom level: EMD method with Green-Kubo function and NEMD method with Fourier's Law [27, 29]. The former strategy is based on the fluctuation dissipation theorem stemmed from the theory of linear response, in which the thermal conductivity can be obtained by integrating the heat current autocorrelation function (HCACF). The latter approach is based on the Fourier's Law derived from the steady state heat flux and temperature gradient, in which the thermal conductivity can be expressed as the ratio of steady state heat flux to the temperature gradient. Currently, although lots of studies have been reported to successfully predict the lattice thermal conductivity of some atomic crystals such as argon, silicon, diamond, silicon carbide and carbon nanotubes by molecular dynamic simulations for its high efficiency and low cost [9-13] and results suggests that the thermal conductivity can be governed by many factors, such as the thermal expansion, impurity, the simulation domain size, system strain, grain size and temperature. To date, however, no both the theoretical and experimental studies on the thermal conductivity in both monocrystalline LiCoO2 material and polycrystalline LiCoO2 material or the thermal conductance of grain boundary in bicrystalline LiCoO2 material have been conducted. The intention of this work is to develop the method constructed polycrystalline LiCoO2 and systematically investigate the anisotropic thermal transport mechanisms of both the monocrystalline LiCoO2 and polycrystalline LiCoO2 under different influencing factors by using the EMD method and explore the effects of different boundary tilt angles, different rotation direction and different grain size on the interfacial thermal conductance in bicrystalline LiCoO2 by employing the NEMD method.

II. SIMULATION METHODS AND MODELS

In this paper, three LiCoO2-based systems with different crystalline type: monocrystalline, polycrystalline and bicrystalline interface, which will be discussed and respectively shown in Figure 1a, Figure 2a and Figure 3a. The EMD or NEMD approach will be employed for exploring the buck thermal conductivity or boundary thermal conductance of the three crystalline types as implemented in the LAMMPS package [14].