Carbon Nanotube – Nanodiamond Li-Ion Battery Cathodes with Increased Thermal Conductivity

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ABSTRACT

Prevention of excess heat accumulation within the Li-ion battery cells is a critical design consideration for electronic and photonic device applications. We report the results of our investigation of the thermal conductivity of various Li-ion cathodes with incorporated carbon nanotubes and nanodiamonds in different layered structures. The cathodes were synthesized using the filtration method, which can be utilized for synthesis of commercial electrode-active materials. The thermal measurements were conducted using two transient techniques – the "hot disk" and "laser flash" – which allowed us to determine separately the in-plane and cross-plane thermal conductivities of the samples. It has been established that the cathode with the carbon nanotubes-LiCo$_2$ and carbon nanotube layered structure possesses the highest in-plane thermal conductivity of above ~200 W/mK at room temperature. The cathode containing nanodiamonds on carbon nanotubes structure revealed one of the highest cross-plane thermal conductivity values. The measured in-plane thermal conductivity is up to two orders-of-magnitude greater than that in conventional cathodes based on amorphous carbon. The obtained results demonstrate a potential of carbon nanotube incorporation in cathode materials for the effective thermal management of Li-ion and other high-powered density batteries.

Keywords: Lithium ion electrodes, carbon nanotubes, nanodiamonds, thermal conductivity, thermal management

1. INTRODUCTION

Li-ion batteries are known for their low weight and high power density[1] which make them attractive for applications in many fields including the automotive and aerospace industries. Recently emerging research on electrode materials has led to an improvement in the overall design of light weight, high power density Li-ion batteries[2]. However, limited work has been done in improving the overall safety of Li-ion batteries[3]. Although Li-ion batteries efficiently convert the stored chemical potential into electric energy, a noticeable amount of energy is lost through Ohmic heating[4]. Additionally, the chemical reactions that take place during their normal operation also contribute to heat buildup within Li-ion batteries[5]. Overheating issues in Li-ion batteries have to be properly addressed to prevent catastrophic failure and to prolong the battery life and performance of Li-ion batteries. Presently, the thermal management of Li-ion battery packs consists of active cooling using liquid or air as a convective heat transfer media or passive cooling using phase change materials and an aluminum packaging. Active cooling is normally used in industrial scale applications in the aerospace and automotive fields, while passive cooling is used in more miniature scales such as small electronic vehicles. Both active and passive cooling have drawbacks that must be considered. Active cooling systems can become complex resulting in large costs and an overall increase weight. Passive cooling systems exploiting the phase change materials' heat absorbing properties to transfer heat away from batteries and out to the surrounding environment. However, their intrinsic low thermal conductivity results in a poor heat dissipation rate which creates unwanted thermal gradients within Li-ion batteries during their operation[6].

Recent studies have shown that the thermal conduction within a battery cell determines its overall heat dissipation ability[7]. It is believed that the thermal resistance between the electrode and separator interface limits the overall thermal conduction of the battery cell. This finding has led to a refocus in the material selection and design of the various components of a Li-ion battery. The conventional structure of a Li-ion battery electrode is a variation of a mixture of electrochemically active electrode material, carbon material, binder, and an aluminum foil or mesh used a collector. This structure is known for

achieving effective electrochemical performance. However, current dry battery electrode materials have been shown to possess very low thermal conductivity values of 0.4 W/mK[8]. Previous studies have shown that dry electrodes based on Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ and multi walled carbon nanotubes (CNTs) had significantly increased cross plane thermal conductivity values as compared to conventional electrodes based on carbon black[1]. However, those electrodes demonstrated a poor electrochemical performance. In this work, we report the thermal conductivity and electrochemical performance of electrodes based on LiCoO$_2$ and 100 µm long multi walled CNTs. LiCoO$_2$ was used an electrode material in the first commercially available Li-ion battery for its ease of use, charge cycle stability, and high power density[9]. The thermal conductivity values and electrochemical performance of the structured LiCoO$_2$/CNTs electrodes are described in the following sections. The present report is focused on the thermal conductivity measurements and thermal characteristics of the electrode. The details of electrochemical measurements will be reported elsewhere.

2. METHODOLOGY

The fabrication used commercial LiCoO$_2$ particles (Aldrich) and C-grade multi-walled CNTs (NanoTechLab; ≥95% purity, 100 nm long, diameter in the range of 5-30 nm). All electrodes used for thermal conductivity and electrochemical tests were fabricated via the vacuum filtration of corresponding solutions through a microporous polyolefin separator[1]. The CNTLCO, CNTLCOND and CNTLCOMD electrodes have three-layered structure in which the middle layer containing LiCoO$_2$ particles was sandwiched between two layers of CNTs. The control CNT sample was obtained via filtration of suspension of CNTs dispersed in isopropanol. The suspension of CNTs was then filtrated by vacuum, forming a black CNT film on the filter. After the filtration, all samples were annealed in an oven at 200 °C for 12 hours, and prepared for electrochemical testing. The samples were inspected with the scanning electron microscopy (SEM). The electrochemical tests were performed using 2032 coin cells with a lithium metal foil as a counter electrode and a 1.2 M LiPF$_6$ in an ethylene carbonate/ethyl methyl carbonate electrolyte. Tests done at half-cell cycles were performed at a 70 mA/g between 2.75 – 4.2 volts and 2.75 – 4.5 volts vs Li/Li$^+$ voltage range using a battery tester at room temperature. The rate performance of each electrode was tested by cycling between 2.75 – 4.2 volts vs. Li/Li$^+$ range at 0.2C, 0.5C, 1C, 2C and 4C discharge rates at constant charge rates run at room temperature.

The in-plane thermal conductivity of the electrodes was measured using the transient plane source technique (Hotdisk). In this technique, an electrically insulted flat nickel sensor with a radius of 0.5 mm is placed in between two identical pieces of an electrode sample (Figure 1a). The sensor acts as both a heat source and a temperature monitor. The thermal properties of the electrodes are calculated by recording the temperature rise as a function of time using the equation $\overline{\Delta T(\tau)} = P\left(\pi^{\frac{3}{2}}rK\right)^{-1}D(\tau)$, where $\tau = (t_m\alpha/r^2)^{1/2}$, α is the thermal diffusivity of the electrode , t_m is the transient measurement time, r is the radius of the hot disk sensor, P is the input heating power, and $D(\tau)$ is the modified Bessel function. The power and time parameters are input values that are chosen so that the heat flux is within the electrodes' boundaries and the temperature rise of the sensor is not influenced by the edge boundaries of the electrodes. More details of the measurement procedures were reported by us elsewhere[10-12]. The cross-plane thermal conductivity of the electrodes was measured using an optical "Laser flash" technique (LF, Netzsch). To measure their thermal diffusivity, the electrode samples were placed into a sample holder (Figure 1b) which is then transferred into the LFA stage where a xenon flash lamp produces shots of energy of 10 joules/pulse on the electrodes' surface while their temperature rise is monitored at the opposite end with an infra-red detector. The thermal conductivity is then calculated from the equation $K=\rho\alpha C_p$, where ρ is the electrode's mass density, and C_p is its specific heat (measured separately).
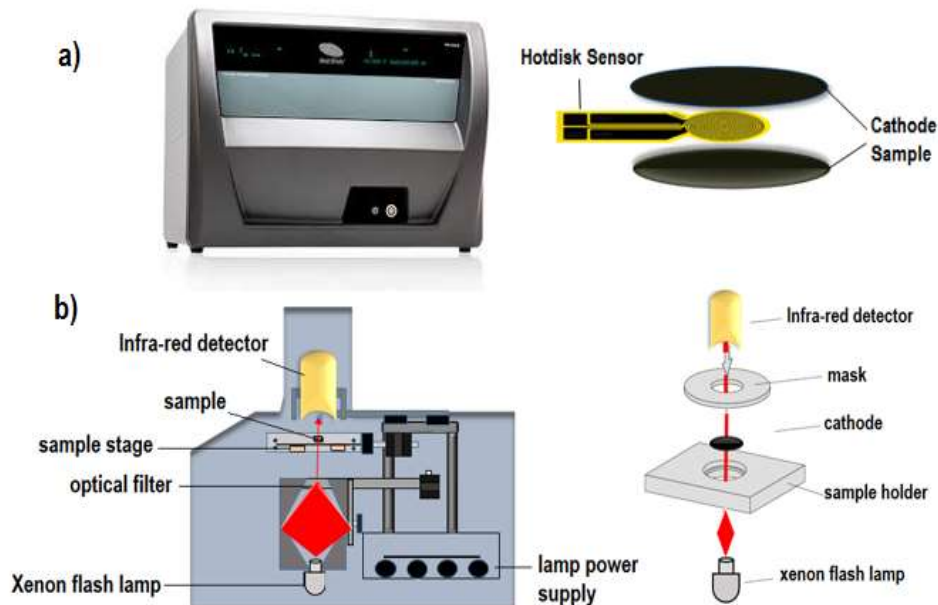
Figure 1: a) A schematic of Hotdisk TPS 2500s instrument used for in-plane thermal conductivity measurements and b) components of the LFA 447 instrument used for cross-plane thermal conductivity measurements

3. RESULTS AND DISCUSSION

Four different types of electrode samples were fabricated via the vacuum filtration method[13]. The samples were then prepared for thermal conductivity and electrochemical performance testing. A reference electrode sample (CNT) was fabricated using 10 mg of CNTs. To study the interaction of CNTs and $LiCoO_2$, the electrode sample (CNTLCO) composed of a mixture 51 mg $LiCoO_2$ particles and 2 mg of CNTs sandwiched between a top layer of 4 mg of CNTs and a bottom layer of 4 mg of CNTs. In order to study the interaction between micro and nano sized diamond particles with CNTs and $LiCoO_2$ particles, two separate samples, CNTLCOND and CNTLCOMD, were fabricated. The CNTLCOMD electrode was composed of an interlayer of 51 mg of $LiCoO_2$, 2 mg of CNTs, and about 1 mg of micro diamond particles, sandwiched between a top and bottom layer of a CNT/micro diamond mixture composed of 4 mg CNTs and around 1 mg of micro diamond particles. Similarly, a CNTCOND electrode was fabricated with the same structure of CNTCOMD while substituting micro sized diamond particles with nano sized diamonds.

In the previous study, we observed a significant increase in the thermal conductivity value for composite electrodes based on polydispersed CNTs[1]. We initially studied the effect of the CNT length on the thermal conductivity and electrochemical performance and found that the electrodes containing short CNTs (5-20 µm) faded abruptly. Consequently, we focused our work on electrochemically stable electrodes based on long (100 µm) CNTs. The results of our electrochemical tests revealed that CNT-based electrodes with $LiCoO_2$ as their active material have a Li-ion capacity in the range of 123 to 142 mAh/g, good performance stability and a high coulombic efficiency (99.9%) when cycled between 2.75 and 4.2 volts at 70 mA/g. $LiCoO_2$ material was added at 84% by weight which is comparable with traditional laminate electrodes. A stable performance of these electrodes was reached at 10 testing cycles. An overall decrease in polarization was also observed during cycling and a gradual capacity drop and impedance increase was also seen. However, the overall capacity retention of the CNT-based electrodes was superior to conventional laminate electrodes that are currently available. For all CNT-based electrodes tested, we observed a capacity drop between 3-4% after 50 cycles at 2.75 and 4.2 volts. We attributed this variation to the fluctuation in the amount of $LiCoO_2$ particles in the tested electrodes. We observed a significantly better cycling performance of CNT-based electrodes at a 4.5-volt cut-off as compared with conventional laminate electrodes. The CNTLCO electrode performed the best in the 2.75 – 4.2 volt cycling range. The electrodes containing diamonds demonstrated the worst performances. This could be attributed to the higher porosity created by the addition of diamonds in the CNT/$LiCoO_2$ structure. We assumed that the CNTLCO electrodes possess a better connection between

the $LiCoO_2$ particles and the CNTs. The high porosity of CNTLCOND and CNTLCOMD electrodes, as compared to CNTLCO, is indirectly confirmed by their superior rate performance and overall lower polarization

SEM inspection was used to analyze the CNTs incorporated in the electrode samples. It was found that CNTs were entangled and randomly orientated in lateral planes (figure 2). It is widely known that bulk diamond has an excellent thermal conductivity (~2000 W/mK)[14]. In this work, we studied the effect of micron and nanometer sized diamond particles on the in-plane and cross-plane thermal conductivity values. Although the thermal conductivity of µ and nano size diamond is expected to substantially decrease as a result of the phonon boundary scattering[15-17], it is still significantly higher than conventional electrode base materials. The average thicknesses of the CNT, CNTLCO, CNTLCOND, and CNTLCOMD electrode samples were 30 µm, 45 µm, 35 µm, and 33 µm, respectively. The thicknesses of the top and bottom CNT layers ranged from 7 µm - 8 µm. The individual multi-wall CNTs were aligned parallel to the filter.
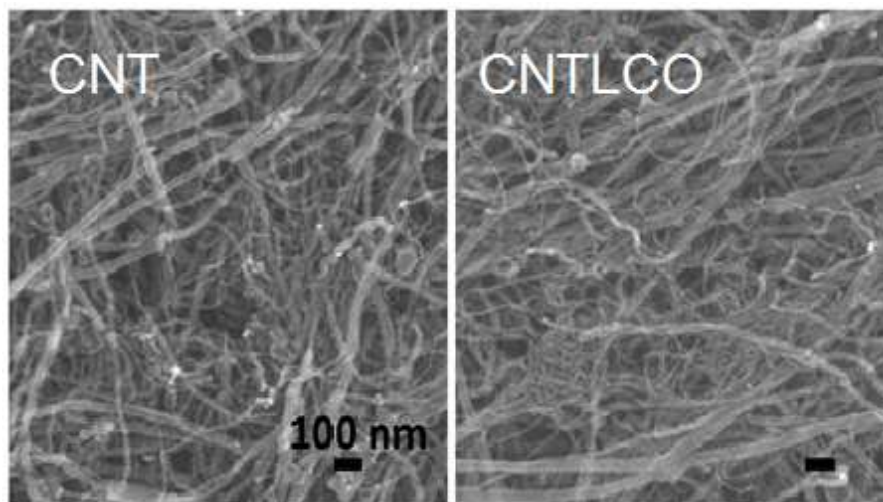
**Figure 2.** SEM images of the lateral plane of a control CNT bundle array and a composite $LiCO_2$/CNT electrode sample.

The in-plane and cross-plane thermal conductivity was measured using the Hotdisk and Laser flash techniques, respectively. For the cross-plane thermal conductivity measurements, a xenon flash lamp emits shots of energy of 10 joules/pulse on the surface of the electrode sample and a liquid nitrogen cooled In-Sb (Indium-Antimonide) infra-red detector measured the temperature rise on its opposite side. The temperature evolution on the rear of the electrode is read and converted into an amplified signal. A mathematical model (Cowan model) was used to fit the recorded curve in order to determine the thermal diffusivity and then the thermal conductivity was calculated using the known density and specific heat value of the sample. Figure 3 shows a representative temperature rise curve (blue curve) of the reference CNT electrode sample, which has been fitted using the Cowan model (red curve).
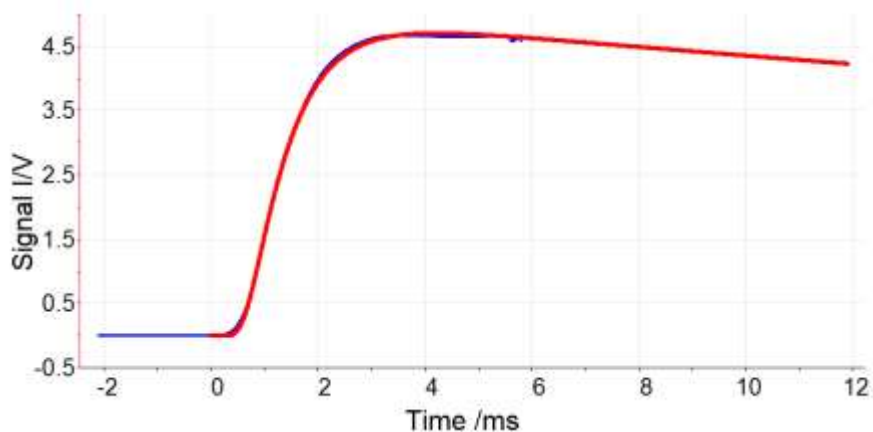
Figure 3. Representative temperature rise curve of a reference CNT electrode sample measured using an InSb detector.

Figure 4 summarizes the in-plane and cross-plane thermal conductivity values for CNT-based $LiCoO_2$ and a control CNT sample. The CNTLCO electrode sample is shown to have an in-plane thermal conductivity value as high as ~206 W/mK, which is comparable to that of Aluminum. Aluminum is a known material used as a current collector in Li-ion cells and an effective heat sink. The thermal conductivity measured for our fabricated electrodes is around three orders of magnitude higher than those of traditional laminate electrodes. The cross-plane thermal conductivity values of our electrodes were three orders of magnitude lower than its in plane value but it was still comparable to conventional laminate electrodes (0.07 – 0.41 W/mK)[8]. Both the in-plane and cross-plane thermal conductivity of our CNTLCO electrode was significantly greater than that of the control CNT bundle array. The mass density and microstructure analysis of our electrode samples have not shown any correlation with their high thermal conductivity value. We believe that the highest thermal conductivity values achieved by the CNTLCO electrode results from a lower disorder and a better coupling between the CNTs and $LiCoO_2$ particles
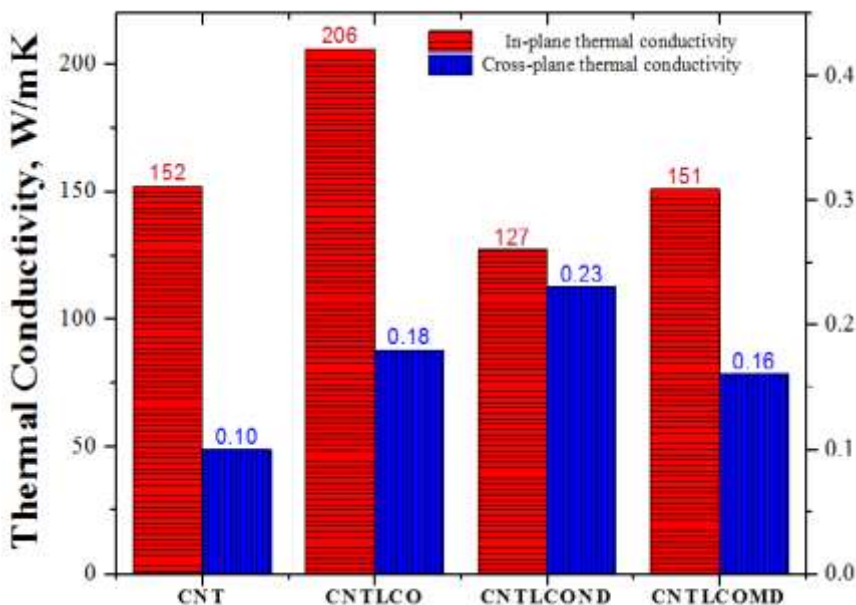
Figure 4. Comparison of the in-plane (uniform color bars) and cross-plane (shaded color bars) thermal conductivity values of the fabricated electrode samples.

The results demonstrate that the in-plane thermal conductivity values of CNTLCOMD and CNTLCOND electrodes were lower than that of the CNTLCO electrode. The reduction in in-plane thermal conductivity can be a result of additional scattering of phonons propagating in individual CNTs near adjacent diamond particles. An improvement of cross plane thermal conductivity in CNTLCOND over CNTLCO was observed and explained by superior coupling between the CNTs and nano sized diamonds in the cross plane direction. The cross-plane thermal conductivity of the electrode sample fabricated with long CNTs (100 µm) was measured to be significantly lower than that of previously reported CNT-based electrodes assembled using polydispersed CNTs[1]. This can be attributed to the more pronounced lateral stacking arrangement of longer CNTs. These results showed that the arrangement of CNTs and their alignment are important factors in determining thermal conductivity. More work must be done to optimize the size of diamond particles to improve their coupling to other electrode active materials and the overall thermal conductivity of the electrode.

4. CONCLUSIONS

We demonstrated that Li-ion electrodes fabricated from commercially available $LiCoO_2$ particles and multi-walled CNTs (~100 µm long) can reach an in-plane K value as high as that of aluminum (205 W/mK). The reported values of in-plane K of the CNT-based electrodes exceeded that of conventional laminate electrodes by three orders of magnitude. While their cross-plane K values were not as high, they compared well within the range found in dry conventional laminate electrodes. The electrochemical performance of CNT-based electrodes was observed to exceed that of laminate electrodes both in terms of stability and rate performance. Although the addition of micro and nano sized diamonds did not improve the thermal conductivity of CNT-based electrodes, their presence improved the overall electrochemical rate performance.

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