



Design of lithium cobalt oxide electrodes with high thermal conductivity and electrochemical performance using carbon nanotubes and diamond particles



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ABSTRACT

Thermal management remains one of the major challenges in the design of safe and reliable Li-ion batteries. We show that composite electrodes assembled from commercially available 100 μm long carbon nanotubes (CNTs) and LiCoO₂ (LCO) particles demonstrate the in-plane thermal conductivity of 205.8 W/m²K. This value exceeds the thermal conductivity of dry conventional laminated electrodes by about three orders of magnitude. The cross-plane thermal conductivity of CNT-based electrodes is in the same range as thermal conductivities of conventional laminated electrodes. The CNT-based electrodes demonstrate a similar capacity to conventional laminated design electrodes, but revealed a better rate performance and stability. The introduction of diamond particles into CNT-based electrodes further improves the rate performance. Our lightweight, flexible electrode design can potentially be a general platform for fabricating polymer binder- and aluminum and copper current collector-free electrodes from a broad range of electrochemically active materials with efficient thermal management.

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1. Introduction

Since the first demonstration of Li-ion batteries based on layered TiS₂ cathode and metallic lithium anode in 1976 [1], it took about 15 years to release the first rechargeable commercial Li-ion battery [2]. Now rechargeable Li-ion batteries became common in consumer electronics and their popularity continues to grow for electric vehicle and aerospace applications. Such batteries have a number of attractive properties. They are lightweight; provide high energy density; and have low self-discharge. Recent progress in battery materials research allowed significant improvement in design of high energy density and high power Li-ion batteries [2–6]. However, the safety aspects of Li-ion batteries are still not properly addressed [2,7]. Transportation and grid-scale energy storage applications require high energy density battery systems

that are realized via assembly of large format cells into packs. Even though Li-ion batteries have high efficiency (~85–90%) in converting of the stored chemical free energy into electric work, still a certain amount of energy will be lost as a result of ohmic heating owing to the current flow through the internal resistance during operation of any battery [8–10]. In addition, thermodynamics of the chemical reactions during charging and discharging cycles, especially within the cathode materials can also contribute to heating events in Li-ion batteries [11–13]. While dendrite growth is a concern for anodes, especially in Li-metal batteries [14], the low thermal stability of the cathode material and its tendency to release pure oxygen, promoting combustion, when over-charged [2,15] impose safety problems for cathodes in Li-ion batteries. Overheating of the battery results in the performance degradation, decreased battery life, and more seriously, increased risk of fire or explosion. Another problem of the Li-ion battery is their temperature-dependent performance [12,16–19]. Therefore, thermal management becomes a serious issue that impedes the spreading of high energy density batteries for large-scale

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applications [15].

The thermal management at the pack level can be achieved via circulating air or liquid heat transfer media around the battery packs. This active cooling approach is mainly applied to large scale electric automotive and aerospace applications since it requires complex, large, heavy, and expensive universal active cooling systems. For smaller electric vehicles and devices, it is more appropriate to utilize a passive cooling strategy that does not require cumbersome additional cooling systems. For example, cells can be surrounded by phase change materials (PCM) that absorb the generated heat in Li-ion cells and melt up upon heating. When cells cool off, the PCM hardens releasing the heat into the outside media. However, the poor thermal conductivity of PCM can result in slow heat dissipation which can create unfavorable thermal regime for battery operation [20]. Combination of PCM and aluminum heat transfer matrix is suggested to improve the low heat conductivity of the PCM.

Besides thermal management at the pack level, there are more direct approaches to improve the safety of batteries at the individual cell level. It has been known that the poor heat transfers across the interface of a cathode and a separator limits the heat dissipation, and the heat built up at the interface region causes the decomposition of solid electrolyte interface and shortage of the circuit as a result of separator failure [21]. Therefore, multilayer separators, ceramic particle coatings and thermoresponsive polymers that decrease conductivity due to expansions upon heating have been adopted to prevent the catastrophic failures by permanent shut down of the battery in the event of overheating [7]. Therefore, a great number of interesting ideas have been considered to minimize the consequences of battery failure with the assumption that the conventional design of the electrodes remains unchanged.

The conventional design of the electrodes in Li-ion battery is based on the laminated composite film, which consists of electrochemically active material, carbon black conducting agents, and polymer binder, coated on metal foil current collector [22]. Such electrode design is proved to be effective for achieving good electrochemical performance and for mass production. Even with small loadings, the carbon black takes large volume fraction in the structure of conventional cathode electrodes and plays a critical role in creating good electrical connections between the active material particles and the aluminum current collector. However, the carbon black is a poor thermal conductor. The low thermal conductivity of the carbon black, which is typically in the range between ~ 0.1 and $1 \text{ W/m}^2\text{K}$ at room temperature, is the main reason for the overall low heat dissipation property of the conventional cathode electrodes [23,24]. Moreover, the electrodes fabricated via conventional laminate process have high porosity and a granular microstructure that are not optimal for fast thermal conduction. Poor thermal conductivity may also create thermal and electrical gradients within the electrodes that can lead to locally unbalanced states of charging and discharging (i.e., local overcharging and discharging) [25]. It is noteworthy that the dry conventional cathode electrodes demonstrate thermal conductivity in the range between $0.27 \text{ W/m}^2\text{K}$ and $0.79 \text{ W/m}^2\text{K}$ [26–28]. The wetting of the dry electrode with electrolyte and interfacing it with aluminum foil can increase the thermal conductivity up to $8.23 \text{ W/m}^2\text{K}$ [27]. In the light of raising concerns of thermal management for safer Li-ion batteries, it is imperative to consider alternative approaches of electrode assembly that can provide material-level thermal management solution without compromising the electrochemical performance.

A possible approach for addressing the low thermal conductivity issue is to replace the carbon black with other carbon allotropes that have better intrinsic thermal conductivity. In this

scenario, graphene [29] and carbon nanotubes (CNTs) [30,31], have become promising alternatives for the design of the electrode matrix [32]. The concept of using different carbon allotropes such as graphene, CNTs and fibrous carbon aerogels has been explored in order to fabricate binder free, flexible electrodes for Li-ion batteries [33,34] and Zn-air batteries [35]. The high quality single layer graphene reveals thermal conductivity in the range from $2000 \text{ W/m}^2\text{K}$ to $5000 \text{ W/m}^2\text{K}$ [29]. The graphene based structures obtained by annealing of graphene oxide demonstrated thermal conductivities of $\sim 61 \text{ W/m}^2\text{K}$ [36]. The thermal conductivity of the reduced graphene oxide is lower than that of graphene owing to the high concentration of defects, structural disorder and relatively small size of sp^2 domains. However, composites assembled from extended graphene monolayers can present a challenge for electrolyte diffusion due to the lodging of the pores [37]. In turn, thermal conductivity of individual CNTs was experimentally reported to be in the range from $1750 \text{ W/m}^2\text{K}$ to $5800 \text{ W/m}^2\text{K}$ [38]. The electrical conductivity of compacted CNT structures was found to be even higher than that of the compacted graphene structures [39]. Generally speaking, both CNTs and graphene offer excellent electrical and thermal conductivities attractive for Li-ion battery applications. However, most of the studies on the alternative electrode designs utilizing carbon allotropes focus mainly on the electrochemical and mechanical aspects of the batteries and only limited number of studies discuss the thermal management aspects [32,34].

Previously, various types of binder-free electrode designs have been suggested. However, most of them are only applicable to nano-scale active materials, such as nanoparticles [40,41], nanowires [42–44], and hierarchical structures [45,46]. Hasegawa et al. [47] demonstrated moderate performance of binder-free LiCoO_2 electrode prepared with CNT (less than 10 wt%). However, their $\text{LiCoO}_2/\text{CNT}$ composite electrodes without current collector indicated significant rise in cell impedance particularly at high current density. Herein, we report on thermal conductivity and electrochemical performances of free-standing $\text{LiCoO}_2/\text{CNTs}$ composite electrodes without using carbon black, polymeric binder, and Al foil current collector. The novel composite electrodes demonstrated excellent lateral thermal conductivity up to about $205.8 \text{ W/m}^2\text{K}$, which is three orders of magnitude higher than the thermal conductivity of the conventional laminated electrodes, without compromising specific capacity of LiCoO_2 . The rate capability and deep cycling stability of the composite electrodes are even better than those of the conventional laminated electrode. We also discuss the effect of micron sized diamond particles and diamond nanoparticles on the thermal conductivity and electrochemical properties of the $\text{LiCoO}_2/\text{CNT}$ composite electrodes.

2. Experimental section

2.1. Materials and sample preparation

LiCoO_2 (LCO) particles were purchased from Sigma-Aldrich and used without any further modification/optimization. We used c-grade multi-walled CNTs purchased from NanoTechLab ($\geq 95\%$ purity, $100 \mu\text{m}$ long, diameter of CNTs is in the range of $5\text{--}30 \text{ nm}$). The nanosized ($\sim 2.3 \text{ nm}$) diamond and micron-sized ($\sim 8\text{--}16 \mu\text{m}$) diamond powder samples were obtained from International Technology Center, Raleigh and NC Diamond Innovations, respectively. All samples for thermal conductivity and electrochemical tests were obtained by vacuum filtration of corresponding solutions through the filter such as microporous glass fiber filter (Wachman GF-F). Table 1 provides the information on the amounts of materials used for different types.

Corresponding amounts of materials were dispersed in 250 mL

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