



Analysis of geometric and electrochemical characteristics of lithium cobalt oxide electrode with different packing densities



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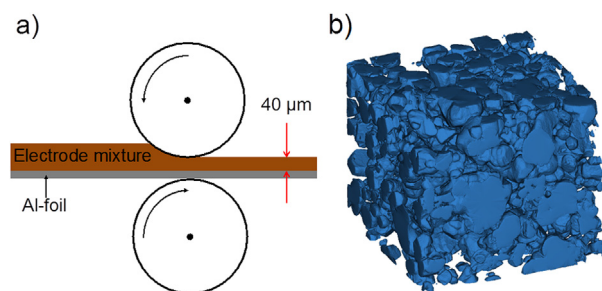
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GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 3 February 2016

Received in revised form

30 June 2016

Accepted 31 July 2016

Keywords:

Li ion battery

Synchrotron nano-computed tomography

Calendering

Packing density

Geometric characteristics

ABSTRACT

To investigate geometric and electrochemical characteristics of Li ion battery electrode with different packing densities, lithium cobalt oxide (LiCoO_2) cathode electrodes were fabricated from a 94:3:3 (wt%) mixture of LiCoO_2 , polymeric binder, and super-P carbon black and calendered to different densities. A synchrotron X-ray nano-computed tomography system with a spatial resolution of 58.2 nm at the Advanced Photon Source of the Argonne National Laboratory was employed to obtain three dimensional morphology data of the electrodes. The morphology data were quantitatively analyzed to characterize their geometric properties, such as porosity, tortuosity, specific surface area, and pore size distribution. The geometric and electrochemical analysis reveal that high packing density electrodes have smaller average pore size and narrower pore size distribution, which improves the electrical contact between carbon-binder matrix and LiCoO_2 particles. The better contact improves the capacity and rate capability by reducing the possibility of electrically isolated LiCoO_2 particles and increasing the electrochemically active area. The results show that increase of packing density results in higher tortuosity, but electrochemically active area is more crucial to cell performance than tortuosity at up to 3.6 g/cm^3 packing density and 4 C rate.

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1. Introduction

Over the last decade, rechargeable Li ion batteries (LIBs) have been widely utilized in portable electronics and become a popular power source for electric vehicles. The energy and power capabilities of LIBs have been considered crucial factors to determine the commercial values of the LIB powered applications. Many efforts have been done to improve the energy density and rate capability of LIBs. According to intrinsic material properties of anode and cathode active materials, high energy and power densities are achieved with high charge/discharge capacity, voltage and rate capability per unit mass or volume. In addition to material properties, the structure of electrode at micro and nano scales also plays a critical role in determining the energy density and rate capability of a LIB. Typically, a LIB electrode consists of active material, polymeric binder, and conductive carbon additive. The micron-sized active material particles are electrically connected via the nanometer-sized conductive carbon particles and maintained the mechanical integrity of the porous microstructure with polymeric binder. Using standard calendaring process, present-day LIBs have ~50% of their volume occupied by the active materials [1,2]. Increased calendaring can increase the packing density of active materials in LIB electrodes, thereby increasing the volumetric energy density. The specific energy density is also increased by calendaring via decreasing the percentage of inactive materials, such as current collector and separator. However, higher fraction of active materials in LIB electrodes can change electrodes' structural properties significantly, such as porosity, specific surface area, pore size distribution and tortuosity. In addition, the packing density of active materials also can change the distribution of polymer binder and carbon additives in the porous microstructure of LIB electrodes [3]. These factors could have impacts on the performance of a LIB.

To this end, some research work has been conducted to study the calendaring effect on electrochemical properties of LIB electrodes [4–6] and the impact of weight fraction of polymeric binder and conductive carbon additive on the performance of LIB electrodes [3]. For instance, Zheng et al. investigated calendaring effects on the physical and electrochemical properties of $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2]$ (NMC) cathode [4,7]. They found that calendaring improves the electrical conductivity between active material particles at relatively high porosities, but increases charge transfer resistance at electrode/electrolyte interface at relatively low porosities. van Bommel et al. investigated the effect of calendaring LiFePO_4 electrodes and found that calendaring resulted in a large decrease in contact resistance at the current collector - electrode interface and maintained their capacity better than uncalendered electrodes at high charge/discharge rates [5]. Haselrieder et al. studied the influence of the calendaring process on surface morphology, mechanical, structural and electrochemical properties of graphite electrodes [8]. They found that the calendaring doesn't have significant impact on power performance. Dahn et al. have reported the electrode compression effects on the LIB performance by enhancing the electrical connection of a low carbon contained cathode electrode [9]. Lai et al. reported a sintered binder-free lithium cobalt oxide (LiCoO_2) electrode with up to 87 vol% density for microscale applications [1]. Liu et al. introduced a physical model in which acetylene black and active material particles compete for polymer binder, which forms fixed layers of polymer on their surfaces [3].

However, there are few reports on the geometric characteristics and their impact on the electrochemical performance of LIB electrodes with different packing densities due to the inhomogeneity, complexity, and three-dimensional (3D) nature of the electrode's microstructure. The effects of geometric properties have been studied based on various mathematical models, such as particle

size distribution [10,11], porosity distribution [12], and the contact resistance of various sizes of particles [13]. These models are based on the assumed homogeneous electrode microstructure or computer generated 3D electrode microstructures. Recently, porous electrode microstructures have been reconstructed by advanced tomography techniques such as X-ray nano-computed tomography (nano-CT) [14–20] and focused ion beam scanning electron microscope (FIB-SEM) [21–23]. The reconstructed microstructures have been employed to investigate the geometric characteristics and spatial inhomogeneity of porous electrodes [24–29]. Moreover, these techniques facilitated numerical studies of electrochemical systems by providing realistic microstructures [30–34]. By using synchrotron radiation X-ray tomographic microscopy, Ebner et al. studied the influence of compression and carbon black and binder content on NMC cathode electrode porosity and discharge capacity as a function of discharge rate [35]. However, more detailed geometric and electrochemical characteristics were not discussed in this report and the voxel size of the synchrotron radiation X-ray tomographic microscopy is $0.37 \times 0.37 \times 0.37 \mu\text{m}^3$, which is relatively large if smaller active material particles are investigated.

Therefore, the purpose of this paper is to investigate the realistic geometric characteristics of LiCoO_2 cathode electrode microstructures with different packing densities and their impacts on electrochemical performance using synchrotron X-ray nano-CT technique with high spatial resolution. Although FIB-SEM tomography enables the detection of carbon-binder matrix, it was not chosen in this study due to the time consumption and difficulty of operation [30]. As mentioned earlier, the porous microstructure of LIB electrodes is dominated by the active and inactive materials and fabrication methods. In this study, LiCoO_2 was chosen as the model material and five LiCoO_2 electrodes were fabricated from a same composition of materials, and calendered to an identical thickness under different packing conditions. We reconstructed the porous microstructures of differently packed electrodes to examine geometric characteristics by employing synchrotron transmission X-ray microscopy (TXM) at the Advanced Photon Source (APS) of the Argonne National Laboratory (ANL). The electrodes were assembled in coin cells with a Li counter electrode for investigating the electrochemical characteristics. The fixed electrode thickness and material composition allow us to investigate the effects of packing density on the porous microstructure and electrochemical performance of LiCoO_2 electrodes.

2. Experimental

2.1. Materials

LiCoO_2 active material (99.5% 5 μm APS powder) was received from Alfa Aesar, Ward Hill, MA, super-P carbon black (C65, TIMCAL Ltd.) was from MTI, Richmond, CA, polyvinylidene difluoride (KF 1120 polymer – 12 wt % PVDF) binding agent was from Kureha, New York, NY, and *N*-methyl-2-pyrrolidinone solvent (NMP, anhydrous 99.5%) was from Sigma-Aldrich, St. Louis, MO, USA. EC/DEC Electrolyte containing 1 M LiPF_6 in a 1:1 volume-ratio mixture of ethylene carbonate and dimethyl carbonate was received from BASF, Elyria, OH, USA.

2.2. Electrode fabrications and cell assembly

The active material, binder, and carbon black current conductor (94:3:3 of weight ratio) were added in NMP solution. There are two reasons that we chose low carbon black and binder content in this study. The first one is that low carbon black and binder content can achieve high energy density which is very important in battery industry. The second one is that carbon black and binder cannot be

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