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Multi-scale 3D investigations of a commercial 18650 Li-ion battery with correlative electron- and X-ray microscopy

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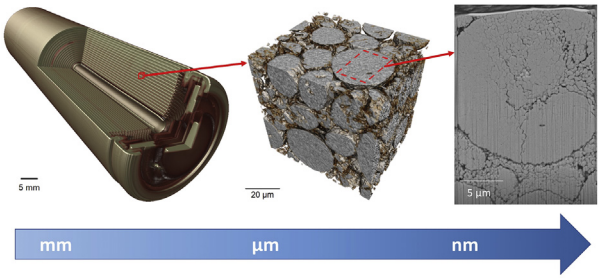
HIGHLIGHTS

- A commercial 18650 battery was studied using correlative microscopy (XRM & SEM).
- A virtual model of the battery microstructure and composition was constructed.
- Porosity, tortuosity, and effective diffusion coefficient were quantified.
- The Bruggeman exponent was determined, using standard image processing routines.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, a commercial 18650 Li-ion cylindrical cell is investigated with non-destructive 3D X-ray microscopy across a range of length scales, beginning with a survey of the entire cell and non-destructively enlarging a smaller section. Active materials are extracted from a disassembled cell and imaging performed using a combination of sub-micron X-ray microscopy and 2D scanning-electron microscopy, which point toward the need for multi-scale analysis in order to accurately characterize the cell. Furthermore, a small section is physically isolated for 3D nano-scale X-ray microscopy, which provides a measurement of porosity and enables the effective diffusivity and 3-dimensional tortuosities to be calculated via computer simulation. Finally, the 3D X-ray microscopy data is loaded into a correlative microscopy environment, where a representative sub-surface region is identified and, subsequently, analyzed using electron microscopy and energy-dispersive X-ray spectroscopy. The results of this study elucidate the microstructural characteristics and potential degradation mechanisms of a commercial NCA battery and, further, establish a technique for extracting the Bruggeman exponent for a real-world microstructure using correlative microscopy.

1. Introduction

There is considerable and growing research interest in Li-ion batteries driven largely by an increase in dependence on energy storage solutions, for applications ranging from mobile electronics to stationary power supplies and electric vehicles [1–3]. In the coming years, increasingly demanding applications from mW to MW, will require advanced Li-ion batteries to operate under extremes of temperature, rate, and pressure. Li-ion batteries are expected to deliver high performance, over long lifetimes, at a reduced cost as compared to existing solutions. With growing dependence on Li-ion technologies, in particular due to the

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growing popularity of hybrid- and fully-electric vehicles [2], it is of paramount importance to understand how batteries perform, age, and degrade under real-world conditions [4,5]. Recent high profile failures have emphasized the need to better understand these processes [6–8].

There are a range of Li-ion battery architectures commercially available, such as pouch, prismatic, and spiral wound cells; by far the most common geometry is the 18650 cell, which has found diverse applications from consumer electronics [9] to aerospace equipment [10] and automotive power trains [11]. While the chemistry within these cells may vary, there are common components across most available commercial cells: the functional cell comprises two porous electrodes, electrically isolated by a porous separator material, the three layers are spiral wound into the 18650 casing, and various safety components including positive temperature coefficient (PTC) devices, pressure relief valves, and current interrupt devices are connected and crimped into the casing [9].

In recent years, there has been growing interest in the relationship between the complex and often heterogeneous microstructure of the porous electrodes and the electrochemical performance of the device. It is hypothesized that microscopic heterogeneities and defects [12] within these materials may act as nucleation points for macroscopic failures and, consequently, there is a need to understand these material microstructures in greater detail [13]. For example, the expansion and contraction of active electrode materials can cause SEI and particle fracture on the micro scale [14,15], whereas the same chemo-mechanical forces can result in severe delamination and electrical isolation of the bulk electrode [5,16]. The authors and others have led work over the past 5 years in the application of X-ray tomography to explore these materials both ex-situ [14,17–21] and in-situ [14,15,22,23]. Additional work using tomography and radiography to characterize cell architecture during failure [22] and post mortem [24,25] as well as to understand the role of safety features [26–28] help to build a comprehensive understanding of the role of each component in driving device degradation and failure. This work is complemented by extensive investigations using SEM [29,30]and FIB-SEM [31], TEM [32], XRD [33], and AFM [34], as well as multi-scale investigations that demonstrate the need for the integration of various imaging instruments to characterize batteries [35,36].

Collectively, these studies highlight the importance of understanding the multi-scale nature of Li-ion batteries from the pack to the particle levels [25,36]; it is essential that researchers identify appropriate length scale(s) for understanding key mechanisms that affect the performance and reliability of cells [36]. Macro-scale features, such as assembly issues, may affect the mechanical and chemical stability, while micro-scale features, such as particle assembly and porosity/tortuosity may affect the overall capacity and operational properties. Furthermore, nano-scale features, such as SEI growth, dendrite formation, and intraparticle cracks may affect the long-term safety and reliability of a battery, but must be understood in the context of other features [37]. There are many aspects of the battery's microstructure that may dictate its performance, but it is important to simultaneously consider features ranging from the macro-to the micro- and nano-scales [35,36].

This multi-scale challenge can be effectively addressed by correlative lab-based imaging instrumentation, using optical, electron and ion beam microscopy and 3D micro- and nano-XRM [25]. Using this correlative imaging approach, each modality is used for its unique strength: for example, the tunable magnification of SEM in 2D and switchable energy dispersive X-ray spectrometry for chemical analysis, along with the non-destructive 3D and 4D imaging capabilities of XRM [38,39].

Recent progress in 3D imaging techniques have indicated deviations between theoretical models and actual formations in battery microstructures and, in so doing, have grown in popularity. Historically, microstructure investigations have hinged on stereological techniques, but the results are often inconclusive [40]. Recent 3D imaging studies have illustrated the anisotropic, non-ideal nature of a “typical” Li-ion battery electrode microstructure, which has demonstrated that models based purely on single 2D images may not be sufficient to accurately describe the transport properties of electrode materials [41]. Using 2D stereological approaches alone may, thus, lead to inaccurate representations of the microstructures leading to ultimate errors in characterization; these issues can be mitigated by employing 3D imaging approaches, such as XRM and FIB-SEM [40].

The present study demonstrates, for the first time, the application of both XRM and SEM to probe a single commercial 18650 Li-ion battery across multiple length scales, starting with the full cell and moving all the way down to examining sub-particle features. X-ray techniques afford the unique capability for non-destructive imaging, allowing the same sample to be imaged multiple times under different conditions. Using this advantage, the present study thus paves the way for future investigations in which 18650 batteries may be studied before, during, and after aging cycles, in a so-called “4D” imaging experiment. This information forms a foundation for several such future imaging studies and illustrates the unique abilities of modern microscopy techniques to aid in the advancement of Li-ion battery research and development.

2. Materials and methods

2.1. Materials preparation

Commercially sourced Panasonic NCR 18650-B cylindrical cells were used for the present study. These high energy density cells contain a nickel-cobalt-aluminum oxide (NCA) positive electrode and have demonstrated applications for mobile electronics and electric vehicles [42].

2.2. X-ray microscopy

X-ray microscopy (XRM) was used to non-destructively collect 3D volumetric data on the specimens and survey them before any dismantling. XRM, discussed extensively elsewhere [35,38,43–45], uses the X-ray computed tomography (CT) approach to collect 3D images of specimen interiors by collecting a series of projection X-ray radiographs at various viewing angles (achieved by rotating the specimen and exposing it to the X-ray beam). The resulting projection images were subsequently reconstructed using a Feldcamp-Davis-Kress (FDK) or filtered back projection (FBP) algorithm (the former for micron-to sub-micron imaging, and the latter for nano-scale imaging) [46], and the 3D datasets produced by this process were rendered and analyzed for porosity using ORS Visual Si Advanced (Object Research Systems, Montreal, QB, Canada) [38,44]. Further simulation studies were performed using GeoDict (Math2Market, Gmbh, Kaiserslautern, Germany) [47], which computed effective diffusivity [48,49], tortuosity [50], and, by means of morphological manipulation, a Bruggeman coefficient for the specimen under study.

Initial investigations were performed using a ZEISS Xradia 520 Versa X-ray microscope (Carl Zeiss X-ray Microscopy, Pleasanton, CA, USA), equipped with a 0.4 × objective lens to provide a 3D isotropic voxel size of 22 μm across the entire imaging volume. This allowed the entire width of the 18650 cylindrical cell to be captured in a single field of view in ca. 1 h, after which further imaging was performed along the vertical axis to cover the entire length of the cylindrical cell. The resulting five datasets were then stitched