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Three-dimensional high resolution X-ray imaging and quantification of lithium ion battery mesocarbon microbead anodes

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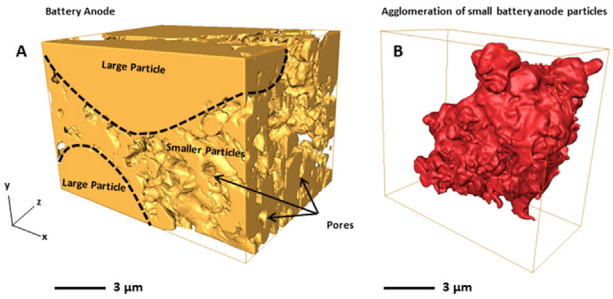
HIGHLIGHTS

- High resolution 3D nano-CT was used to image MCMB anodes down to 16 nm voxel size.
- A specimen labelling methodology was used to enhance image contrast.
- The 3D MCMB anode had a heterogeneous and bi-modally distributed microstructure.
- Anode was quantified via surface area, volume, connectivity and tortuosity factors.
- Complexity of both MCMB and electrolyte phases suggests inhomogeneous anode use.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to improve lithium ion batteries it is important to characterise real electrode geometries and understand how their 3D structure may affect performance. In this study, high resolution synchrotron nano-CT was used to acquire 3D tomography datasets of mesocarbon microbead (MCMB) based anodes down to a 16 nm voxel size. A specimen labelling methodology was used to produce anodes that enhance the achievable image contrast, and image processing routines were utilised to successfully segment features of interest from a challenging dataset. The 3D MCMB based anode structure was analysed revealing a heterogeneous and bi-modally distributed microstructure. The microstructure was quantified through calculations of surface area, volume, connectivity and tortuosity factors. In doing so, two different methods, random walk and diffusion based, were used to determine tortuosity factors of both MCMB and pore/electrolyte microstructures. The tortuosity factors (2–7) confirmed the heterogeneity of the anode microstructure for this field of view and demonstrated small MCMB particles interspersed between large MCMB particles cause an increase in tortuosity factors. The anode microstructure was highly connected, which was also caused by the presence of small MCMB particles. The complexity in microstructure suggests inhomogeneous local lithium ion distribution would occur within the anode during operation.

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1. Introduction

Meeting increasing energy demands, storage requirements and energy portability will be expedited through an ability to directly image battery micro/nano structures at high resolutions in three dimensions (3D). In doing so, it is possible to relate battery structure with behaviour. An ability to circumvent current contrast limitations when imaging state-of-the-art lithium ion battery electrodes and quantify them provides an important step towards achieving this goal. This capability offers the future optimisation of lithium ion batteries through better microstructure designs.

A typical lithium ion battery consists of three components; a graphite based anode, metal oxide cathode and a separator composed of a polymer and organic electrolyte. It is beyond the scope of the paper to review different bulk and surface processes responsible for battery functioning, ageing or failure. Nonetheless it is well known that some of these bulk processes are associated with structural transformation of the solid phase of battery electrodes and that in certain cases (e.g. or Sn electrodes) they can induce large volumetric expansions of up to 300% [1]. Other processes are linked to the surface reactions between lithium and electrolyte to form a thin, passive solid electrolyte interphase (SEI) film [2,3]. Therefore the microstructure of the electrodes will affect, and also be affected by, these processes.

The effects of electrode microstructure on cell level performance and degradation have been widely acknowledged, however it is only relatively recently that the availability of high resolution tomography tools have enabled the capture of complex 3D geometry of battery electrodes with sufficient detail. Recent studies present the application of focused ion beam tools [4–6] as well as laboratory and synchrotron X-ray CT [7–10] to resolve electrode structures into 3D, and these data have also been successfully combined with modelling tools to explore the relationship between microstructure and performance [11,12]. In this paper we report the application of nano-scale resolution X-Ray tomography to study the microstructure of graphite-based electrode materials and then quantify both the pore and MCMB phases.

Until now, imaging of graphite particles at sub-100 nm resolution in 3D has been difficult due to (i) the low X-ray attenuation coefficient of graphite and (ii) the interaction of graphite with focused ion beams, which can lead to highly non-uniform nano-scale milling. Therefore the precise nanostructure of graphite-based anodes at high resolution has been poorly understood. This paper applies a labelling technique to improve contrast between the polymer binder and the electroactive mesocarbon microbead (MCMB) particles used for lithium ion battery anodes. As the labelled binder coats MCMB particles during anode fabrication, this also helps in the identification of MCMB particle edges. The use of MCMB particles is also useful for simulation purposes due to their sphericity [13,14]. We demonstrate here a methodology to obtain 3D micro/nano structural information of battery anodes and use it to characterise complex anode geometries, and thereby begin to understand how they function. In doing so, new insights are gained that could be used to develop improved anode designs.

2. Experimental

X-ray nano-tomography (nano-CT) involves using an X-ray beam to produce a series of transmission projection images of an object as it is rotated though multiple angles (Fig. 1). The resulting contrast in each acquired image is a function of the attenuation coefficients or interference effects of the phases through which the X-ray is transmitted. While X-ray sources themselves may be laboratory based, synchrotron X-ray sources provide parallel, monochromatic illumination with both good signal-to-noise and high-resolution capabilities [15]. The validity of X-ray tomography as a technique in imaging battery electrodes has been demonstrated in several studies [7,16,17]. As nano-CT instruments have a limited field of view, samples must be carefully prepared to ensure they fit within it [18].

Graphite anode mesocarbon microbeads (MCMB 6-28, Osaka Gas Co.) particles were fabricated in the following manner: an anhydrous LiI salt (Sigma–Aldrich) used as a labelling agent and polyethylene oxide (PEO, Sigma–Aldrich, 5×10^6 M.W.) was dissolved in acetonitrile followed by addition of the corresponding amount of MCMB graphite. The resulting solution was then cast on thin copper foil. The final composition of the anode consisted of 88%w/w MCMB, 10%w/w PEO and 2%w/w LiI. LiI was selected due to presence of heavy iodide ion that creates a contrast between graphite and the binder for X-rays. The PEO is known for its ability to dissolve LiI and form solid state complexes with various stoichiometry [19]. Similarly, the iodine-based compounds, called radiocontrasts, are widely used in medical CT [20]. It is worth noting the PEO binder was selected to serve as a complexing agent for LiI which cannot be achieved using more conventional binders based on polyvinylidene fluoride (PVDF). Although PEO is not a common binder it can be used as a binder for both cathode and anode fabrication [21]. For further details concerning PEO and LiI the reader is referred to other studies [22–29].

Following preparation, the MCMB sample was imaged in scanning electron mode using a Zeiss Auriga dual beam (FIBSEM) microscope with an accelerating voltage of 2 kV. X-ray imaging was subsequently conducted using an Xradia nanoXCT-S100 TXM at synchrotron beamline 6-2-C at the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, USA (Fig. 1). A field of view of $\sim 15 \times 15 \times 12$ μm was acquired with 721 transmission images taken at 0.5° rotation intervals using 6.5 keV incident X-ray beam energy. The transmission images were reconstructed using a standard parallel beam filtered back-projection algorithm (Xradia Reconstructor) producing a final dataset with isotropic voxel size ca. 16 nm following alignments and reconstruction.

The acquired grey-scale 3D datasets were analysed using image processing techniques to segment MCMB particles and porous (electrolyte) regions out of the bulk volume. The anode structure was then evaluated using both commercial and in-house routines by calculating surface areas, volume fractions and tortuosity factors. Further details are provided in subsections of the paper.

Image analysis techniques had to be applied in order to segment and quantify the 3D imaged data. The general procedure involves

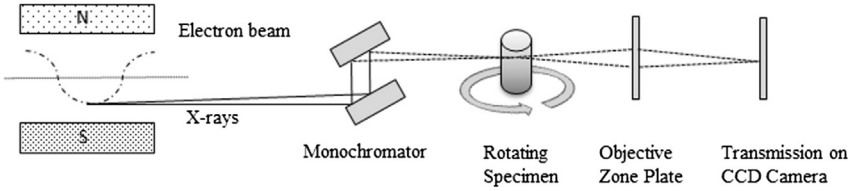

Fig. 1. The X-ray nano-tomography beam-line setup at 6-2-C at SSRL. Samples are rotated relative to the source-detectors with field of view determined by post-sample Fresnel zone plates that focus X-rays prior to the CCD camera.