Chemical Engineering Science 154 (2016) 27–33

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

The use of contrast enhancement techniques in X-ray imaging of lithium–ion battery electrodes

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HIGHLIGHTS

- Micro- and nano-scale XRM were used to characterize a Li-ion graphite electrode.
- Enhanced X-ray image contrast was obtained by signal blending and optimization.
- Imaging resolution requirement varied with the investigated electrode parameter.

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form
30 March 2016
Accepted 11 April 2016
Available online 12 April 2016

Keywords:
Phase-contrast
X-rays
Graphite electrode
Image contrast

ABSTRACT

Understanding the microstructural morphology of Li–ion battery electrodes is crucial to improving the electrochemical performance of current Li–ion battery systems and in developing next-generation power systems. The use of 3D X-ray imaging techniques, which are continuously evolving, provides a non-invasive platform to study the relationship between electrode microstructure and performance at various time and length scales. In addition to characterizing a weakly (X-ray) absorbing graphite electrode at multiple length scales, we implement an approach for obtaining improved nano-scale image contrast on a laboratory X-ray microscope by combining information obtained from both absorption–contrast and Zernike phase-contrast X-ray images.

1. Introduction

Li-ion batteries have achieved widespread use in a variety of electronic applications, ranging from portable consumer electronic devices to electric vehicles and aircraft to grid storage applications. Electrochemical reactions which take place within Li–ion batteries are supported by porous composite electrodes, which consist mainly of particles of active material mixed with a conductive material and binder. The microstructure of these electrodes is inherently three-dimensional and has a strong influence on battery performance metrics such as durability, capacity retention, cyclability, and safety.

In recent years, the understanding of the microstructure within electrochemical devices has been revolutionized through the use of tomographic imaging techniques, mainly using X-rays (Ebner et al., 2013; Shearing et al., 2010a, 2010b; Yan et al., 2012) and focused-ion beam milling (Ender et al., 2011; Hutzenlaub et al., 2014; Wilson et al., 2011). Although destructive in operation, focused-ion beam tomography techniques provide sufficiently high resolution (typically <100 nm) and contrast suitable for understanding nano-scale properties within a porous electrode. X-ray computed tomography (CT) is a diagnostic tool that has been used to non-invasively explore a variety of real-life electro-active materials, thus providing unique insight not only into their complex, three-dimensional nature but also on their degradation, aging, and failure upon reaction or during device operation (Finegan et al., 2015a, 2015b; Yufit et al., 2011).

Tomographic imaging has been used to examine battery cathode materials, even at multiple length scales (Shearing et al., 2012); however, for low atomic number (low-*Z*) anode materials (e.g. graphite), conventional tomographic imaging approaches have some limitations. For instance, the Ga^+ focused-ion beam interacts with graphitic structures, often resulting in highly non-uniform surface milling; moreover, with conventional absorption contrast X-ray imaging, it is difficult to obtain high-contrast images due to the extremely small X-ray absorption coefficients of low-*Z* materials, especially at the nanometer length scale.

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http://dx.doi.org/10.1016/j.ces.2016.04.023

The proliferation of phase-contrast X-ray imaging modalities (Davis et al., 1995; Holzner et al., 2010; Irvine et al., 2014; Schmahl et al., 1994; Wilkins et al., 1996) has helped enhance contrast in X-ray images of weakly absorbing materials by utilizing phase shifts across the incident X-ray beam. For nanoscale imaging in particular, Zernike phase contrast X-ray imaging has been used to improve the contrast in CT images of graphite anodes (Eastwood et al., 2014) and of the conductive additive-binder phase in a Li–ion battery cathode (Komini Babu et al., 2015), enhancing the visibility of sub-micron features of interest within the electrode materials. Unfortunately, Zernike phase-contrast tomography on low-*Z* materials produces undesired artifacts, such as "halos" and "shade-off" (Otaki, 2000), which preclude the use of traditional image segmentation techniques that employ a single value threshold; however, images laden with such artifacts may be restored with use of algorithms which model the phase contrast optics (Kumar et al., 2015).

To address this problem, we develop and apply a combined contrast approach to characterize the three-dimensional (3D) microstructure in a graphite-based electrode material using image information obtained subsequently from both absorption–contrast and phase-contrast X-ray CT imaging. Previously, Komini Babu and coworkers (Komini Babu et al., 2015) successfully used Zernike phase-contrast and absorption–contrast X-ray CT imaging to separately resolve the active material and carbon-binder phases in a $LiCoO_2$ cathode material by merging the resulting segmented image data from both X-ray CT images with mathematical image operations. However, we have demonstrated the combination of absorption and phase contrast information from sequential X-ray imaging in a laboratory X-ray microscope without prior image segmentation by blending and optimizing the weighting of the signal from both X-ray images in order to create a final enhanced image with improved contrast. This technique leverages the benefits of both phase and absorption imaging: maintaining the fine detail of electrode cracks characteristic of phase images with the ease of image analysis of absorption imaging, which enables the use of single-threshold image segmentation and minimal post-processing of image reconstructions.

Here, we also present microstructural investigations at two length scales, using laboratory X-ray Microscopy (XRM) to image the bulk electrode and to identify a region of interest for subsequent investigation using nano-scale XRM. For the first time, we present the results of high-resolution studies on a graphite anode material using our unique combined phase/absorption approach.

2. Materials and methods

Graphite electrodes were prepared by mixing graphite powder (TIMREX® SLP30, TIMCAL, Switzerland), carbon black (Super P, Sigma Aldrich, UK), and PVDF binder (Pi-KEM, UK) in the respective percentage weight ratios 87:3:10 with *n*-methyl-pyrrolidone (Pi-KEM, UK) in a mixer (ULTRA-TURRAX, IKA-Werke GmbH, Germany). The resulting slurry was dried at 80 °C under vacuum for 24 h. The surface morphology of the prepared electrode was captured using scanning electron microscopy (ZEISS EVO MA 10, ZEISS, USA).

X-ray microscopy, or XRM, is an imaging technique that employs digital geometry processing to reconstruct a 3D image of the internal structure of an object from a series of two-dimensional (2D) X-ray projection images, which are recorded as the object is rotated about a single axis. When X-rays are incident upon an object, they are absorbed, transmitted, and/or scattered. In standard X-ray computed tomography (X-ray CT), the 2-D projection images are progressively obtained by passing a beam of X-rays from an X-ray source through the sample object as it is rotated at certain angular increments. The transmitted X-rays are then recorded by an X-ray detection system, in which the beam of high-energy photons is converted to visible light by a scintillator, imaged through an objective lens onto a CCD detector and read out into a computer for further processing. A 3D digital image of the object is then created by mathematically reconstructing the acquired series of 2D projection images where each voxel (volume element or 3D pixel) represents the X-ray absorption at that point.

Following electrode preparation, the three-dimensional microstructure of an electrode sample was examined using two X-ray tomography platforms: laboratory-based micron-scale XRM (ZEISS Xradia Versa 520, Carl Zeiss X-ray Microscopy Inc., Pleasanton, CA) and nano-scale XRM (ZEISS Xradia 810 Ultra, Carl Zeiss X-ray Microscopy Inc., Pleasanton, CA). Schematic representations of the micro-XRM and nano-XRM imaging setups are presented in Fig. 1a and b respectively. The micro-XRM system can perform non-destructive 3D X-ray imaging achieving true spatial resolution to

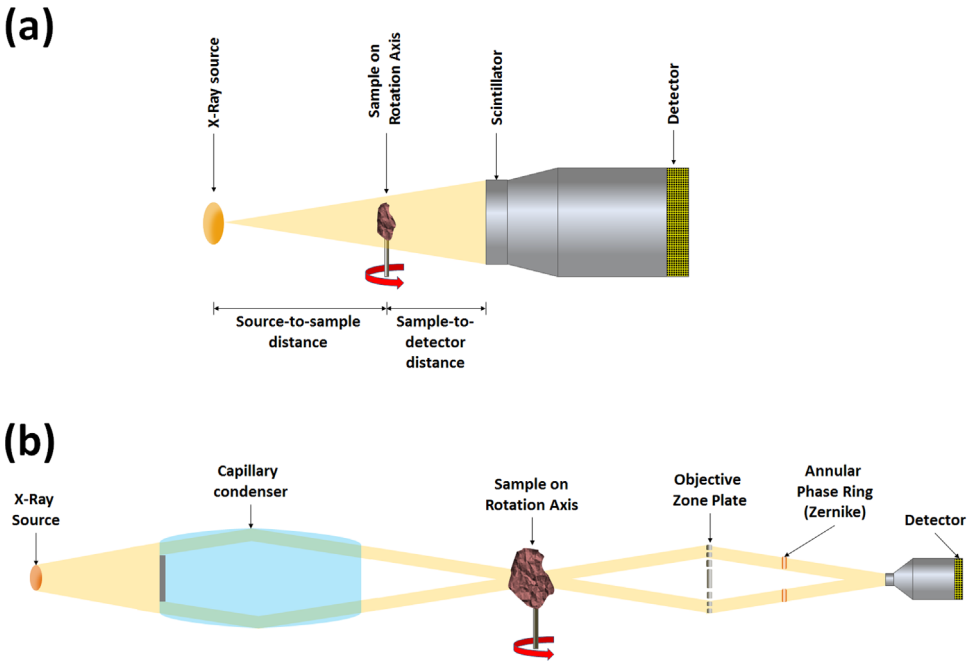

Fig. 1. Schematic of (a) a typical micro-scale laboratory XRM setup and (b) a nano-scale laboratory XRM setup operating in Zernike phase contrast mode.