Electrochemistry Communications 12 (2010) 374–377

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Characterization of the 3-dimensional microstructure of a graphite negative electrode from a Li-ion battery

P.R. Shearing [a], L.E. Howard [b], P.S. Jørgensen [c], N.P. Brandon [a,*], S.J. Harris [d]

[a] Department of Earth Science and Engineering, Imperial College London, London, United Kingdom
[b] Department of Mineralogy, The Natural History Museum, South Kensington, London, United Kingdom
[c] Risø National Laboratory, Roskilde, Denmark
[d] General Motors R&D Centre, Warren, Michigan, USA

ARTICLE INFO

Article history:
Received 10 December 2009
Received in revised form 23 December 2009
Accepted 24 December 2009
Available online 4 January 2010

Keywords:
X-ray tomography
Microstructure
Representative volume element
Battery
Graphite electrode

ABSTRACT

The 3-dimensional microstructure of a porous electrode from a lithium-ion battery has been characterized for the first time. We use X-ray tomography to reconstruct a $43 \times 348 \times 478$ μm sample volume with voxel dimensions of 480 nm, subsequent division of the reconstructed volumes into sub-volumes of different sizes allow us to determine microstructural parameters as a function of sub-division size. We show that the minimum size for a representative volume element is about $43 \times 60 \times 60$ μm for volume-specific surface area, but as large as the full sample volume for porosity and tortuosity.

1. Introduction

Li-ion batteries are generally analyzed using a macro-homogeneous porous electrode model [1,2]. Model input includes particle radius and porosity; otherwise, it assumes that the electrode is an isotropic, homogeneous, 1-dimensional porous material constructed from mono-disperse, non-porous isotropic spherical particles small compared to the electrode thickness. This model has been highly successful in optimizing electrode properties such as film thickness and porosity [3].

The ability to predict cell degradation is a challenge, however, because so many seemingly unrelated degradation mechanisms have been identified [4]. Analysis of specific degradation mechanisms can in some cases provide a rationale for experimentally observed phenomena [5–8], but without additional experimental data, quantitative cause-and-effect relationships between observation and degradation pathway are difficult to develop. Measurements showing the evolution of the 3-dimensional microstructure will help enable deconvolution of these effects.

There are a number of experimental techniques that can provide such information. For example, Yoshizawa et al. [9] used electron tomography (3D TEM) to observe the internal structure and connectivity of carbon nanospheres. Thorat et al. [10] have developed a novel technique to determine electrode and separator tortuosity, in contrast to its more common treatment as an adjustable parameter [2].

The use of tomographic techniques in the field of fuel cell research has provided unprecedented access to microstructural information. Two commonly used techniques are high resolution X-ray computerized tomography [11] and focused ion beam tomography [12,13]. Of these, focused ion beam milling has been used to examine battery electrodes [14–19]; however, to date there have been no 3-dimensional reconstructions of a battery electrode presented.

This paper presents the results of tomography experiments to characterize graphite electrode microstructures with subsequent geometrical analysis of the reconstructed volume. Any tomography procedure must balance the dual requirements of reconstructing a sufficient sample volume while maintaining imaging resolution. The high stopping distance of ions in graphite means that graphite specimens are highly resistant to ion beam milling, thus limiting the sample volume that can be reconstructed. After preliminary investigations, X-ray nano-CT has been selected as the most appropriate technique to characterize our sample. As material failure is often a result of local inhomogeneities and defects [20,21], we focus here on the validity of the widely used assumptions of homogeneity and isotropy in battery electrode modeling.

* Corresponding author. Tel.: +44 2075945704.
E-mail address: n.brandon@imperial.ac.uk (N.P. Brandon).

1388-2481/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2009.12.038

2. Experimental

About 1 cm^2 from a graphite negative electrode was harvested from a Lishen 18650 battery of 2.2 A h capacity. The copper current collector was dissolved in nitric acid, and an area of the electrode was identified for examination and mounted onto an aluminum pin using silver paint. Dissolution of metals from carbon using nitric acid is a standard process (e.g. [22]).

The Gatan X-ray ultramicroscope (XuM) system was used for high resolution computerized tomography (nano-CT) [23,24]. Projected X-ray images were acquired at 1° rotation increments over 190° and reconstructed using Gatan's cone-beam back-projection algorithm to generate a 3D volume. The images were acquired with an 80 s exposure time (total acquisition time of 4.2 h) and a total magnification of 41.4×, corresponding to 480 nm voxel dimensions.

Table 1
Dimensions of sub-division levels.

Sub-division level	*Z* thickness (voxels)	*X* width (voxels)	*Y* depth (voxels)
Bulk	90	726	996
1	90	242	249
2	90	242	124
3	90	121	124
4	90	121	62
5	90	60	62
6	45	60	62
7	45	60	31
8	45	30	31
9	22	30	31

The total reconstructed sample volume was 43 × 348 × 478 μm; subsequent geometrical analysis was conducted to extract porosity, pore-connectivity, particle and pore size distribution, surface area and tortuosity. The analysis considered the entire bulk volume as well as a number of sub-volumes (which, when combined, represent the entire bulk volume); sub-volume dimensions are provided in Table 1. We then extracted standard deviations at each sub-volume dimension, allowing us to suggest the minimum representative volume element (RVE) size.

Graphite surface area was calculated by creating polygons along the surface defined by the pore-graphite interface. Tortuosity is calculated based on the geometrical definition provided by Shen [25] and is determined as follows: for a given pore structure the minimum distance from one side to the other is termed "*D*". The shortest distances ($L1$) from every pixel on one side to the closest pixel on the opposing side is calculated, ensuring that the path is maintained within the 3-dimensional pore structure. Tortuosity, calculated for each of these $L1$ values is defined as tortuosity = $L1/D$, and tortuosity factor is defined as the square of tortuosity. Pore size distribution was calculated by the 3-dimensional "continuous PSD" method described in [26].

3. Results and discussion

Fig. 1a shows an individual "slice" from the reconstructed tomography sequence; Fig. 1b shows the rendered solid graphite

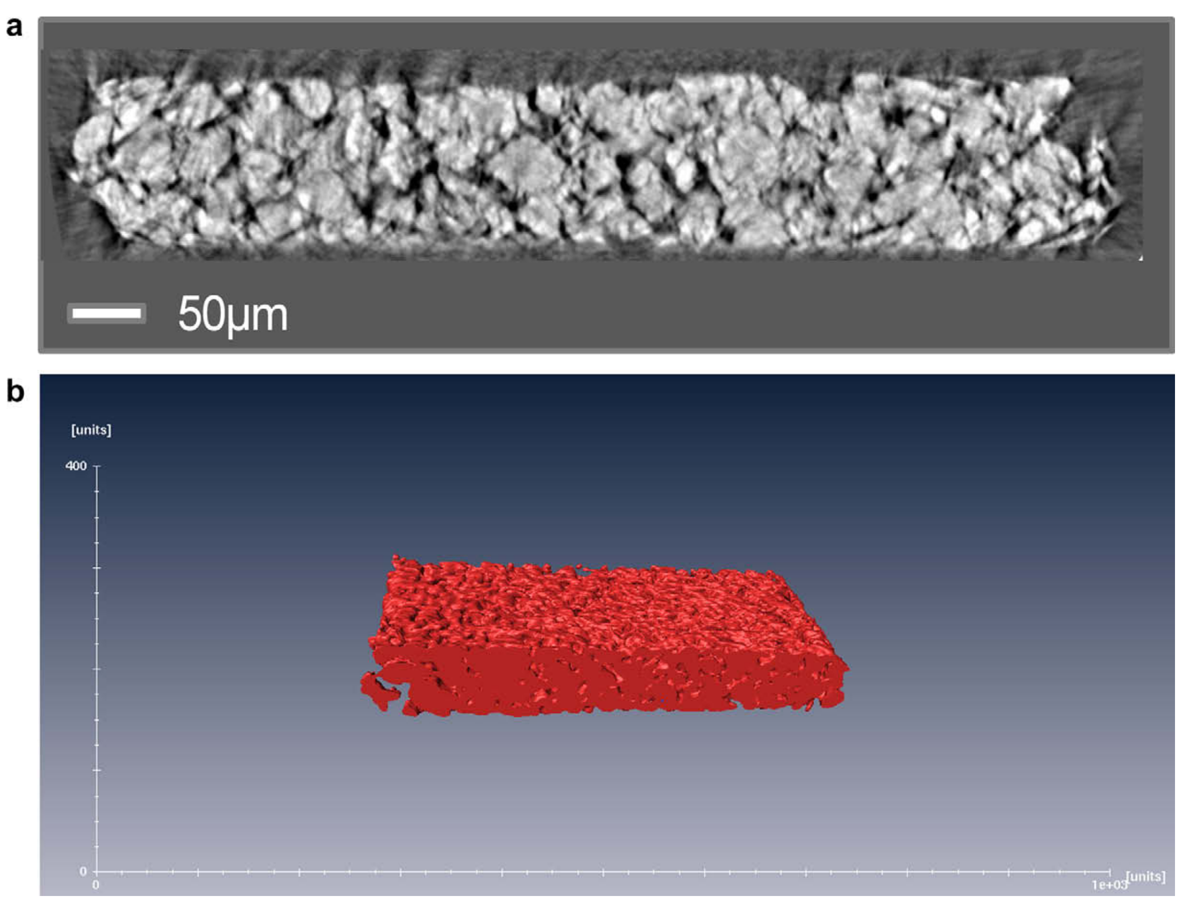

Fig. 1. (a) Individual slice from the tomography sequence. (b) Rendering of 300 individual tomography slices (dimensions 43 × 348 × 144 μm).