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# Stochastic simulation model for the 3D morphology of composite materials in Li–ion batteries

Ralf Thiedmann [a,*], Ole Stenzel [a], Aaron Spettl [a], Paul R. Shearing [b], Stephen J. Harris [c], Nigel P. Brandon [b], Volker Schmidt [a]

[a] Institute of Stochastics, Ulm University, 89069 Ulm, Germany
[b] Department of Earth Science & Engineering, Imperial College, London SW7 2AZ, UK
[c] R&D Center Electro-Chemistry and Battery Systems, General Motors, Warren, MI 48090-9055, USA

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ABSTRACT

Battery technology plays an important role in energy storage. In particular, lithium–ion (Li–ion) batteries are of great interest, because of their high capacity, long cycle life, and high energy and power density. However, for further improvements of Li–ion batteries, a deeper understanding of physical processes occurring within this type of battery, including transport, is needed. To provide a detailed description of these phenomena, a 3D representation is required for the morphology of composite materials used in Li–ion batteries. In this paper, we develop a stochastic simulation model in 3D, which is based on random marked point processes, to reconstruct real and generate virtual morphologies. For this purpose, a statistical technique to fit the model to 3D image data gained by X-ray tomography is developed. Finally, we validate the model by comparing real and simulated data using image characteristics which are especially relevant with respect to transport properties.



## 1. Introduction

Batteries are a very important and already well-engineered technology. However, not all physical phenomena within batteries are well understood so far. Most models for transport processes only take global parameters into account, so that the detailed 3D morphology of the media within which the transport processes of lithium ions are occurring is not considered, see Ref. [25]. One reason for this is the fact that imaging of the 3D morphology in high resolution is a difficult task. The first 3D images of both positive and negative composite electrodes used in Li–ion batteries have been obtained very recently, see e.g. Refs. [18,27]. They allow a deeper insight into the interior of this type of batteries. Hence, in Ref. [18], a first descriptive analysis of the 3D structure of Li–ion batteries has been performed with respect to transport-relevant properties, where the lithium-transporting phase is interpreted as a 'pore phase' and the graphite as a 'solid phase'. We will use this terminology in the present paper as well.

Here, we go one step further than simply analyzing the 3D morphology in a purely descriptive way by developing a stochastic simulation model for the pore phase based on the above mentioned 3D image data of Li–ion batteries, see Fig. 1. More precisely, the model, which we propose in the present paper, is based on tools from stochastic geometry, especially on point-process models. Hence, for image segmentation, we use an algorithmic approach described in Ref. [23] to come up with a suitable representation of the pore phase by unions of overlapping spheres. It can be seen as a realization of a random marked point process, where the centers of spheres are the points and the corresponding radii are the marks. See also Refs. [28,29], where unions of overlapping ellipsoids have been considered for structural analyzes of Li–ion electrode materials.

In addition to our model itself, we present a method of spatial statistics to estimate the model parameters, i.e., to fit our model to the data obtained in Ref. [18] by means of X-ray tomography. For validating the fitted model, we consider structural image characteristics which describe transport-relevant properties, and compare them for simulated data obtained from the model and for real data, respectively. Comprehensive surveys on recent results in the fields of stochastic geometry and spatial statistics can be found in Refs. [8,13].

In a next step of investigating Li–ion batteries and especially the transport processes therein, which will be discussed in a forthcoming paper, the proposed model will be used to generate virtual

* Corresponding author. Tel.: +49 731 50 23617; fax: +49 731 50 23649.
*E-mail address:* ralf.thiedmann@uni-ulm.de (R. Thiedmann).

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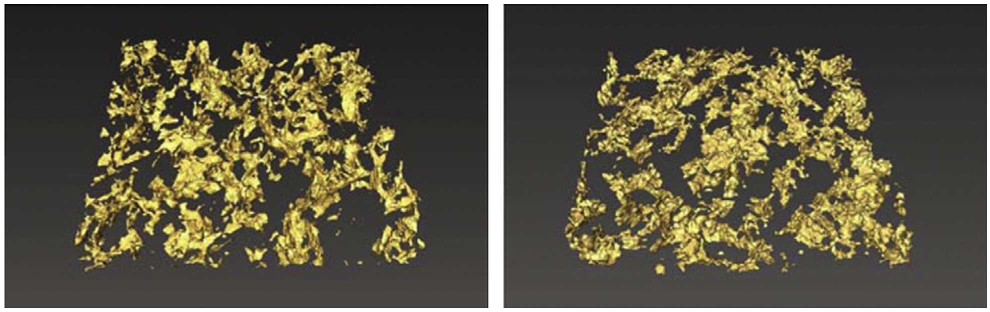

**Fig. 1.** Left: 3D cutout of original data from Li–ion batteries and right: 3D cutout of a realization of the stochastic simulation model.

structures for the 3D morphology of Li–ion batteries. Such a computer-based approach allows us to analyze the influence of morphology on the performance of batteries. Thus, our stochastic simulation model can be used for virtual material design based on computer experiments, i.e., to predict and construct morphologies of Li–ion batteries that are optimal w.r.t. transport. This kind of analysis can help to reduce expensive and time-consuming physical experiments and measurements. Note that the fitting of the model to real data and its subsequent validation are necessary pre-conditions for virtual material design. In this sense the fitting is an adjustment of the model, and the validation shows whether the morphological structure observed in real data can be reconstructed by the model sufficiently well.

In these porous materials, there are inherent statistical deviations in microstructure; these deviations must be compensated for by characterizing sufficiently large volumes to be representative of the bulk microstructure. The ability to accurately reproduce microstructures derived from high-resolution tomography experiments can enable large-scale replication of electrode analoges in silica. This may be especially useful for simulation of transport phenomena in porous materials, which often requires some microstructural framework.

The paper is organized as follows. In Section 2 the real 3D data, their exploration and preprocessing is briefly described. Then in Section 3 a stochastic segmentation algorithm is considered to find a suitable representation of the pore space by unions of overlapping spheres. In Section 4 the modeling approach including a technique for model fitting is explained, whereas Section 5 deals with the validation of the stochastic simulation model by means of structural image characteristics. Finally, in Section 6 a brief summary and an outlook to possible future research using the stochastic simulation model is given.

## 2. 3D images of Li–ion batteries

This paper deals with 3D images of composite materials used in Li–ion batteries, which have been obtained by X-ray tomography as described in Ref. [18]. These images allow, for the first time, a detailed investigation of the inner 3D structure of Li–ion batteries. To begin with, we give a short description of the imaging techniques, the images themselves, and the methods for image segmentation which have been applied in this context.

### *2.1. Experimental*

Tomography studies have been performed on the graphite composite electrode from a commercial Lishen 2.2 Ah 18650 laptop cell. The battery was completely discharged and then opened, and the graphite electrode was harvested. The graphite electrode of the working cell is bonded to a Cu current collector. In order to facilitate X-ray tomography studies, the Cu layer was removed by dissolution in nitric acid – this dissolution process is also expected to remove any residual electrolyte material. EDS and SEM images of the electrode composite show (see Ref. [9]) that the graphite particles are typically 10–15 μm in diameter. Since the electrode is only about 60 microns thick, the electrode is unlikely to be structurally homogeneous, but inherent statistical deviations in microstructure can occur.

An area of the isolated graphite electrode layer was subsequently identified and mounted on a pin for analysis by X-ray tomography. The SEM hosted Gatan X-ray ultramicroscope (XuM) system was used for high resolution computerized tomography (nano-CT). 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. The reconstructed gray-scale tomography data was analyzed using the Avizo software package (mercury computer systems, 2008): the raw data was filtered using the 'Edge Preserving Smoothing Tool' (also known as anisotropic diffusion – see e.g. Ref. [26]) before binarization by global thresholding.

The considered data set for composite graphite electrodes used in Li–ion batteries has a size of $750 \times 499 \times 89$ voxels, where each voxel has a size of $(480\ \text{nm})^3$, see Fig. 1 (left). This is a cutout of the complete 3D data set which is chosen to avoid edge effects. Note that all parameter values in the present paper are given in voxels, where we will regard the lithium-transporting phase as 'pore space' considering it as (black) foreground phase, and the solid as the (white) background phase, see Fig. 2. To fix notation, let $B$ be the pore phase of the binarized data set, and $B^c$ its complement, i.e., the solid phase.

**Fig. 2.** Cutout of a 2D slice of composite materials in Li–ion batteries.