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Stochastic 3D modeling of the microstructure of lithium-ion battery anodes via Gaussian random fields on the sphere

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ABSTRACT

The performance and durability of lithium-ion batteries are highly dependent on the microstructures of their components. Recently, methods have been developed that make possible the simulation of electrochemical processes on 3D representations of lithium-ion batteries. However, it is difficult to obtain realistic microstructures on which these simulations can be carried out. In this paper, we develop a stochastic model that is able to produce realistic microstructures of lithium-ion battery anodes, which can serve as input for the simulations. We introduce the use of Gaussian random fields on the sphere as models for the particles that form the anodes. Using this new approach, we are able to model realistic particle geometries. The stochastic model also uses a number of techniques from stochastic geometry and spatial statistics. We carry out validation of our model, in order to demonstrate that it realistically describes the key features of the anode's microstructure.

1. Introduction

Lithium-ion batteries used in electric vehicles need to fulfill a number of requirements. They should charge quickly, especially at low temperatures, be highly durable under a wide range of climatic conditions, and provide sufficient energy storage capabilities for long driving ranges [1]. A number of challenges remain, however, in satisfying these requirements. These are largely due to the complex nature of the batteries' microstructures. For example, lithium plating can occur at low temperatures; see [2–5]. This is caused by the slow transport of lithium ions in the electrolyte and bulk material, which is a direct result of the geometry of the microstructure; see [6,7]. Cyclic aging is also related to the microstructure; see, e.g., [5,8,9]. The influence of different operating conditions on cell degradation has been studied using electrochemical principles; see, e.g., [7,10]. Much of this research has made use of 1D or pseudo-2D models developed by Newman and co-workers [7]. For example, aging has been studied in [11] and lithium plating has been studied in [10,12]. However, these models do not fully take into account the importance of the microstructure and use only averaged structural characteristics like tortuosity, volume fraction and mean particle radius. Recent research, however, shows that the microstructure plays a key role in determining functional characteristics of the material; see, e.g., [13,14].

Recently, significant advances have been made in the simulation of electrochemical processes in 3D models of lithium-ion batteries [6,15–18]. Using these simulations, it is possible to carry out detailed studies of the relationships between the morphologies of battery materials and their corresponding transport behaviors. This approach has proven very effective in studying other energy materials, such as fuel cells; see, e.g., [19,20]. Important processes such as degradation can also be investigated and connected to the properties of the materials. A limitation of these simulation based approaches, however, is that it is very difficult to obtain realistic 3D microstructure models to use as input. This is because the small scales make 3D imaging of sufficiently large and representative material samples very difficult; see [21–25]. In addition, it would be desirable to investigate realistic microstructures that do not correspond to materials that have already been physically produced [26].

Stochastic modeling has proved to be a very effective method of producing realistic microstructures without the need for microscopy or computationally expensive physics-based simulations; see, e.g., [27–35]. Stochastic models have also been successfully coupled with numerical simulations; see, e.g., [28,36,37]. Using fast and flexible stochastic models, it is then possible to investigate the relationships between microstructure characteristics and material functionality [38].

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In this paper, we develop a stochastic model for the microstructure of lithium-ion battery anodes, which consists of a network of connected graphite particles. The model uses a number of techniques from stochastic geometry and spatial statistics; see, e.g., [39–41]. As a major innovation, it introduces the use of Gaussian random fields on the sphere to model particle shapes. In most standard approaches, particles are described by simple geometric objects such as balls and ellipsoids. However, the particles we consider are not adequately described by such shapes [42,43]. Using spherical harmonics expansions of Gaussian random fields, we are able to represent particles with much more complex shapes [42,44].

Our stochastic model uses a random tessellation to roughly describe the shape, size and position of the particles. A random graph is then used to describe how the particles connect with one another, in order to replicate the connectivity structure of the material itself. Using the tessellation and the connectivity graph, the particles themselves are produced. We exploit properties of Gaussian random fields to force the particles to connect in the desired manner. In the final step, the structure is morphologically smoothed to resemble the empirical microstructures as closely as possible.

The paper has the following structure. We first briefly describe the material and the methods by which we image it and extract its microstructure. We then describe the stochastic model itself. Afterward, we carry out validation of the model, by considering a number of important microstructure characteristics. In the last section, we provide a summary of the paper and describe future research that we will carry out.

2. Experimental data

The experimental data in this paper consists of four samples that are extracted from a large scale lithium-ion battery used in automotive applications. The cell did not contain electrolyte in order to ensure that the microstructure of the anode was not altered by electrical operation. The cell was disassembled and four samples were extracted from different positions and layers in the cell. This was done to ensure that the samples were as reflective as possible of the material's structure; see [23]. The obtained image data is shown in Fig. 1 alongside the binarized and segmented versions.

2.1. Description of samples and imaging technique

The 3D data sets were created at the Synchrotron X-ray imaging facility BAMLine at BESSY (Berlin, Germany). The setup consists of a PCO4000 detector system with 4008×2672 pixels and an optical system (Optique Peter) with a CWO scintillator screen that was used to convert X-rays into visible light. An X-ray energy of 19 keV was used. The pixel size was about 0.44 μm^2. During the tomographic measurement, 2200 single radiographic projections were taken at equidistant angles over a range of 180°. A filtered back-projection algorithm was used for 3D data reconstruction.

Details on the measurement and on the sample preparation method that was used to minimize the differences in the samples induced by varying measurement conditions are described in [23]. After imaging and reconstruction, the sample data is in the form of four 3D images, each $2097 \times 828 \times 119$ voxels. Each voxel has a grayscale value, which ranges from 0 to 255.

2.2. Structural segmentation

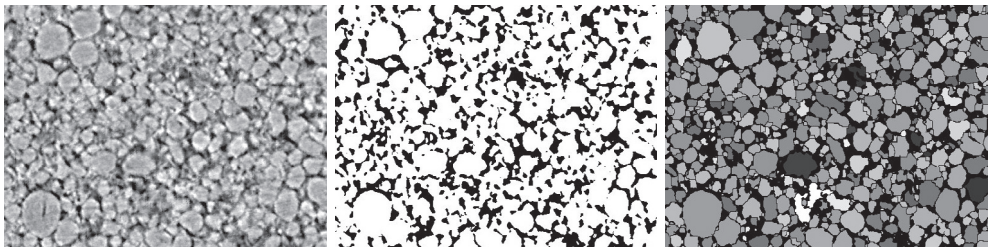
A graphite electrode comprises a fully connected network of particles. In order to extract information about the individual particles from the image data, we carry out a structural segmentation procedure consisting of four steps: (1) we binarize the original grayscale image; (2) we remove holes within the particles; (3) we remove irregularities such as parts extruding from the surfaces of the particles; (4) we segment the image into separate particles using a watershed procedure.

In the binarization step, we allocate each voxel to either the solid (graphite) phase or to the pore space. We first apply a Gaussian filter with $\sigma = 1.0$ in order to reduce the noise in the image data. We then use a global threshold to produce a binarized image. More precisely, every voxel with a grayscale value greater than or equal to 32 is assigned to the solid phase and every voxel with a value less than 32 is assigned to the pore phase; see [45] for more details. The threshold value is chosen to reproduce the volume fraction of the solid phase, which is known to be 73% for this material.

In the second step, we remove holes within the solid phase in order to avoid over-segmentation which would otherwise occur; see [46]. These holes are mainly caused by artifacts in the imaging and thresholding procedures. The particles themselves should not contain holes. We remove the holes using a Hoshen–Kopelman clustering algorithm (see [47]) on the pore phase of the thresholded image. Every cluster consisting of less than 5000 pore space voxels is removed by relabeling all the member voxels as belonging to the solid phase. The threshold of 5000 was chosen to ensure that hollow regions within particles were removed, but isolated pores still remained.

We then remove regions where the pore space intrudes significantly into the particles. The procedure is as follows. We generate a one voxel thick skeletonization of the pore phase. The skeleton, S_1, is generated using Lee thinning [48]. The 'dead-end' branches of S_1, which are only connected at one end, represent intrusions into the solid phase. We generate a second skeleton, S_2, which is simply S_1 with the 'dead-end' branches removed. We remove the intrusions by reassigning to the solid phase all voxels in the pore space that are closer to S_1 than S_2.

In the last step, the four binary images are segmented into disjoint parts, with each part containing only one particle. The segmentation is performed for each binary image using a marker



(a) Grayscale image. (b) Binary image. (c) Segmented image.

Fig. 1. 2D cutout of experimental data.