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Parametric stochastic 3D model for the microstructure of anodes in lithium-ion power cells

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ABSTRACT

The microstructure of anodes in lithium-ion batteries has a strong influence on their electrochemical performance and degradation effects. Thus, optimizing the morphology with respect to functionality is a main goal in battery research. Doing so experimentally in the laboratory causes high costs with regard to time and resources. One way to overcome this problem is the usage of parametric 3D microstructure models, which allow the realization of virtual morphologies on the computer. The functionality of microstructures generated with such models can be investigated by means of numerical transport simulations. The results of this procedure, which is called virtual materials testing, can be used to design anodes with improved morphologies that lead to a better electrochemical performance. Recently, a particle-based stochastic microstructure model for anodes in lithium-ion energy cells has been proposed. In the present paper, an extension of this model to describe the morphology of anodes in power cells, whose structure strongly differs from energy cell anodes, is introduced. The extensions include techniques to model anisotropic morphologies with a low volume fraction of the particle phase and strongly irregular particle shapes. The model is fitted to 3D image data of a power cell anode and validated using morphological image characteristics. Furthermore, we show examples of modifications of our microstructure model that can be made for generating further virtual morphologies. Finally, we briefly explain how electrochemical characteristics can be estimated using thermodynamically consistent transport theory. To illustrate this, we compute the cell potential over time during lithiation for image data of real microstructures as well as corresponding microstructures simulated by our model.

1. Introduction

Lithium-ion batteries have a wide field of applications, ranging from small mobile devices up to large-scale applications, e.g., in electric vehicles. However, there are still unresolved problems concerning capacity, power, safety, duration and aging effects, see, e.g., [1–4]. For an overview of challenges regarding lithium-ion batteries we refer to [5].

It is well known that the morphological properties of the electrodes strongly contribute to these problems. Thus, the microstructure of anodes and cathodes is of high interest in battery research [6–8]. Many theoretical investigations are based on the famous model introduced by Newman [9]. However, Newman's model does not take into account the full 3D information of the microstructure. This can be overcome using microstructure-resolved transport models, see [10]. Given the 3D morphology of the electrodes, such models can be used to predict the electrochemical performance of battery cells. Thus, if a tool is on hand that systematically generates virtual 3D microstructures with varying morphological properties, microstructure-resolved transport models can be used to identify electrochemically preferable structures, a procedure called virtual materials testing. Stochastic microstructure modeling has proven to be an ideal tool for the generation of such structures for various energy materials, see, e.g., [11,12]. In particular, virtual materials testing based on stochastic modeling has been performed in [13,14] for a wide class of 3D

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structures, which are closely related with microstructures observed in tomographic image data for electrodes of solid oxid fuel cells (SOFC). Thus, it is desirable to develop a parametric stochastic model that is capable of creating a broad range of battery electrode morphologies, which can be used as input for microstructure-resolved transport models. By doing so, an efficient tool (compared to experimental manufacturing and testing of electrodes in the laboratory) to identify preferable structures is provided.

Depending on the application of a battery, either power cells or energy cells are used. While for an energy cell the capacity is of high priority, which is reflected in a high volume fraction of the particle phase, for power cells a fast ion transport is necessary for high charge and discharge currents, and therefore the volume fraction of the pore phase needs to be rather high. For a discussion of the morphological differences between energy and power cells we refer to [15].

Recently, a parametric stochastic model for the microstructure of anodes in energy cells has been developed [16]. The model is particle-based, and each particle is modeled using so-called spherical harmonics [17]. The particles are placed in a system of convex polytopes that forms a decomposition of the region of interest. Due to the high volume fraction of the particle phase in energy cell anodes, it is easily possible to force each particle to touch a previously chosen subset of neighbors, in a way that the whole 3D structure is completely connected.

In the present paper, a parametric stochastic microstructure model for power cell anodes is introduced, which is based on the approach considered in [16]. The model accounts for the lower volume fraction of the particle phase, but still ensures its complete connectivity. In addition, techniques for modeling particles with more irregular shapes (compared to [16]) as well as anisotropy of the particle phase (which results from the calendering process) are presented. We fit the model to tomographic 3D image data (which we will call 'real data set' or just 'real data' in the following) of a power cell anode and compare morphological characteristics between real and simulated data.

In addition, we show various kinds of modifications of the microstructure that can be realized by the model. Finally, we briefly discuss how the thermodynamically consistent transport theory developed in [10] can be applied to image data of real microstructures and virtual ones generated by the model. To give an example, we compute the cell potential over time during lithiation of the electrode. Those two aspects (the ability to generate virtual, but still realistic structures and to perform electrochemical simulations) provide the basis for virtual materials testing.

The paper is organized as follows. In Section 2, a brief overview of the considered material and data preprocessing steps is given. The stochastic microstructure model as well as the fitting procedure to real data are introduced in Section 3. The validation based on morphological image characteristics is shown in Section 4. An outlook towards virtual materials testing is given in Section 5. In Section 6, the results are summarized and possible further work is discussed.

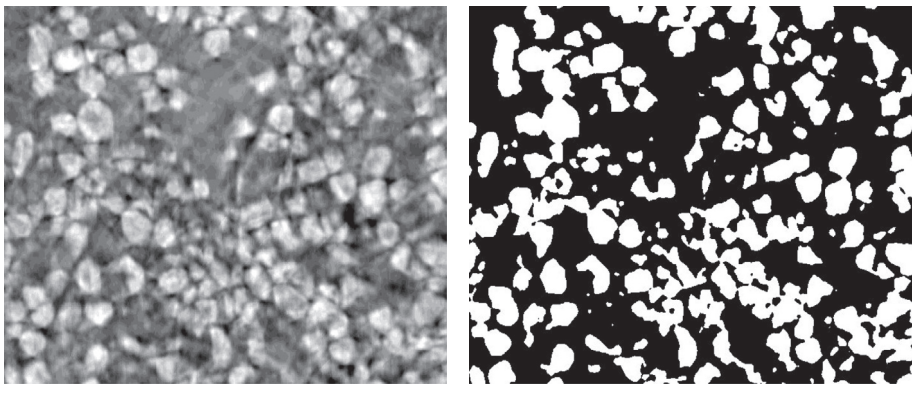
2. Material description and data preprocessing

The real data, to which the model is applied, is taken from a plug-in hybrid vehicle's battery cell. The cells have been exposed to moderate cyclic aging, i.e., no too strong structural changes due to aging are expected. The imaging was performed at a synchroton X-ray facility (BAMLine, BESSY, Berlin). For details regarding the imaging process, we refer to [18], where the technique has been introduced in detail. The imaging procedure resulted in an 8-bit 3D grayscale image with $1601 \times 1401 \times 109$ voxels, where the voxel size is $(0.44\ \mu\text{m})^3$.

This grayscale image is binarized, i.e., each voxel is either assigned to the particle phase or to the complementary phase, the pore phase. First, in order to remove noise in the image data, a Gaussian filter (see, e.g., [19]) with parameter $\sigma = 1$ is applied. After that, a (manually chosen) global threshold of 34 is applied, as this value leads to the best binarization considering visual comparison. We expect the particles not to have holes, however, due to artifacts in the data, after binarization, some holes are visible. Those holes are detected using the Hoshen-Kopelmann clustering algorithm [20] and removed, i.e., the corresponding voxels are assigned to the particle phase. This is done for clusters found up to a size of 10,000 voxels. Finally, as we expect the particle phase to be completely connected, a clustering algorithm is performed (now on the particle phase) and only the largest cluster (and clusters touching the edge of the image, as their connectivity across the border is not known) are kept, which removes a few artifacts in the background.

As an example, Fig. 1 shows a cutout of a 2D slice from the grayscale image and the corresponding binarization. The complete binarized 3D data set is visualized in Fig. 2.

As the parametric stochastic model is particle-based, we need a segmentation of the binary image that allows identification of individual particles. This is necessary for parameter estimation, see Section 3.4. The segmentation is done using a watershed algorithm, see, e.g., [21] for detailed information. The algorithm is adapted from [22] and is based on so-called regional local minima, which extend the concept of simple local minima in order to prevent oversegmentation. We consider the so-called negative Euclidean distance transformation of the binary image, i.e., the value of each



(a) Grayscale image. (b) Corresponding binarization.

Fig. 1. 2D planar cutout of the real data set.