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Generation of virtual lithium-ion battery electrode microstructures based on spatial stochastic modeling

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ABSTRACT

It is well known that the microstructure of the active material in lithium-ion battery electrodes has a strong influence on the battery's performance. In order to improve functional properties of lithium-ion batteries, designing optimized electrode morphologies is an important task. As exploring a large set of possible design concepts via laboratory experiments is very expensive in cost and time, model-based simulations have become an important tool to explore a broad range of possible microstructures on the computer. They allow a preselection of promising design concepts. This procedure, which is called virtual materials design, involves two main tasks. First, a tool for creating virtual, but realistic electrode morphologies is needed. This tool must be able to generate a broad range of electrode microstructures on the computer. In a second step, the performance of these virtual electrodes must be evaluated using spatially resolved numerical transport simulations. In the present paper, the first part of this procedure is addressed. A general framework based on tools of stochastic geometry is presented, which can be used to create a broad range of different electrode microstructures on the computer. To demonstrate the wide spectrum of possible outcomes of the microstructure generator as well as its ability to describe real electrode microstructures, we show how the microstructure of three types of electrodes, which exhibit rather different morphologies, can be described using different adaptions of the framework. A comparison of structural characteristics of the model outputs and tomographic image data of real electrodes indicates a good fit of the model. Moreover, we show how design concepts can be implemented for generating virtual electrode microstructures that can be used as input for spatially resolved transport simulations.

1. Introduction

Although lithium-ion batteries are, due to their high energy density, widespread in many applications [1], production costs are high while the energy density is still too small for an entirely satisfying application in the automotive sector [2]. As it is well-known that the microstructure of battery electrodes strongly influences their performance [3], it is highly desired to identify optimal electrode morphologies. With laboratory experiments being expensive in cost and time, many approaches are based on modeling and simulations, see, e.g., [4]. In [5], a tool for spatially resolved electrochemical transport simulations has been developed, which has recently, e.g., been applied to analyze properties of thick electrodes [6]. However, for systematic investigations of the relationships between the microstructure of electrodes and their electrochemical properties, it is necessary to have a broad range of electrode microstructures as input for spatially resolved electrochemical simulations. In the present paper, a framework for such a microstructure generator is described. The basic idea is to model the individual active particles of the electrodes using spherical harmonics expansions of Gaussian random fields. Note that spherical harmonics can be used to represent functions defined on a sphere, see [7] for an overview. Modeling of particles using spherical harmonics has successfully been performed in [8,9]. In [10], an approach to ensure a realistic arrangement and connectivity of particles in the sampling window is presented for modeling of battery electrodes. This method is extended in [11,12]. The modeling approaches considered in [10–12] are based on tools of stochastic geometry [13]. The main idea is to subdivide the region of interest into a space-filling system of polytopes, a so-called Laguerre tessellation, see [14] for details on this topic. Subsequently, the individual particles are placed inside the polytopes, where a pre-defined connectivity of particles is ensured using a connectivity graph (see [15] for details on graphs). While exhibiting a remarkably good fit to experimental data for different scenarios (anodes in energy and power cells as well as pristine and aged cathodes), these models also have some limitations which make their application for virtual materials testing difficult. On the one hand, the model

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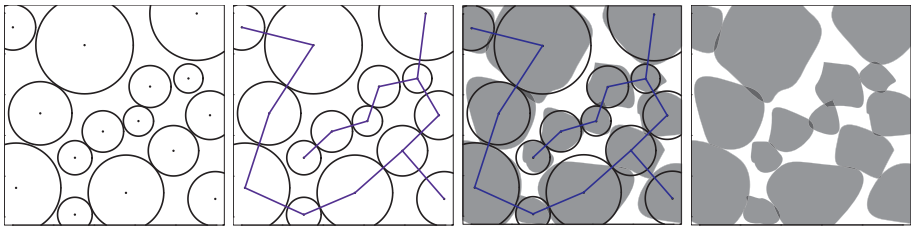

Fig. 1. (a) Approximate locations and sizes of particles are modeled using a random allocation of spheres (black circles). This can, e.g., be achieved using the force-biased algorithm for random sphere packing. (b) A connectivity graph (blue) determines how particles should be connected with each other. This can, e.g., be the minimum spanning tree. (c) For each sphere, a particle with approximately the same size is modeled using a Gaussian random field on the sphere (grey), where the connectivity conditions are fulfilled. (d) Spheres and graph are deleted and only the (connected) system of particles is retained. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

construction via Laguerre tessellations is rather complicated and the number of parameters is quite large, and, on the other hand, the parameters are rather abstract variables with no direct geometrical interpretation. This makes it difficult to systematically vary and adjust morphological parameters. For instance, even predetermining a specific particle size distribution is difficult, as the particle size distribution can not be directly expressed as a function of model parameters. Therefore, in the present paper a simplified version of these models is presented, where the number of model parameters is kept small, and many model parameters have a direct geometrical interpretation. In particular, the particle size distribution is a direct, adjustable input parameter. The basic idea is to omit the construction via a random tessellation, and, instead, use a random packing of spheres to control the spatial arrangement of particles. These spheres are subsequently replaced with particles which are generated using spherical harmonics, whereby their volume is retained. This procedure has three main advantages. First, as already mentioned above, the particle size distribution can be directly adjusted by predetermining the size distribution of the spheres being packed. Moreover, sphere packing algorithms are reproducing the production process of electrodes in a more natural way than the approach via tessellations, i.e., a random packing of spheres can be interpreted to mimic the random allocation of particles when casting the suspension of an electrode. It turns out that, surprisingly enough without further presets, this approach leads to a good representation of how particles are in contact with each other in real data. Finally, the small number of parameters, which mainly have a direct geometrical interpretation, allows for a systematic variation of morphological properties.

The model described in the present paper is constructed in a modular concept, which consists of three main modules. Each module can be adjusted to the specific needs in a given application, where "adjustment" does not only mean a different choice of parameters, but slightly changing the setup of the individual modules. We first present the general framework with a simple example, i.e., each of the modules is kept in the most simple way. Afterwards, we show how the three modules can be adjusted to three different battery scenarios, anodes in energy and power cells as well as cathodes. Finally, we give examples for adjusting the modules for generating virtual electrode microstructures. The modular concept has the great advantage that a collection of slightly different implementations of each module can be created. When generating virtual structures, a choice for each module can be made and the different modules can be combined with each other.

Note that the framework described in the present paper is not only applicable for lithium-ion battery electrodes, but similar methods can be used to model other particulate materials.

The outline of the paper is as follows. The general framework of the modeling idea is presented in Section 2. Examples using specific adaptions of the framework are presented in Section 3. For the three examples under consideration, a comparison of structural characteristics of model realizations and tomographic image data is performed to show that the simulation outcomes are realistic. Applications for virtual materials design using the framework are described in Section 4. Conclusions are drawn in Section 5.

Note that in Section 4 only two examples for the generation of virtual microstructures are presented. For an overview of further virtual structures that can be generated using the framework described in the present paper, we refer to the supplementary material.

2. Modeling framework

2.1. Overview

In order to model a system of connected particles, three main steps are necessary. This is (a) modeling of locations and approximate sizes of particles, (b) determining how particles should be in contact with each other and (c) modeling of particles themselves according to the specifications of the first two steps. These steps are illustrated as a 2D sketch in Fig. 1. A 3D view can be found in Fig. 2. The main difference of the approach proposed in the present paper compared to the ones in [10–12] is to use a random packing of spheres in the first step instead of random tessellations. These spheres act as a placeholder for the particles that will be created in a later step. Thus, they define their approximate locations and sizes. We will denote this set of random spheres by $\Xi = \{(S_i,R_i), i = 1,...,N\}$ with $S_i \in W \subset \mathbb{R}^3$ a random vector in the sampling window W, a random radius $R_i > 0$ of the corresponding sphere and N the random number of spheres in the sampling window. Such a random packing of spheres with predefined radii can be generated using the force-biased algorithm [16,17]. Based on these spheres, a connectivity graph $G = (V,E)$ is constructed, where the vertex set $V = \Xi$ is the system of spheres, and the edgeset $E \subset \Xi \times \Xi$ consists of pairs of spheres. If there is an edge between two spheres, this indicates that the corresponding particles are supposed to touch each other. In contrast to the tessellation-based approach, in a random allocation of spheres generated by a packing algorithm it is much easier to implement such connectivity conditions, due to the fact that, if two spheres (almost) touch each other, it is easy to model two touching particles with the same volume as the spheres. The particles themselves

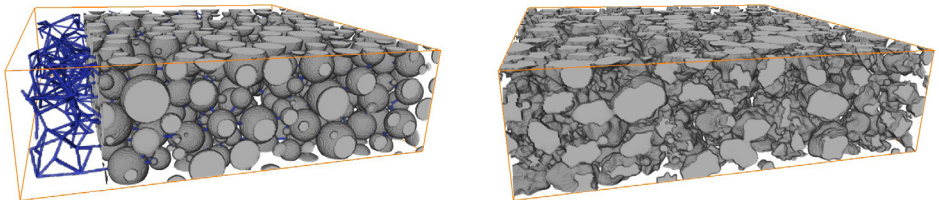

Fig. 2. Left: Random sphere packing (grey) and connectivity graph (blue) in 3D. Right: System of particles simulated based on sphere packing and connectivity graph on the left. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)