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Modeling the evolution of lithium-ion particle contact distributions using a fabric tensor approach

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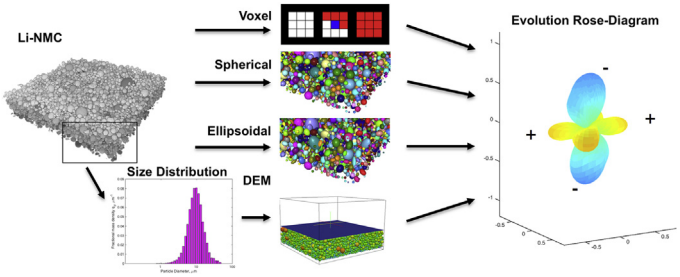
HIGHLIGHTS

- We examine the microstructure of lithium nickel manganese cobalt oxide cathodes.
- We search for active material contacts in tomography by geometric approximations.
- Fabric tensors can be used to model directional contact distribution.
- DEM models built from particle size distribution do not reflect experimental data.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrode microstructure and processing can strongly influence lithium-ion battery performance such as capacity retention, power, and rate. Battery electrodes are multi-phase composite structures wherein conductive diluents and binder bond active material to a current collector. The structure and response of this composite network during repeated electrochemical cycling directly affects battery performance characteristics. We propose the fabric tensor formalism for describing the structure and evolution of the electrode microstructure. Fabric tensors are directional measures of particulate assemblies based on inter-particle connectivity, relating to the structural and transport properties of the electrode. Fabric tensor analysis is applied to experimental data-sets for positive electrode made of lithium nickel manganese cobalt oxide, captured by X-ray tomography for several compositions and consolidation pressures. We show that fabric tensors capture the evolution of inter-particle contact distribution and are therefore good measures for the internal state of and electronic transport within the electrode. The fabric tensor analysis is also applied to Discrete Element Method (DEM) simulations of electrode microstructures using spherical particles with size distributions from the tomography. These results do not follow the experimental trends, which indicates that the particle size distribution alone is not a sufficient measure for the electrode microstructures in DEM simulations.

1. Introduction

Lithium-ion batteries are currently a storage technology of choice for applications ranging from automotive to consumer electronics due to their high energy density, performance, and versatility [17]. An increasing demand for high-capacity, high-

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power batteries for hybrid and electric vehicles [46] and grid energy storage [22] has resulted in the development of new active materials for Li-ion electrodes and battery chemistries [30,51]. The microstructure and processing of the Li-ion battery electrodes has a strong influence on their performance and life [44,6,48]. The electrode microstructure is set at the electrode manufacturing step and evolves during battery operation usually causing deterioration of the battery performance. As the demands for Li-ion technology grow in terms of delivering high energy and power, consideration must be given to the transport, mechanical, and thermal behavior of the electrode microstructures in order to optimize storage, useful life, and thermal safety [3].

Li-ion positive electrodes are multi-phase materials comprising both active and inactive phases. The active phase is usually in the form of crystalline or semi-crystalline powder and accounts for about 90% of the total mass of the electrode. The remaining mass is partitioned between the two inactive materials: binder and conductive agent. The positive active materials for Li-ion batteries are typically lithiated transition-metal oxides such as $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC), $LiCoO_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $LiMn_2O_4$, $LiFePO_4$, and $LiMn_{1.5}Ni_{0.5}O_4$ [17]. Carbon black is used as a conducting additive for enhancing the electrical contact between particles. Polyvinylidene fluoride (PVDF) is a common binder that holds the active particles together and onto the current collector. The interplay between the three electrode constituents is more complex than their primary roles suggest, especially under processing conditions where mechanical effects such as calendaring can induce significant changes in the electrode microstructure [52]. As an example, too little binder results in a low connectivity between the active particles, impeding electronic conductivity and electrochemical performance [52]. Too much binder makes the overall electrode more insulating. An electronically-conducting additive may boost local electronic conductivity but may constrict the overall ionic transport at electrode level.

The active electrode material, binder, and conductive agent form a porous solid skeleton. The overall porosity can range from 20 to 30% which allows the liquid electrolyte to access the active material [17]. Currently, the main parameters for electrode microstructure characterization are active particle average size, size distribution, and electrode porosity [6,7]. These parameters can be related to battery performance, especially in the post-production stage [42,52], but they often require empirical correlations and are insensitive to many types of changes in the microstructure that occur at the electrode level [23,13]. For example, Ebner et al. [12] shows that positive electrode assemblies forming an anisotropic structure suffer increased tortuosity perpendicular to current collection, which can negatively impact power density and battery performance. This shows that the particle size distribution and porosity alone are insufficient to describe the transport mechanisms in the electrode. Another example is adhesion loss between the binder/conductive agent and active particles; this may reduce the electrical conductivity of the assembly but changes neither the active particle size distribution nor the overall porosity. Similarly, particle rearrangement does not change the size distribution, although it may change the electrode porosity.

One method to simulate and analyze electrode particulate microstructures is the Discrete Element Method (DEM). Originally developed by Cundall and Strack [8] for modeling granular mechanics, it has been recently applied to various aspects of electrode microstructures [6,7]. However, these models must be upscaled to the continuum scale in order to be of a practical use, and methods of scaling are yet to be developed for electrode structures.

The transport properties in the electrode are strongly influenced by the connectivity of the active material particles and the connectivity of the interstitial space. The electrode microstructure and transport domains are similar to those of the saturated granular materials and bonded porous aggregates [37], so our idea is that some of the descriptive and analytical tools [20,36] of the latter can be applied to electrodes. In fact, the electrical conductivity and percolation are often used as analogs for modeling strength and material breakdown [29]. In granular media, the mechanical connectivity, force networks, and transport are described using Fabric Tensor (FT) formulations. FTs are well-established, non-local directional measures of internal connectivity and structure of granular media and solids. They are also extensively used in the field of damage mechanics [45,47,37] to describe the deterioration of material due to cracks and the reduction in the connectivity and force transport pathways. They provide granular and damage mechanics with a measurable and clear physical interpretation of microstructure effects and correlate to macroscopic properties such as skeleton stress tensors and stiffness tensors.

In the remainder of the paper, we investigate the use of FTs to describe microstructure of battery electrodes. We focus on the directionality of the active material contact network and structural mechanics aspects of the material as they are the most closely related to the disciplines where FT formulations have been extensively used. Following the same ideas for thermal, charge, and species transport gives us exciting new possibilities for creating unified framework for modeling battery performance based on the electrode microstructures. We seek to show that FTs are an appropriate measure of particle contact for lithium-ion positive electrode microstructures, and further, how the particle assembly responds to processing steps such as calendaring pressure. This will provide a metric for evaluating and standardizing the microstructural evolution under such conditions. The concept is illustrated on the experimental scanned microstructure of NMC electrodes and their DEM simulated models. By combining experimental imagery and DEM simulations, the FT framework can be employed to build constitutive models of the electrode microstructure, as has been done with granular media, which will be subject of subsequent publications.

2. Experimental data

Tomographic imagery used in this study was collected by Ebner et al. [13] using the synchrotron radiation X-ray tomographic microscopy (SRXTM) technique, yielding an imagery set which can be assembled to form a three-dimensional image of the cathode microstructure. Tomographic measurement was performed on electrodes that were earlier calendared at pressures of approximately 300, 600, and 2000 bar (30, 60, and 200 MPa, respectively) as well as uncalendared samples (0 bar, 0 MPa). The sample preparation for tomography involves placing electrodes in cylindrical molds (15 mm diameter), immersing them in epoxy resin, and heating them for 24 h at 55 °C under vacuum [13]. Cylindrical samples 0.7 mm in width are then milled using a lathe [13].

The Laboratory of Nanoelectronics at the Eidgenössische Technische Hochschule Zürich (ETHZ) performed the step of particle identification using the watershed algorithm for particle segmentation, detailed for granular contact problems by Saadatfar [40]. The database is hosted by ETHZ Library and is publicly available [21]. It includes the raw imagery files, time-series data of charging cycles, and a tabulated description of the identified particles. The imagery slices are approximately 330 μm × 330μm square with voxels that measure 370 nm × 370nm × 370nm.

The materials used to make the cathode composite were NMC compound from 3M, Super C65 carbon black from TIMCAL Ltd., and Kynar 761 binder (polyvinylidene fluoride) from Arkema [13,6]. Chung et al. [6] notes that the NMC compound was selected due to the high sphericity of the particles, which are distributed log-