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Original Research Paper

# Structural and mechanical characterization of lithium-ion battery electrodes via DEM simulations

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ABSTRACT

Electrode structural stability and mechanical integrity is of major importance regarding not only lithium-ion battery performance but also safety aspects. The goal of this study is to design a simulation procedure to reproduce the microstructural and mechanical properties of such lithium-ion battery electrodes. Taking into consideration the particulate state of these electrodes, a discrete element method (DEM) approach is proposed, which comprises a procedure to reproduce real electrode structures and the application of a proper contact model to capture the bulk mechanics. This is accomplished by considering particle interactions as well as the performance of the binder. Three different electrodes are manufactured with the aim of calibrating and validating the Hertzian-bond contact model. Experimental nanoindentation measurements prove to be in good agreement with the simulation outcome, concluding that the method constitutes a valuable physical and mechanical basis for further applications.



## 1. Introduction

Lithium-ion batteries (LIBs) are widely used as electrochemical power sources for mobile telephones, personal computers, cameras and other modern-life appliances. They are also remarkably successful in the electric power vehicle market due to their long life cycles and high-rate capabilities. However, as lithium-ion batteries increase in popularity, there is still room to improve their performance and durability. Within this framework, the importance of electrode structural stability and mechanical integrity has been already pointed out by several research groups. Peterson et al. [1] experimentally investigated the effect of several relevant structural factors on electronic and ionic conductivity. By presenting various scenarios, it was demonstrated that electronic conductivity is greatly increased by raising the carbon black volume fraction and reducing the electrode porosity, whereas the ionic conductivity decreases by increasing the amount of carbon black and binder. Among other interesting results, Bockholt et al. [2] showed that the positive or negative impact of calendering on battery performance is directly linked to the change in the structure of the electrode. With regard to active material particle size, Michaels et al. [3] experimentally confirmed that smaller particles give rise to higher electrode adhesive strength and lower electrode conductivity.

Concerning mechanical aspects of lithium-ion battery electrodes, it is well-known that stress generation within the electrodes is one of the main causes for capacity fade and eventual failure of lithium-ion batteries. For this reason, mechanical instabilities, including structure disintegration and particle fracturing, loss of contact between the electrode and the current collector or plastic deformation have been a major subject of extensive research activities [4–6]. In this regard, the work of Mukhopadhyay et al. [7] must be noteworthy underlined. They presented an overview of the sources and relative magnitudes of stresses within the electrodes and introduced recently developed techniques for *in situ* measurements of stress evolution.

Since experimental research implies costly processes in terms of raw materials, resources and time, modelling and numerically simulating lithium-ion batteries have been recently in the spotlight as an alternative approach [9–11]. Bearing in mind the effect of electrode microstructure on voxel performance, numerical methods have specifically become more popular due to the additional complexity of experiments. In order to be able to model the electrode microstructure accurately, it is necessary to acknowledge the particulate nature of such structures. So far, this fact has been only partially contemplated. Within this context, this work proposes a discrete element method (DEM) approach. This method,

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first developed by Cundall and Strack [8], is based on the characterization of contacts between a number of discrete particles forming the bulk material. Even though its application to electrode simulations is to date in an early phase, DEM has been already proven to be a feasible tool in the subject. Schneider et al. [9] analyzed the effect of electrode thickness and composition on the Triple Phase Boundary (TPB) length by computing several composite electrodes consisting of spherical monosized particles. Liu et al. [10] generated various numerical microstructures by sintering in order to assess the importance of macroscopic porosity and pore surface area of SOFC (Solid Oxide Fuel Cells) electrodes. Also in this line of research, Forouzan et al. [11] developed a mesoscale particle-based simulation technique to predict the microstructure of lithium-ion battery electrodes considering the manufacturing process. These contributions have helped to improve the understanding of fundamental structural parameters such as electrode porosity, thickness or composition on the voxel performance. Nevertheless, they constitute an overall approximation of the real microstructure. In particular, the mechanical characteristics, which are directly affected by the structure, have not been fully comprehended for lithium-ion battery electrodes so far.

In the scope of this work, the focus is set on designing a simulation procedure and an appropriate DEM contact model that can reproduce not only the microstructure but also the mechanics of lithium-ion battery electrodes. Combining simulations with nanoindentation experiments, the contact model is calibrated and validated, bringing reliability to the developed method. It is believed that this study offers an interesting tool which constitutes an accurate structural and mechanical foundation for future investigations. For instance, with the aim of studying stress evolution within electrodes during lithium-ion intercalation or investigating the effect of manufacturing processes such as calendering.

This work is organized as follows: In Section 2, the DEM contact model is fully explained. Section 3 includes the numerical generation of the electrode microstructures. For calibration and validation, several electrodes were manufactured; Section 4 briefly introduces the materials as well as the experimental characterization. Simulation results are gathered in Section 5. Concluding, the outcomes are summarized.

## 2. Materials and experimental characterization

In the scope of this contribution, three electrodes were manufactured and physically characterized; one electrode for calibrating the contact model (C1), and the other two for validating the simulation results (V1 & V2).

The composite anode electrodes were prepared with MesoCarbon MicroBeads graphite powder (MCMB, Osaka) as active material and a mixture of styrene-butadiene copolymer (SBR, Lipaton SB 5521, Synthomer) and carboxymethyl voxelulose (CMC, Walocel Na-CMC2000 PA, Dow Wolff Voxelulosics GmbH) as binder. The MCMB powder and the CMC were firstly dry-mixed for 15 min in a rotary drum mixer (Turbula® T2F, Willy A. Bachofen Corp.) with a rotational speed of 49 $min^{-1}$ for 15 min. The mixture was then dispersed in deionized water for 70 min using a dissolver (Dispermat CA, VMA Getzmann) with a 50 mm toothed disk. The circumferential velocity of the disk was set to 9 m $s^{-1}$ and vacuum was applied during additional 10 min right after adding the necessary amount of SBR. The resulting suspensions were coated on a 10 μm copper foil using a continuous pilot-plant scale coater (Labco, Krönert GmbH & Co KG) with a comma bar reverse roll application system. Drying was performed in a three stage convective drying process (Drytec, Hamburg, Germany) at a temperature of 65 °C. The coating and drying speed was set to 2 m $min^{-1}$. The active material mass loading for all anodes was set to 8.7 ± 1.2 mg $cm^{-2}$.

With the aim of assuring reliable simulation results, active material was analyzed via laser diffraction to acquire the particle size distribution. Moreover, porosity of the electrodes was determined by means of mercury intrusion and electrode thickness was measured via a digital gauge, as explained in [12]. Table 1 gathers these outcomes as well as additional information regarding electrode composition. Taking anode C1 as the reference, anode V1 was composed of coarser particles maintaining the same composition. Anode V2 was manufactured with the same active material particle size but with a higher amount of binder. Due to these variations, all three electrodes showed different values of porosity and thickness.

The micromechanical properties were characterized via nanoindentation (UNAT, Asmec Advanced Surface Mechanics GmbH) using a flat punch indenter with a diameter of 100 μm. The compressions (80 measuring points per electrode sample) were performed by controlling the maximum indentation displacement under a constant velocity of 0.15 μm $s^{-1}$ during both loading and unloading. As suggested by Fischer-Cripps et al. [13], a total displacement of 10% of the coating thickness was chosen in order to avoid substrate effects. The plastic ($W_{pl}$), elastic ($W_{el}$) and total ($W_{tot}$) deformation energies can be calculated based on the force-displacement curves as follows:

$$W_{tot} = \int_0^{h_{max}} F_{load}(h)dh \quad (1)$$

$$W_{el} = \int_{h_f}^{h_{max}} F_{unload}(h)dh \quad (2)$$

$$W_{pl} = W_{tot} - W_{pl} \quad (3)$$

where $h_{max}$ is the maximum displacement during indentation, $h_f$ is the residual indentation depth and $F_{load}$ and $F_{unload}$ are the indentation forces during loading and unloading respectively. Fig. 1 shows exemplarily an experimental force-displacement curve of a nanoindentation measurement.

**Table 1**
Structural parameters of the manufactured electrodes: Anode composition, thickness, porosity as well as active material particle size.

| Parameter | Anode used for the calibration (C1) | Anode used for the validation (V1) | Anode used for the validation (V2) |
|---|---|---|---|
| Anode composition (AM/Binder, wt.%) | 96:04 | 96:04 | 92:08 |
| Anode thickness, $h_e$ | 76.50 μm | 79.86 μm | 96.43 μm |
| Porosity, ε | 0.45 | 0.59 | 0.59 |
| Active material particle size | $x_{10,3}$ = 4.03 μm<br>$x_{50,3}$ = 5.99 μm<br>$x_{90,3}$ = 8.94 μm | $x_{10,3}$ = 10.34 μm<br>$x_{50,3}$ = 17.45 μm<br>$x_{90,3}$ = 30.89 μm | $x_{10,3}$ = 4.03 μm<br>$x_{50,3}$ = 5.99 μm<br>$x_{90,3}$ = 8.94 μm |

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