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Morphology of nanoporous carbon-binder domains in Li-ion batteries—A FIB-SEM study

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ABSTRACT

FIB-SEM tomography is used to reconstruct the carbon-binder domain (CBD) of a $LiCoO_2$ battery cathode ($3.9 \times 5 \times 2.3\ \mu m^3$) with contrast enhancement by ZnO infiltration via atomic layer deposition. We calculate the porosity inside the CBD (57.6%), the cluster-size distribution with a peak at 54 nm, and the pore-size distribution with a peak at 64 nm. The tortuosities of the pore space (1.6–2.0) and the CBD (2.3–3.5) show a mild anisotropy, which is attributed to the fabrication process. A comparison to a modeled homogenous CBD reveals that clustering in the CBD decreases its electronic conductivity while increasing the ionic diffusivity. To account for the higher calculated diffusivity compared to experimental values from literature, a simple binder swelling model is implemented, suggesting a swelling of 75 vol%. The prevention of both clustering and swelling could increase the volume available for active material and therefore the energy density.

1. Introduction

Li-ion battery cathodes usually consist of three phases: active material, electrolyte, and a carbon-binder domain (CBD) [1,2]. The function of the CBD is to guarantee electrode mechanical stability while providing electronic contact between the active material and the metallic current collector. The CBD has been observed as distinct agglomerations of carbon black and binder (here PVDF) with dimensions similar to those of the active material. The CBD is sparsely distributed inside the battery (carbon and binder constitute 5.5 dry wt% of the electrode in this study), contains nanoporosity, and can be distinguished from mesoscale pores [3]. This nanoporosity allows electrolyte pathways in the CBD while providing the necessary electronic connections. To extract morphological properties and transport parameters of the CBD, a reconstruction of the nanoporosity is required. We and others have attempted to model the distribution of carbon and binder inside porous electrodes [3–5], though experiments are needed to validate such models.

In recent years, FIB-SEM tomography has proven suitable for the reconstruction of nanoporous carbon matrices [6,7]. However, conventional FIB-SEM tomography of nanoporous carbon materials suffers from a lack of contrast between the carbon and the pores having carbon in the background, thus making the automatized discrimination of the phases extremely challenging. While filling the pores with resins [8] to enhance contrast does not fully infiltrate the nanopores, another approach uses an electron beam and a gas to deposit Pt inside the pores [9]. We recently demonstrated the infiltration of nanoporous carbon in a fuel cell electrode via atomic layer deposition [10]. This method has several advantages for the investigation of nanoporous carbon materials: many samples can be infiltrated at a time, the infiltration process is gentle (50 °C, no electron beam at 30 kV, no mechanical alterations like shrinking of the resin) and high SEM contrast of the infiltrated ZnO and CBD allows an almost completely automated segmentation which saves time and enhances reliability.

In this work, we use ZnO to fill the CBD in a conventional battery cathode and reconstruct it in order to calculate porosity, cluster- and pore-size distributions, and tortuosities of the pore and solid portions of the CBD. We compare the results to a modeled homogenous CBD and simulate CBD swelling to compare the values to experimental results from literature.

2. Methods

The investigated battery cathode was fabricated by Saft America (94.5 wt% $LiCoO_2$, 2 wt% carbon black, 3.5 wt% PVDF binder). The film was calendered to 37% porosity. To enhance contrast, the cathode was coated with a ZnO film of 100 nm thickness by allowing diethyl zinc and water to react in a cyclic manner in a vertical-flow, hot-wall reactor

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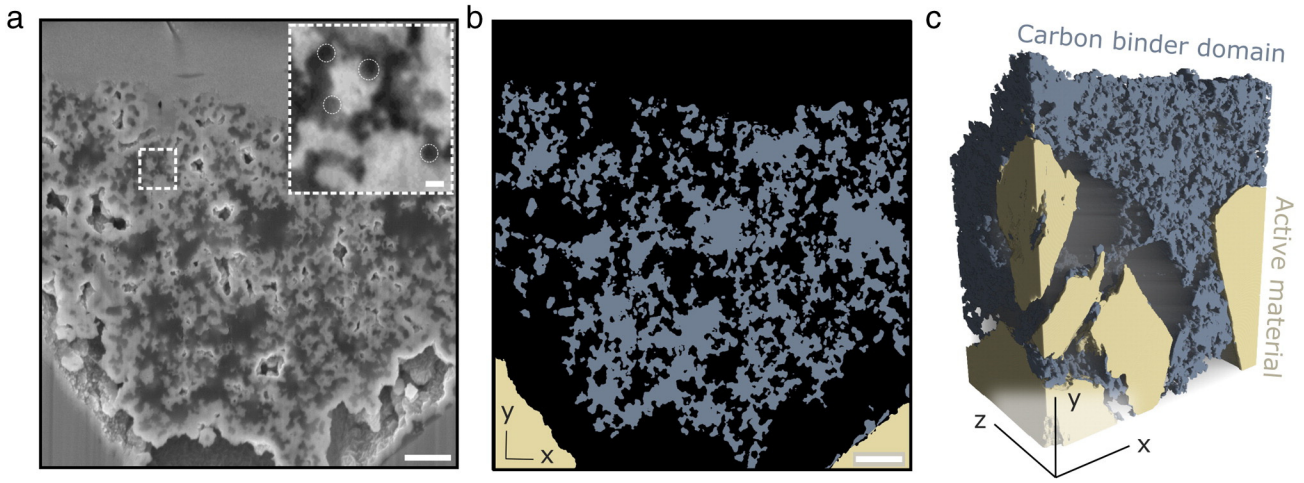

Fig. 1. Reconstructed CBD: (a) Sample image showing high contrast between carbon particles (dark) and nanopores filled with ZnO (bright), (b) the same section after segmentation, (c) three-dimensional representation. Scale bars are 500 nm, with 40 nm for the inset.

(OpAL, manufactured by Oxford Instruments) as described in a previous study [11]. In this work, the temperature was decreased to 50 °C to rule out any temperature-related changes of the sample's structure. At this temperature, the overall duration of the infiltration is approximately 3.5 hours. Closed porosity of the CBD was neglected, as it cannot be infiltrated and contrasted. Cavities, which remain when a volume gets closed by the ALD process, were identified in the three-dimensional representation by island filtering as described in Ref. [10].

FIB-SEM tomography was conducted with a Zeiss 'Auriga 60 dual beam' comprising 261 FIB cuts and SEM images. Each FIB cut was conducted at 30 kV accelerating voltage and 20 pA beam current with a cutting distance of 9 nm. SEM images were acquired at 5 kV with a pixel size of 3 nm using an in-lens detector. To protect the CBD matrix, a Pt layer was deposited on top of the sampling volume with engraved lines to track the cutting distance. The total reconstructed volume was $3.9 \times 5 \times 2.3\ \mu m^3$.

Images were aligned with MATLAB (Mathworks) while image enhancement and segmentation (Otsu threshold and minor manual corrections) were conducted with Fiji [12]. A sensitivity analysis of the calculated parameters as a function of the threshold value can be found in the appendix. Size distributions and transport parameters were calculated using GeoDict (Math2Market GmbH) and MATLAB in three cuboidal, partly overlapping subsets of the reconstructed dataset. The homogenous CBD model was created in GeoDict with weight fractions from the cathode: starting with randomly distributed carbon spheres of 40 nm diameter, the volume was filled with binder based

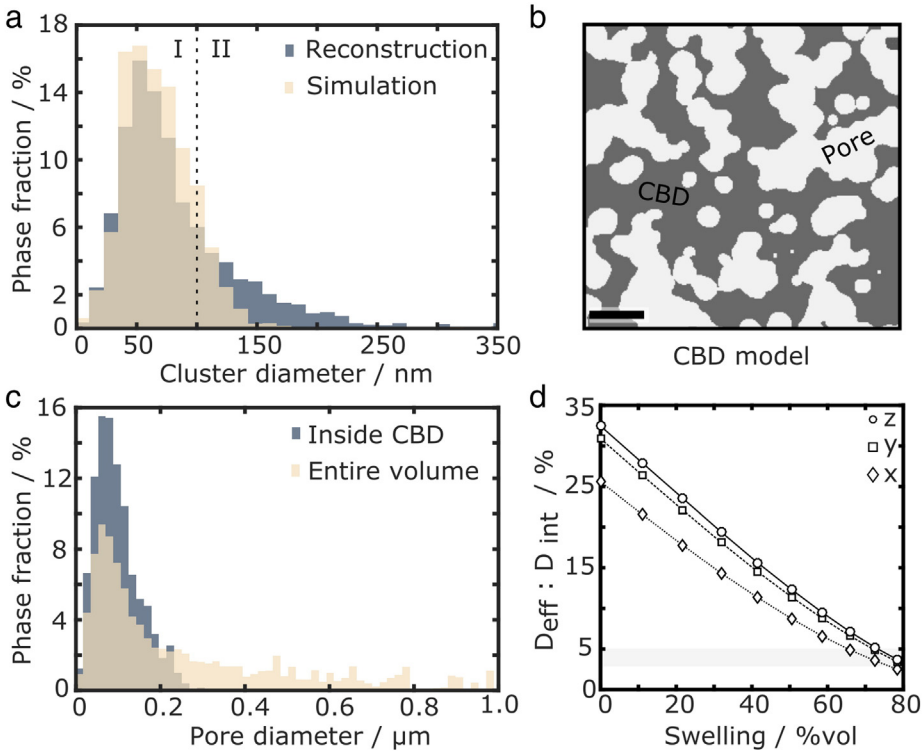

Fig. 2. (a) The cluster-size distribution of the CBD simulation (ocher) and reconstruction (blue), featuring two regimes: 1–3 particle diameters (I) and large clusters (II). (b) Sample section of the simulated CBD with solids (dark gray) and nanopores (white); scale bar is 150 nm. (c) Pore-size distribution inside the CBD (blue) and of the entire reconstructed volume (ocher). (d) Calculated relative effective diffusivity after swelling of the CBD.