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

*Severin Vierrath^{† a}, Lukas Zielke^a, Riko Moroni^a, Andrew Mondon^c, Dean R. Wheeler^d,
Roland Zengerle^a and Simon Thiele^{ab}*

a Laboratory for MEMS Applications

IMTEK - Department of Microsystems Engineering

University of Freiburg

Georges-Koehler-Allee 103, 79110 Freiburg, Germany

b FIT, University of Freiburg, Georges-Köhler-Allee 105, 79110 Freiburg, Germany

c Fraunhofer Institute for Solar Energy ISE, Heidenhofstr 2, 79110 Freiburg, Germany

d Department of Chemical Engineering, Brigham Young University, 350 CB Provo, UT , 84602 , USA

[†] Corresponding Author, E-mail: severin.vierrath@imtek.de

Abstract

FIB-SEM tomography is used to reconstruct the carbon binder domain (CBD) of a LiCoO₂ battery cathode (3.9 μm × 5 μm × 2.3 μm) 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% LiCoO₂, 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 (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 µm × 5 µm × 2.3 µm.

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 on the pore-size distribution, from small to big pores. The size distributions were determined using the method presented by Delerue et al.[13]

3 Results

The SEM images of the tomography featured a high contrast between CBD and the nanopores (Fig. 1a) enabling reliable automatized segmentation (Fig. 1b). The volume of the reconstruction was $3.9\ \mu\text{m} \times 5\ \mu\text{m} \times 2.3\ \mu\text{m}$ and featured mostly CBD and a few LiCoO_2 particles (Fig. 1c). The y direction (Fig. 1b, 1c) is normal to the plane of the electrode film. The calculated porosity (57.6%) of a subvolume containing exclusively CBD is in good accordance with previously estimated nanoporosities of similar samples.[1] Even though carbon black is considered to be of nearly uniform size, clusters or aggregates of carbon black and binder can lead to variable size of solid material. The distribution of cluster diameters for the entire dataset has a peak at 53 nm as depicted in Fig. 2a. This is in good agreement with the diameter of the carbon particles (30–40 nm) plus a PVDF coating. Furthermore, the size distribution exhibits two regimes: while 75% of the CBD consists of clusters with diameters equivalent to 1–3 carbon black particles (regime I), a substantial amount of the CBD forms larger clusters (regime II). The large clusters of the latter regime do not substantially appear in the simple homogenous 3D model with the same composition (Fig. 2b), as indicated by the smaller tail of the distribution in Fig. 2a. The pore sizes inside the CBD are distributed closely

around a peak of 62 nm (Fig. 2c). The pore-size distribution of the entire reconstructed volume, however, features much larger pores, as expected.

The mean chord length of the clusters was calculated to be 71, 81 and 89 nm in x, y and z directions respectively, revealing a slight anisotropy. This anisotropy is also visible in the tortuosity of pore space and solids in the CBD: In both phases, the x direction exhibits higher tortuosity values than do the y and z directions (Table 1). Here the tortuosity is calculated as $\tau = \varepsilon \alpha_0 \alpha_{\text{eff}}^{-1}$ for either ionic or electronic transport, with α_0 being an intrinsic transport coefficient for the conducting phase (ionic diffusivity in the pore space or electronic conductivity in the solid phase), α_{eff} being an effective transport value for the composite and ε being the volume fraction of the transporting phase.[14] These anisotropies could stem from limited sampling or FIB-SEM-reconstruction artifacts, though the off-diagonal entries of both diffusivity and conductivity are negligible as expected, suggesting relatively small errors [10]. Furthermore, cutting distance and image alignment were controlled by fiducial markers, giving no indication for reconstruction artifacts upon visual inspection. Moreover, anisotropy is likely to occur as a result of the interplay of large and irregular active material particles and the additives during the electrode film fabrication process, specifically the coating, drying and calendaring steps.

The calculated tortuosity of the pore space of the CBD ranges between 1.6–2.0. This corresponds to an effective ionic diffusivity of 30–37% of the intrinsic value. This is significantly higher than the experimental value of around 5% reported by Stephenson et al. for a CBD film of similar porosity and composition.[1] To account for this difference, we simulated CBD swelling by simple pixel dilation. Fig. 2c depicts the relative effective diffusivity after swelling of the CBD: in order to reach similar ionic diffusivities as in the experiment, a CBD swelling of 75 vol% is necessary, resulting in a CBD porosity of 17%. This corresponds to a PVDF volume expansion of 114%, which is indeed in good accord with reported swelling of PVDF in EC/DEC electrolyte.[15]

The tortuosity of the solid fraction of the CBD (e.g. for electron transport) was calculated to be 2.3–3.5. Compared to the simulated homogeneous CBD, on average this is 52% higher, while the tortuosity in the pore space is 27% lower. This difference reflects the influence of large CBD clusters: clustering inside the CBD makes pore channels more continuous for a given value of porosity, thus decreasing the tortuosity of the pore space. At the same time, the clustering creates bottlenecks in the CBD solid fraction, increasing its tortuosity. In summary, compared to a homogenous CBD, the observed clustering increases ionic transport and decreases electronic transport.

Two major findings can be concluded from the above results: First, the inhomogeneity of the carbon-binder domain reduces electronic connections that are intended by the added carbon. As a consequence, the amount of CBD in the battery could be reduced by up to 30% to reach the same electronic conductivity, if clustering could be prevented, e.g. by additives. The reduction of CBD, in turn, would allow a larger amount of active material, resulting in a higher energy density. Second, effective ion transport in the CBD structure as investigated by tomographic methods is markedly higher than ion transport observed for a CBD-like film containing electrolyte. This discrepancy can be explained by significant swelling of the PVDF in the CBD, reducing effective pore volume. This reduces ion transport significantly, or equivalently occupies volume that could otherwise be used for active material. Tomographic analysis thus emphasizes the value of replacing PVDF with materials that swell less in electrolytes, e.g. cross-linked polymers [16].

Acknowledgements

We thank Jan Laube and Prof. Zacharias from the Laboratory for Nanotechnology for the atomic layer deposition of ZnO in the battery cathodes. DRW acknowledges funding from the BMR program of the U.S. Department of Energy.

Figure 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.

Figure 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.

Table 1. Morphological and transport parameters of the CBD, comparing reconstruction to simulation. The parameters of the reconstruction are mean value and its standard deviation calculated from three subsets.

	Porosity / %	Tortuosity of pore space			Tortuosity of CBD			Mean chord length / nm		
		x	y	z	x	y	z	x	y	z
<i>Reconstruction</i>	57.6 ± 3	2.0 ± 0.1	1.6 ± 0.1	1.6 ± 0.1	3.5 ± 0.5	2.3 ± 0.1	2.3 ± 0.1	71 ± 6	81 ± 8	89 ± 8
<i>Simulation</i>	57.1	2.4	2.3	2.4	1.8	1.7	1.8	81	81	80

4 References

- [1] D.E. Stephenson, B.C. Walker, C.B. Skelton, E.P. Gorzkowski, D.J. Rowenhorst, D.R. Wheeler, Modeling 3D Microstructure and Ion Transport in Porous Li-Ion Battery Electrodes, J. Electrochem. Soc. 158 (2011) 781–789.

- [2] I.V. Thorat, D.E. Stephenson, N.A. Zacharias, K. Zaghib, J.N. Harb, D.R. Wheeler, Quantifying tortuosity in porous Li-ion battery materials, *J. Power Sources* 188 (2009) 592–600.
- [3] L. Zielke, T. Hutzenlaub, D.R. Wheeler, C.-W. Chao, I. Manke, A. Hilger, N. Paust, R. Zengerle, S. Thiele, Three-Phase Multiscale Modeling of a LiCoO₂ Cathode: Combining the Advantages of FIB–SEM Imaging and X-Ray Tomography, *Adv. Energy Mater.* 5 (2015).
- [4] M. Cerbelaud, B. Lestriez, A. Videcoq, R. Ferrando, D. Guyomard, Understanding the Structure of Electrodes in Li-Ion Batteries: A Numerical Study, *J. Electrochem. Soc.* 162 (2015) A1485–A1492.
- [5] W. Wu, F. Jiang, Simulated annealing reconstruction and characterization of the three-dimensional microstructure of a LiCoO₂ Lithium-ion battery cathode, *Materials Characterization* 80 (2013) 62–68.
- [6] C. Wieser, T. Prill, K. Schladitz, Multiscale simulation process and application to additives in porous composite battery electrodes, *J. Power Sources* 277 (2015) 64–75.
- [7] C. Ziegler, S. Thiele, R. Zengerle, Direct three-dimensional reconstruction of a nanoporous catalyst layer for a polymer electrolyte fuel cell, *J. Power Sources* 196 (2011) 2094–2097.
- [8] M. Ender, J. Joos, T. Carraro, E. Ivers-Tiffée, Quantitative Characterization of LiFePO₄ Cathodes Reconstructed by FIB/SEM Tomography, *J. Electrochem. Soc.* 159 (2012) A972.
- [9] S.K. Eswara-Moorthy, P. Balasubramanian, W. van Mierlo, J. Bernhard, M. Marinaro, M. Wohlfahrt-Mehrens, L. Jörissen, U. Kaiser, An In Situ SEM-FIB-Based Method for Contrast Enhancement and Tomographic Reconstruction for Structural Quantification of Porous Carbon Electrodes, *Microsc. Microanal.* 20 (2014) 1576–1580.
- [10] S. Vierrath, F. Güder, A. Menzel, M. Hagner, R. Zengerle, M. Zacharias, S. Thiele, Enhancing the quality of the tomography of nanoporous materials for better understanding of polymer electrolyte fuel cell materials, *J. Power Sources* 285 (2015) 413–417.
- [11] F. Güder, Y. Yang, U.M. Küçükbayrak, M. Zacharias, Tracing the migration history of metal catalysts in metal-assisted chemically etched silicon, *ACS Nano* 7 (2013) 1583–1590.
- [12] M.D. Abràmoff, P.J. Magalhães, S.J. Ram, Image processing with ImageJ, *Biophotonics International* 11 (2004) 36–43.
- [13] J.F. Delerue, E. Perrier, Z.Y. Yu, B. Velde, New algorithms in 3D image analysis and their application to the measurement of a spatialized pore size distribution in soils, *Phys. Chem. Earth. Pt. A* 24 (1999) 639–644.
- [14] M. Doyle, J. Newman, A.S. Gozdz, C.N. Schmutz, J. Tarascon, Comparison of modeling predictions with experimental data from plastic lithium ion cells, *J. Electrochem. Soc.* 143 (1996) 1890–1903.
- [15] E. Quartarone, P. Mustarelli, A. Magistris, Transport Properties of Porous PVDF Membranes, *The Journal of Physical Chemistry B* 106 (2002) 10828–10833.
- [16] Z. Chen, L. Christensen, J.R. Dahn, Mechanical and electrical properties of poly(vinylidene fluoride–tetrafluoroethylene–propylene)/Super-S carbon black swelled in liquid solvent as an electrode binder for lithium-ion batteries, *Journal of Applied Polymer Science* 91 (2004) 2958–2965.