Combining X-ray tomography with virtual design in $LiCoO_2$ cathodes

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Summary

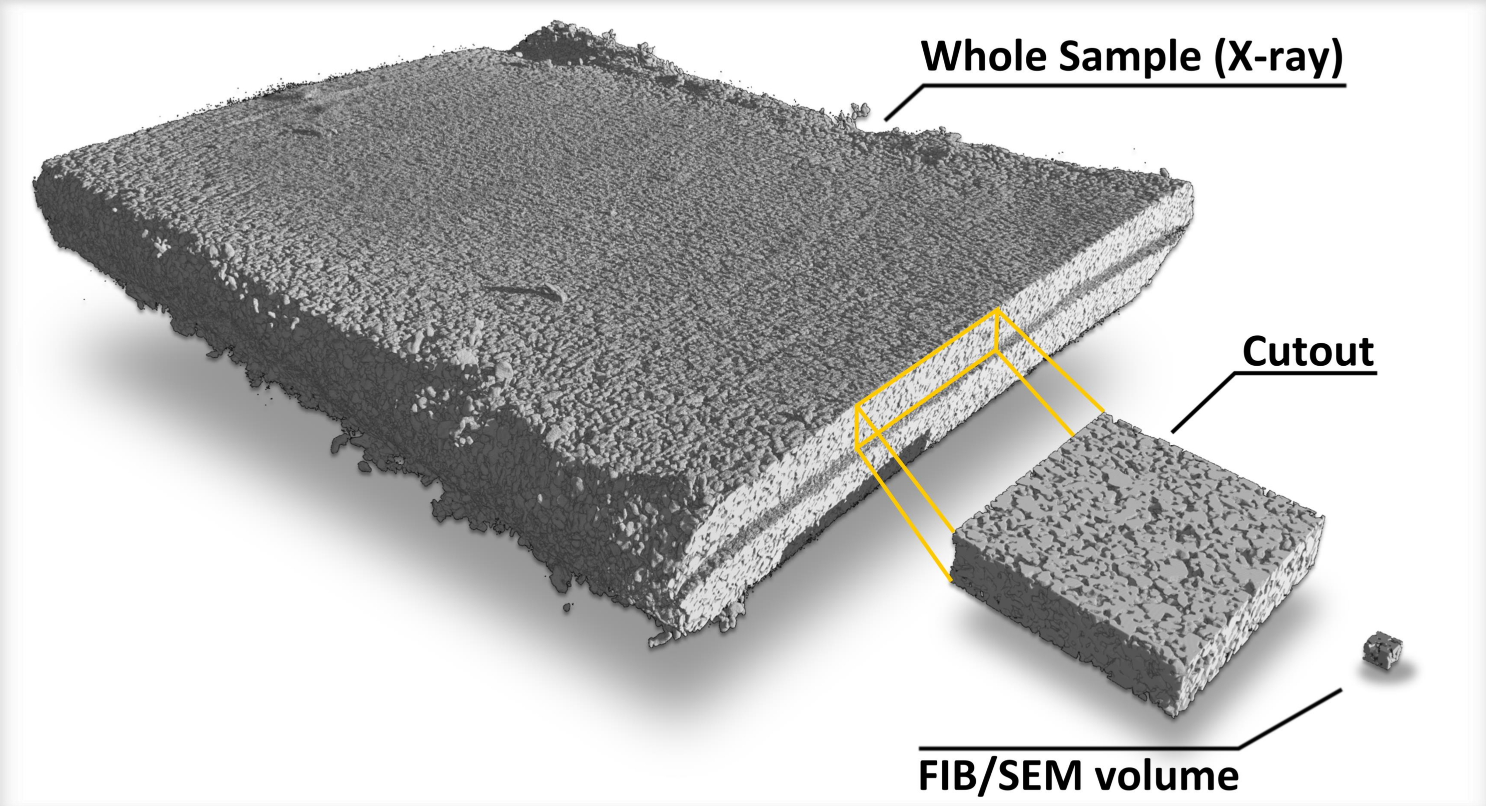
A deficiency of X-ray tomography is that the carbon binder domain (CBD) in $LiCoO_2$ electrodes cannot be imaged. By inserting two virtually designed CBDs into the pore space of an X-ray tomography reconstruction by a computational approach we overcome this deficiency. We find that a fibrous CBD improves conduction significantly at certain operation conditions. We link this to the structural element morphology and percolation of the CBD in the pore space.

Introduction

The microstructure of LiCoO2 electrodes determines transport properties to a large extend. Therefore the electron conducting CBD and the ion conducting electrolyte filled pore space must be understood. FIB/SEM manages to image the CBD, however it is cost intensive and yields small volumes. X-ray on the other hand cannot image the CBD but provides large active domains. We account for all phases by combining X-ray tomography and virtual design.

Reconstruction and CBD Models

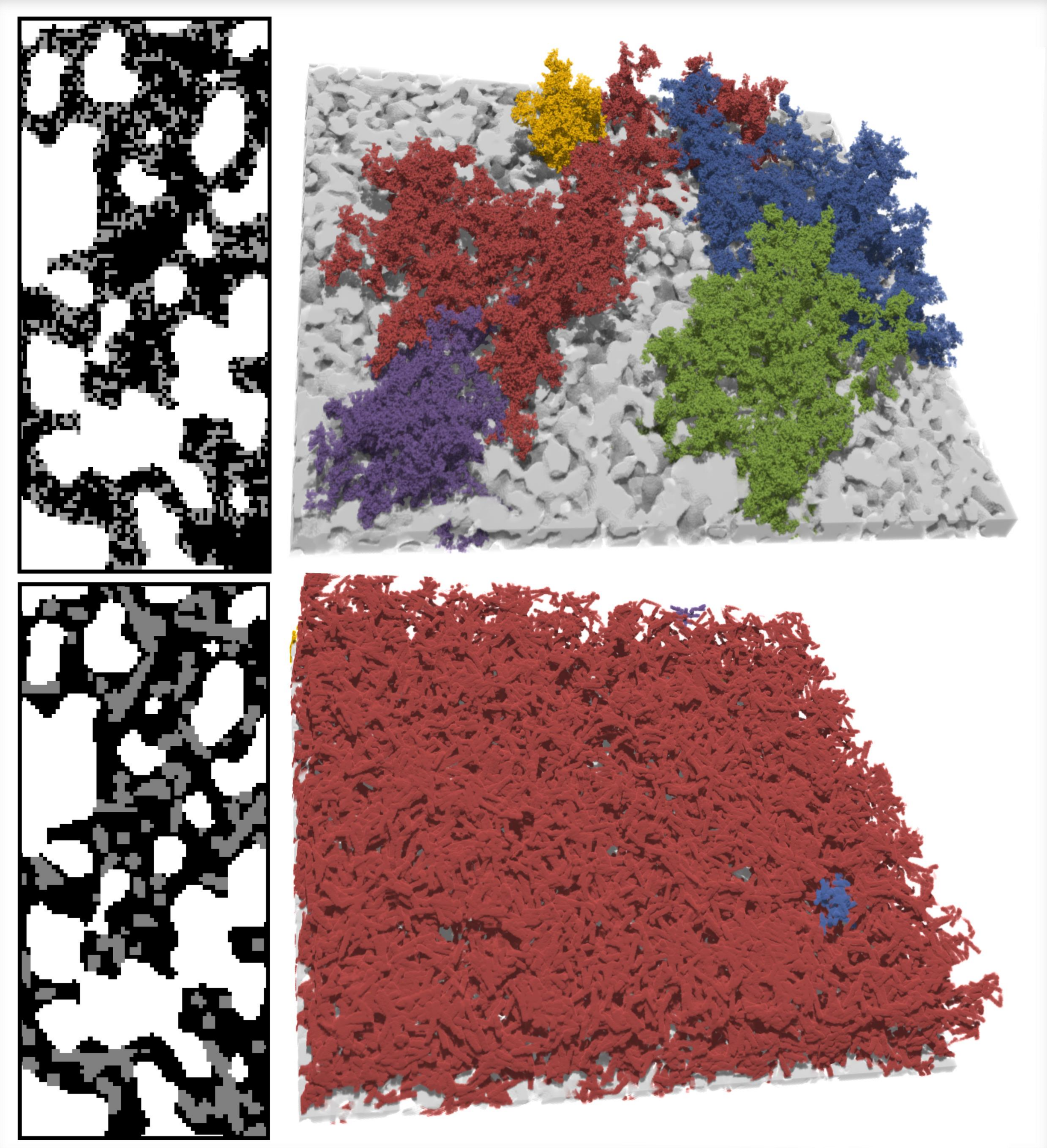
The X-ray images with a resolution of 438 nm per square pixel were aligned and segmented. The whole sample is shown in the following figure. We used a representative cutout being 44x219x197 µm³ for calculations.



For comparison, a typical FIB/SEM volume is shown [1]. Subsequently, we designed a fibrous CBD (Fig.2 bottom) using GeoDict [2] and a cluster CBD (Fig. 2 up) using Matlab and inserted them into the pore space.

The cluster model grows clusters randomly from active material surfaces.

Fig. 2 shows partially 2D slices of a final geometry (left) and the five biggest connected parts of the CBD (right) at equal volume fractions. The fibrous CBD is percolated, the cluster CBD only partially. Here, active material is depicted in white, CBD in grey and pore space in black. When comparing to experimental values for overall tortuosity of the cathode, we find good agreement with carbon black/PVDF mixture CBDs in comparable active domains [3].

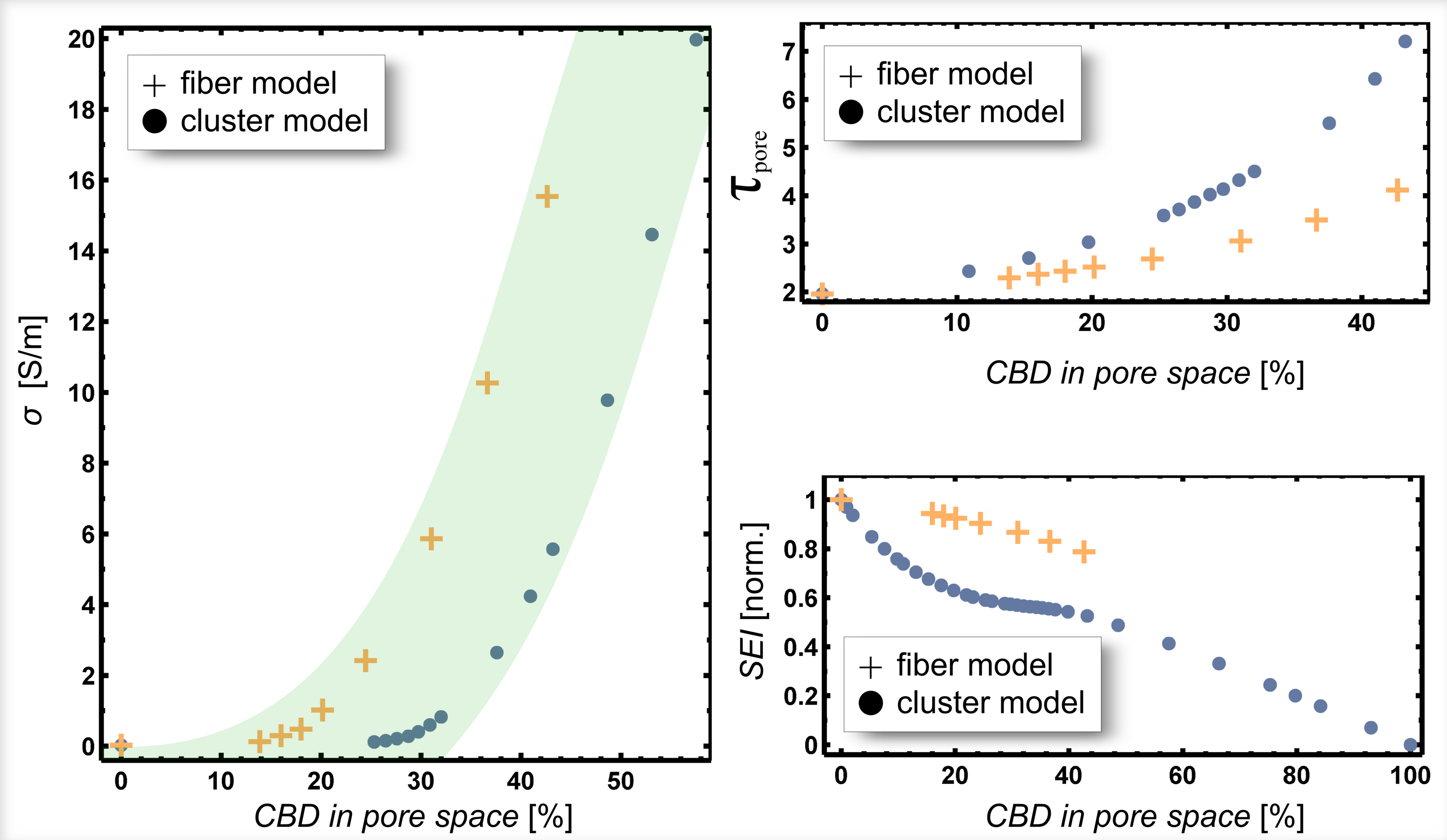


For the fiber model we insert equally shaped fibers into the pore space. The geometries can now be compared.

Results

To compare important transport parameters like SEI, tortuosity and effective electrical conductivity, we insert different volume fractions of the two different CBDs. Subsequently, parameters are calculated using GeoDict and a connectivity analysis is performed to verify percolation.

We find that the fibrous model percolates at half the volume fraction of the cluster model, namely at 13.5% CBD in the pore space. This is made visible by plotting the five largest, connected clusters for both models in figure 2. The percolation is directly linked with a strong increase in the effective electrical conductivity of the cathode. In the following figure, also the solid electrolyte interface and the tortuosity are shown for both models.



The fiber model leaves more surface area and less complicated pathways for Li-ions. However, in reality contact resistances could decrease electrical conductivity. We therefore advise to use a mixture of cluster-like and fibrous CBD [4].

Outlook

Future models should contain more information about the real CBD distribution. Also, the impact of the CBD when it comes to ion conduction must be quantified.

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