

## Supplementary Materials

Additional SEM cross-sectional images of embedded electrodes with the highest (44%) and lowest (18%) porosity – with different SEM settings compared to **Error! Reference source not found.** – are depicted in Figure S1.

To identify the micropore volume within the electrodes with N<sub>2</sub>-physisorption, t-plots [14, 50] of three electrode porosities (39%, 30% and 18%) are shown in Figure S2.

Figure S3 shows the 3D model of the FIB/SEM-tomography results and the simulated CBD within the electrode, created with the GeoDict software.

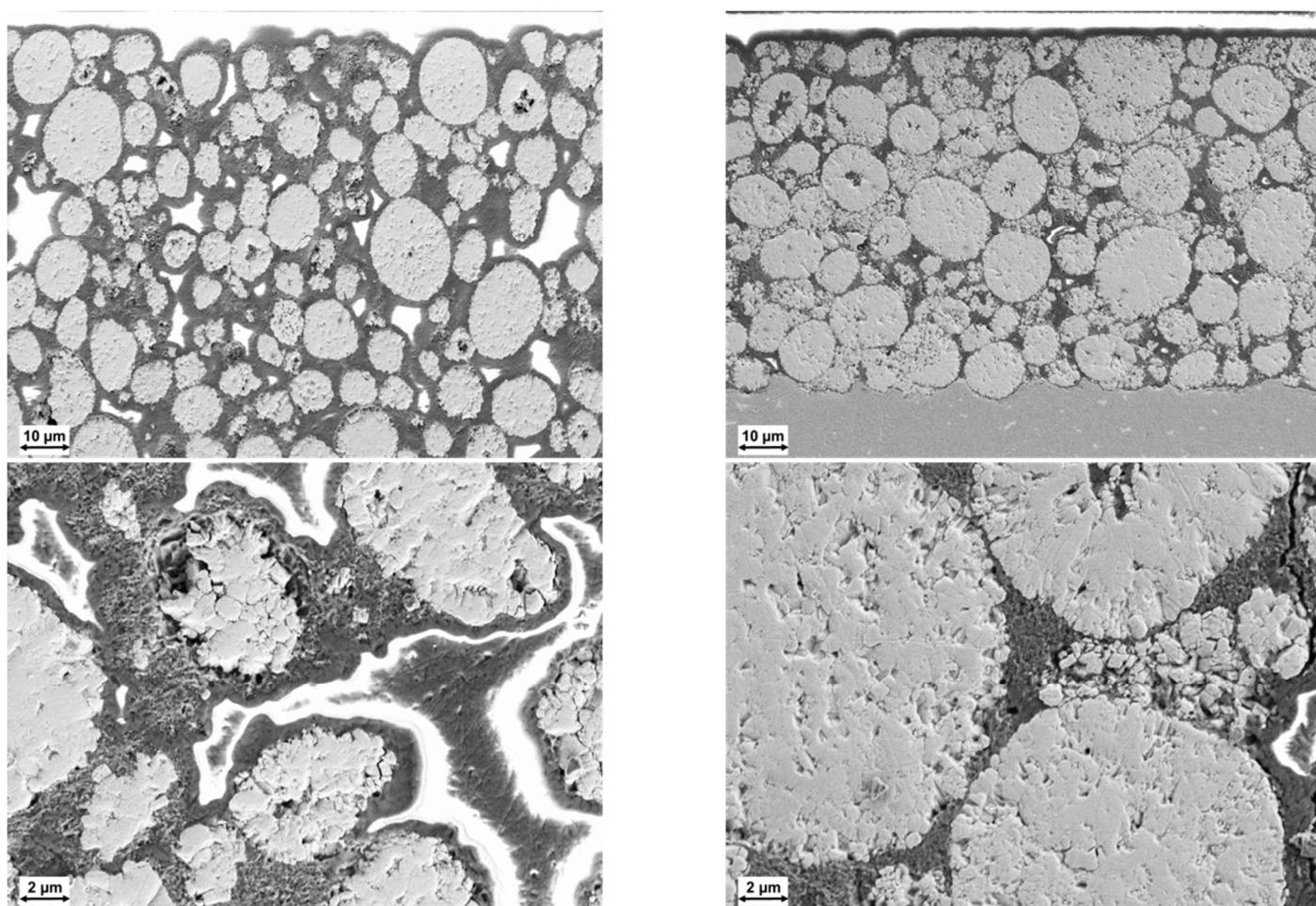


Figure S1 SEM cross-sections of positive electrodes with the highest (44%, left) and lowest (18%, right) porosity in an epoxy resin. The used SEM parameters result in a high surface sensitivity and, thus, electrostatic charging effects of the epoxy resin occur. This way, larger pores, which contain the intruded epoxy resin, show a white color in the uncalendered electrode and are nearly non-existent in the highly densified electrode. In the images with higher magnification (bottom), CBD is identifiable between the AM particles; it fills nearly the whole void space between the AM secondary particles in the calendered electrode (18% porosity).

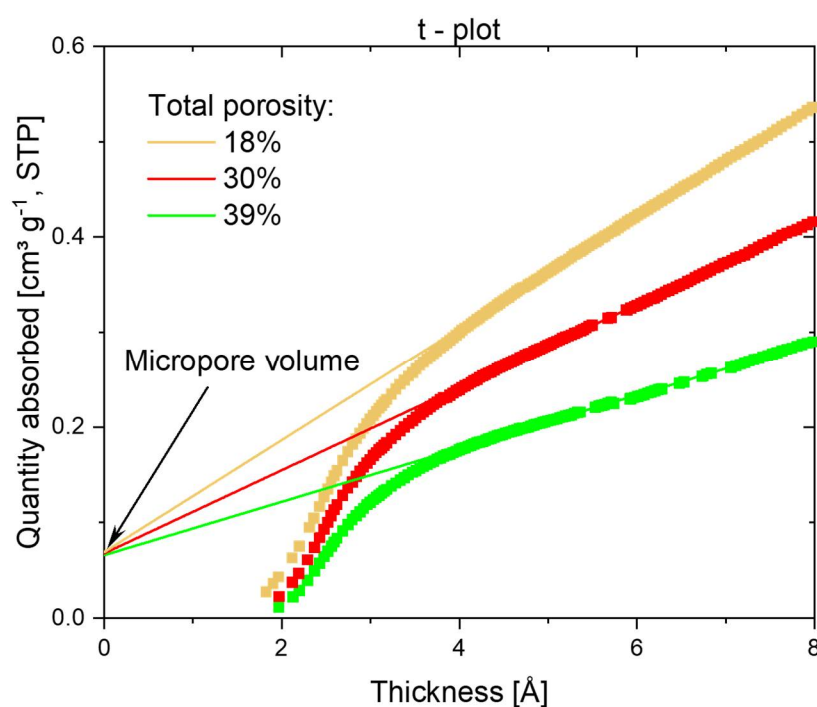


Figure S2 t-plot from  $\text{N}_2$ -physisorption experiments to identify the micropore volume (from y-intercept). All depicted electrode porosities result in the same micropore volume of  $0.1 \text{ mm}^3 \text{g}^{-1}$ , which results in a micropore area of  $0.3 \text{ m}^2 \text{g}^{-1}$ . We used the thickness equation by Harkins and Jura, which was fitted between 4  $\text{\AA}$  and 8  $\text{\AA}$ .

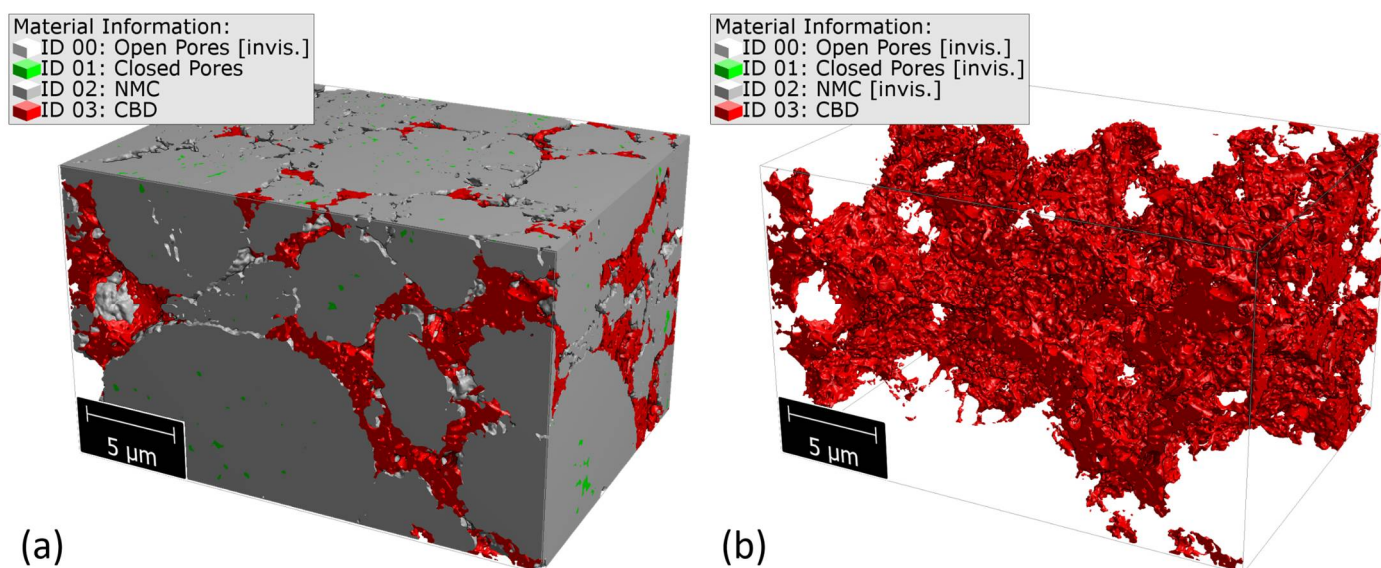


Figure S3 Imported and segmented FIB-SEM 3D image of the positive electrode (a), created with GeoDict software. The CBD is omitted during segmentation and digitally modelled (b). Closed pores within the AM are marked in green; they are distributed within the secondary particles.