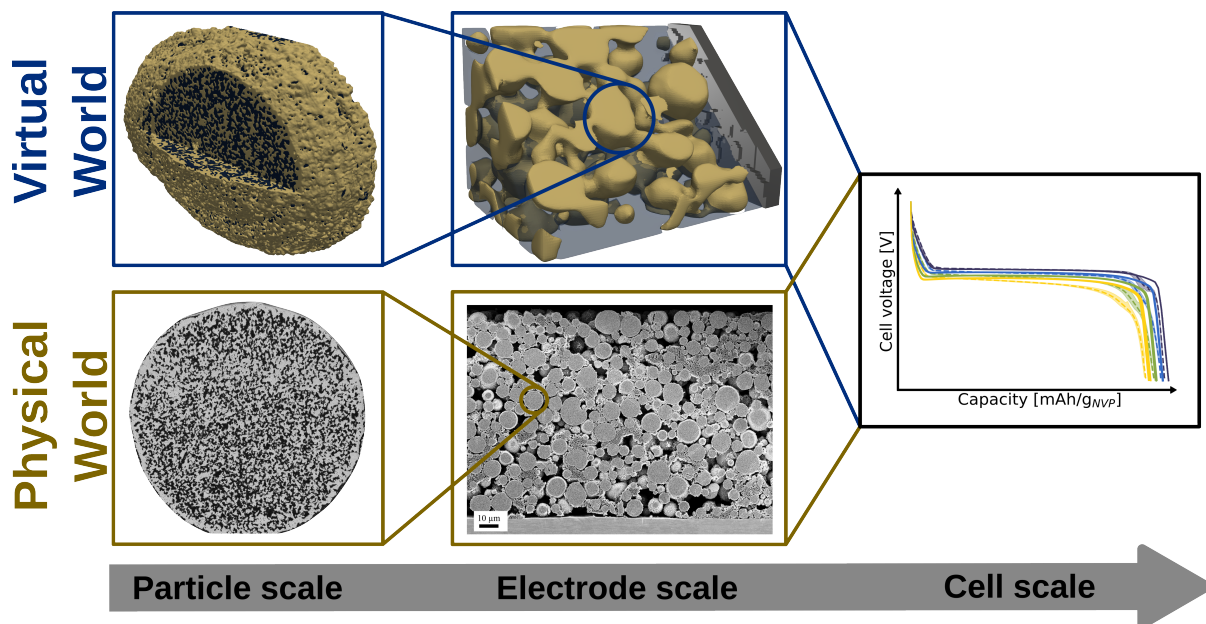


Graphical Abstract

Analysis and optimization of NVP/C electrodes: A multi-scale approach combining experiments with computational modeling

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Highlights

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- Coupling of experimental and modeling techniques for the analysis and optimization of battery materials
- Multi-scale and multi-methodology simulation workflow
- Investigation of NVP/C as cathode for Sodium-ion batteries
- Design guidelines for hierarchically structured electrode materials for sodium-ion batteries

Analysis and optimization of NVP/C electrodes: A multi-scale approach combining experiments with computational modeling

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Abstract

Sodium-ion batteries (SIBs) are expected to play an important role in the transition toward sustainable energy storage, owing to their reliance on more abundant and less critical raw materials compared to state-of-the-art lithium-ion batteries (LIBs). Among the most promising cathode materials is $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP), which combines excellent cycling stability with enhanced safety characteristics. Recently, porous NVP particles interspersed with carbon (NVP/C) have been proposed to substantially improve the rate capability. Further optimization of the particle morphology offers significant potential to increase the material-level energy density while maintaining high power performance. However, the interplay between particle morphology, transport processes, and electrode performance is still poorly understood. In the present paper, we combine complementary experimental and computational modeling methods across multiple length scales to provide a comprehensive analysis of NVP/C. On the basis of these results, we identified the dominant factors limiting electrode performance and performed a morphology optimization study of NVP/C to derive design guidelines for next-generation electrodes with improved energy density.

Keywords: 3D imaging, electrochemical simulations, multi-scale computational modeling, nanoporous NVP/C, sodium-ion batteries

2020 MSC: Primary 00A05, Secondary 00A66.

1. Introduction

Nowadays, lithium-ion batteries (LIBs) represent the dominant electrochemical energy storage technology [1]. However, their widespread deployment relies on critical raw materials such as lithium, cobalt, and graphite, motivating intensive research into post-lithium battery chemistries [2, 3]. Among the most promising alternatives are sodium-ion batteries (SIBs), which benefit from the high abundance and low cost of sodium while offering an operating principle similar to LIBs [4, 5].

While hard carbon has become the established anode material for SIBs, the search for high-performance cathode materials remains an active field of research. $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) has emerged as a particularly promising cathode material due to its excellent structural stability, which results in low capacity degradation and long cycle life. To further enhance its electrochemical performance, nanoporous NVP/carbon (NVP/C) composite particles are manufactured by using a scalable spray-drying process [6]. The nanoporous particle structure significantly improves the rate capability of the material. Comparable concepts have also proven successful for LIB electrode materials [7]. The hierarchical particle architecture facilitates rapid ionic transport through interconnected intra-granular pores, while the conductive carbon network promotes efficient electronic transport throughout the particle. In addition, the primary particles are exposed to electrolyte, which accelerates sodium intercalation kinetics and reduces diffusion pathways within the active material.

However, improved transport properties come at the expense of reduced volumetric energy density. Consequently, key design parameters—including nanoporosity, primary particle size, and carbon content—must be carefully balanced to maximize capacity while maintaining high rate performance. Exploring this multidimensional design space experimentally is both time-consuming and resource-intensive, in particular, when material optimization is coupled with electrode processing and structural design. Consequently, predictive virtual design tools are becoming indispensable for accelerating the development of advanced battery materials and electrodes.

Physics-based modeling provides a powerful framework for guiding material and electrode design. However, battery systems - and hierarchically structured electrodes in particular - are inherently multiscale in nature, with relevant transport processes spanning several orders of magnitude in length and time. Accurately capturing the interplay between material properties, particle morphology, electrode architecture, and cell performance therefore requires a multiscale modeling framework that integrates information across these different scales.

In this work, we present a comprehensive multiscale workflow that combines molecular simulations, advanced imaging, stochastic microstructure reconstruction, physics-based modeling, electrochemical characterization, and data-driven analysis to establish quantitative links between electrode morphology and cell performance. Molecular dynamics simulations are used to parameterize sodium diffusion within NVP. Nanoporous NVP/C particles are synthesized following the approach of [6], electrochemically characterized, and the corresponding image

data is acquired using focused ion beam scanning electron microscopy (FIB-SEM) [8, 9]. Three-dimensional virtual particle structures are reconstructed using methods from mathematical morphology and stochastic geometry [10, 11, 12]. The structures are subsequently analyzed to determine their effective transport properties. Hierarchically structured NVP/C electrodes are fabricated using two different calendering conditions and characterized using synchrotron X-ray tomography [13, 14]. After segmentation into the individual material domains, these three-dimensional electrode structures, together with the material parameters obtained at the lower scales, serve as input for fully resolved three-dimensional electrochemical simulations. Integration of the data of complementary techniques provides a digital representation of NVP/C half-cells. Finally, the proposed workflow is used to identify performance-limiting mechanisms originating from the microstructure of the material and also to derive quantitative design guidelines for the optimization of future NVP/C morphologies.

The remainder of this paper is organized as follows. Section 2 introduces the overall multiscale workflow and the interactions between the different methods and length scales before describing each methodology in detail. The experimental and simulation results are presented and discussed in Section 3, where we also derive design guidelines and predict the performance for next-generation NVP/C materials. Finally, Section 4 summarizes the main findings, discusses the current limitations of the proposed framework, and outlines directions for future research.

2. Methods

2.1. Workflow

In this publication, we develop a multi-scale methodology for a virtual characterization and design of hierarchically structured NVP/C electrodes. Starting at the material level, we use complementary experimental and modeling methods to analyze and optimize limiting processes in NVP/C electrodes. The workflow is illustrated in Figure 1. Advanced analytical techniques, including state-of-the-art imaging methods, bridge the physical and digital worlds by enabling the creation of physico-chemical digital representations of NVP/C cells.

On the experimental side (‘physical world’) the process starts on the material level with the synthesis of nanoporous NVP/C particles (Section 2.2.1). Using this material, we manufacture electrodes with two different degrees of calendering (Section 2.2.2). The electrodes are then electrochemically characterized in half-cell measurements as described in Section 2.2.3.

The development of the digital representation starts similarly on the material level. In particular, we use molecular dynamics simulations (Section 2.3) to determine the chemical diffusion coefficient of sodium within the crystal structure of NVP. Additional material parameters are extracted from either dedicated model experiments or the existing literature. On the particle level, we analyze the morphology of the NVP/C particles and the entire electrode using high-resolution scanning electron microscopy (HR-SEM) and focused-ion beam scanning electron microscopy (FIB-SEM) for 2D and 3D imaging, respectively. Image

segmentation and a 3D stochastic reconstruction of the internal particle structure were performed in [10]. The 3D data are analyzed to determine the characteristic structural and effective properties (Section 2.6). Next we perform synchrotron X-ray tomography of electrodes with different degrees of calendaring (Section 2.4), since the arrangement of NVP/C particles on the electrode scale is decisive for battery performance. Segmentation of the 3D data sets allows to distinguish the different phases in the electrode (Section 2.5), which enables us to characterize the morphology by quantitative statistical image analysis (Section 2.7). Finally, the information on the different length scales is fused to create a digital representation of the electrochemical cell enabling virtual experiments based on detailed multi-scale physico-chemical models (Section 2.8).

The complementary results from the physical, experimental, and virtual characterization allow for a holistic interpretation of material and electrode properties. On the one hand we are able to determine limiting factors for the cell performance (Section 3.5) and, on the other hand the validated digital representation can be used to assess the optimization potential of this new class of nanoporous NVP/C materials. In particular, in Section 3.6 we provide design guidelines to achieve improved energy density and good rate performance.

2.2. Electrode manufacturing and experimental characterization

2.2.1. Material synthesis

The composite material of sodium vanadium phosphate and a carbon-binder matrix (NVP/C) is synthesized by spray drying followed by a calcination process. For this purpose, ammonium metavanadate NH_4VO_3 , sodium carbonate Na_2CO_3 , and ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ are dissolved in deionized water at a molar ratio of 4 : 3 : 6, before β -lactose is added at 16.7 wt%. Spray-drying of the solution is performed with an inlet temperature of 210 °C and an outlet temperature of 112 °C. Calcination of the resulting precursor powders takes place under argon at a heating rate of 1 K min⁻¹ to 450 °C, which is maintained for 2 h. Then, the temperature is increased to 850 °C at a heating rate of 3 K min⁻¹, followed by an isothermal holding time of 5 h. In a agitator ball mill, the powder is ground aqueous for 7.5 h. The obtained suspension is diluted with water to a solids content of 7.5 wt%. Polyacrylic acid and polyethylene glycol dissolved in water are added to the suspension, which is then sprayed again in a spray dryer with inlet temperature of 210 °C and outlet temperature of 112 °C. The second calcination takes place in an argon/hydrogen atmosphere and the heating rate is 3 K min⁻¹ to 800 °C with an isothermal hold time of 5 h. Further details on how the process parameter influence the NVP/C composites can be found in [15].

2.2.2. Electrode preparation

For the preparation of NVP/C cathodes conductive carbon black Super C65 (Imerys Graphite & Carbon) is used as conductive additive and PVDF Solef 5130 (Solvay S.A.) as

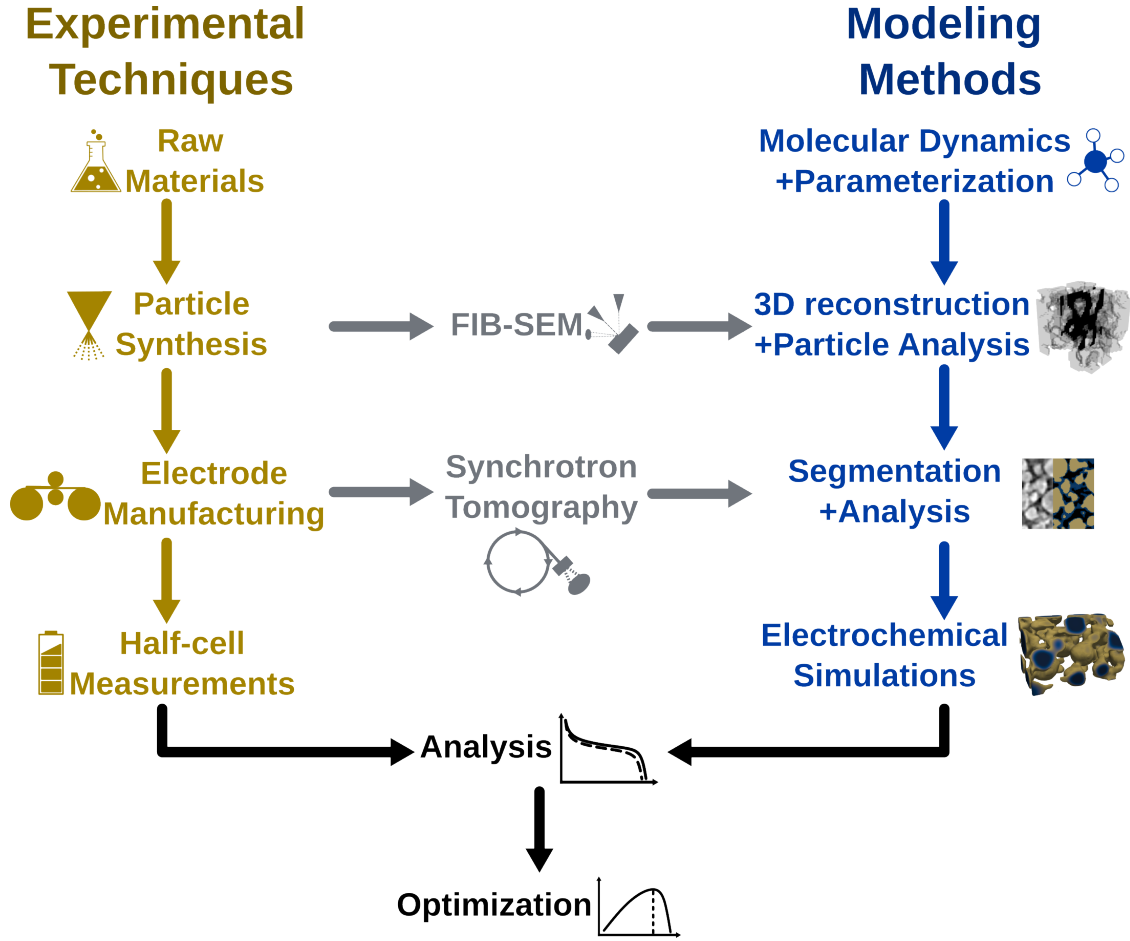


Figure 1: Interactions between the methods used in this paper. Experimental and modeling methods go from the material over particle and electrode scale to cell level. Based on the analysis of experimental data, we use model-based simulations to identify an optimized electrode design with respect to cell performance.

binder. The solvent used for slurry production is N-Methyl-2-pyrrolidone (NMP). The slurry contains 90 wt% NVP/C active material, 5 wt% conductive carbon black and 5 wt% binder.

The slurry is coated by a doctor blade and dried on a KTF-S (Mathis AG, Switzerland) roll-to-roll system. Immediately after doctor blading, a laser triangulation is used to measure the wet film thickness of the coating, which is approximately 210 μm . The film is then transported to a drying area consisting of two separately controllable convective slotted nozzle ovens. The temperature is 80 $^{\circ}\text{C}$ in the first dryer and 120 $^{\circ}\text{C}$ in the second one. The speed of the furnace fans is 1500 rpm and the path speed of the current collector is 0.3 m min^{-1} . The layers are compacted with a GLK 400 calender (Saueressig). The cylindrical calender rolls, which have a diameter of 267 mm, are heated to 50 $^{\circ}\text{C}$. The web speed of the calender rolls is 1 m min^{-1} . For the present paper, two electrodes with the target microporosities (only

counting electrode scale porosity, not porosity in secondary particles) of 60% and 40% are manufactured. Throughout this publication we refer to the two electrodes with mildly and strongly calendered respectively. This process results in electrodes forming a hierarchical structure exhibiting nanopores within and micropores between particles.

2.2.3. Experimental characterization

The microporosity of the manufactured electrodes is measured by mercury intrusion porosimetry. These results serve as input for the segmentation of synchrotron images representing the electrode (cf. Sections 2.4 and 2.5). Note that the nanopores within active material particles cannot be resolved by synchrotron tomography. In addition, the electrodes are cycled against a sodium counter electrode using the rates and numbers of cycles stated in Table 1. After this protocol a series of 1C cycles follows to check for irreversible effects.

Table 1: Cycling protocol for both electrodes with corresponding rate and number of cycles. All rates are applied successively from left to right without a constant voltage phase between cycles.

Rate	$\frac{1}{20}$ C	$\frac{1}{10}$ C	$\frac{1}{5}$ C	$\frac{1}{2}$ C	1C	2C	3C	5C	10C
Number of cycles	2	5	5	5	10	10	10	10	10

2.3. Molecular dynamic simulations for bulk diffusion coefficient

The determination of the bulk diffusion coefficient in NVP is done in two steps: First, we use density functional theory (DFT) to compute the positions of atoms in the crystal lattice using the experience already gained in a previous multiscale simulation study of NVP [16]. In a second step, molecular dynamics simulations are applied to track sodium motions, from which the diffusion coefficient can be calculated.

For the first step, we perform periodic DFT [17, 18] calculations using the Vienna *Ab initio* Simulation Package (VASP) [19, 20, 21]. Exchange–correlation effects were treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional [22]. The interaction between ionic cores and valence electrons was described using the projector augmented-wave (PAW) method [23]. A plane-wave kinetic energy cutoff of 520 eV was employed.

On-site Coulomb interactions of the transition-metal d electrons were accounted for using the DFT+ U approach within the Dudarev formalism [24]. A Hubbard U value of 3.25 eV was applied to the d orbitals of the transition-metal atoms, while no U correction was applied to the remaining elements. Non-spherical contributions inside the PAW spheres were included, and long-range van der Waals interactions were incorporated using the DFT-D3 method with Becke–Johnson damping [25].

Spin polarization was included in all calculations, and systems were initialized with ferromagnetic ordering of the transition-metal atoms. Symmetry was disabled to allow full

structural and magnetic relaxation. Electronic self-consistency was achieved with an energy convergence criterion of 1×10^{-5} eV.

To track the sodium motion in the crystal structure, *ab initio* molecular dynamics (AIMD) simulations were carried out in the canonical NVT ensemble using a Nosé–Hoover thermostat. Simulations were performed for a series of compositions with varying level of sodiation, and for temperatures of 300, 400, 600, 800, 1000, and 1200 K. Initial velocities were assigned according to a Maxwell–Boltzmann distribution corresponding to the target temperature. A time step of 1.0 fs was used, and each trajectory was propagated for up to 15000 ionic steps.

To obtain the diffusion coefficient D , the mean-squared displacement of sodium ions was calculated along the simulation trajectories and the Einstein relation

$$D_{\text{NVP}} = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$$

was used, where $\mathbf{r}(t)$ denotes the position of a sodium ion at time t , and the angular brackets indicate an ensemble average over all ions and multiple time origins.

2.4. 3D imaging

Geometric information about the electrode morphology is obtained by various imaging techniques. On particle level focused-ion beam scanning electron microscopy (FIB-SEM) tomography and high-resolution scanning electron microscopy (HR-SEM) are used. The electrode structure is scanned via synchrotron X-ray tomography. These complementary techniques allow for imaging of the electrode architecture at the micrometer scale and high-resolution reconstruction of secondary particle morphologies at the nanometer scale.

Particle imaging. FIB-SEM and HR-SEM on the particle scale are performed as described in [10]. These images are analyzed and statistically equivalent 3D structures are generated by means of stochastic modeling techniques [10]. This result of this process is a virtual representation of the interior particle structure, which is further analyzed in Section 2.6.

Electrode imaging. Scanning electron microscopy is used to get a qualitative impression of the electrodes [26]. Since these images provide only limited 3D information additionally synchrotron X-ray tomography is used to get more detailed information about the electrode structure.

For synchrotron X-ray tomography, electrode stripes of approximately $1 \times 3 \text{ mm}^2$ are cut from the manufactured electrodes and mechanically clamped between plexiglass rods. This mounting ensured sample stability while preventing contamination by adhesives. Tomography experiments are conducted at the BAMline of the BESSY II synchrotron facility (Helmholtz-Zentrum Berlin, Germany, HZB) [14]. Tomography scans over an angular range of 180° are performed with 2500 projections acquired using a PCO.edge 5.5 detector (2560×2160 sCMOS chip). Each projection is recorded with an exposure time of 0.5 s at a beam energy of 16 keV. The $20\times$ optical magnification is used, resulting in an effective pixel size of

0.360 μm . Reconstruction is performed with in-house Python-based scripts developed at HZB, using the ASTRA toolbox [27] with total-variation-based denoising followed by filtered back projection. For image analysis, the 3D image data representing the strongly and mildly calendered electrode is subdivided into four sub-samples per electrode. Each sub-sample has a size of 144 $\mu\text{m} \times 144 \mu\text{m}$ in lateral direction and takes the full thickness of the electrode into account.

2.5. Experiment informed electrode image segmentation

In this section, an experiment informed segmentation of the 3D image data of the electrode structure, which is measured by synchrotron tomography as described in Section 2.4, is presented. The approach is experiment informed in the sense that it uses segmentation algorithms, which are calibrated based on various experimental measurements. First, we perform a phase-based segmentation, i.e. each voxel is attributed to the active material or to the union of carbon binder domain (CBD) and pore space. For each of the latter voxels, we assign a local volume fraction of the binder-additive phase via its grayscale value. Note that, due to the nanostructure of the binder-additive phase, it is not possible to uniquely attribute each voxel either to the binder-additive phase or to the pore space. The segmented image data is used as an input for locally resolved electrochemical simulations in Sections 2.8 and 3.5.

The segmentation is performed such that the experimentally determined volume fractions of the active material and the binder-additive phase, see Section 3.4, are reflected in the segmented image data. It is important to note that we consider the volume fraction of the active material including the nanopores of the secondary NVP/C-particles, because the nanopores are not resolved by synchrotron X-ray tomography.

For image data of each of the two differently calendered cathodes, we proceed as follows. To begin with, we determine a mask, in which the electrode is contained. For this purpose, a variance filter with a radius of 27 μm is applied. In the filtered image, the value at a given voxel is the variance of all grayscale values of voxels within a distance of less than 27 μm . Since the variability of grayscale values is much higher inside the electrode than outside, global thresholding after application of the variance filter leads to an appropriate first candidate for the mask of the electrode. The threshold is determined as proposed in [28]. This first candidate of the mask is refined in a post-processing step to obtain the final mask. Post-processing is performed in two steps. First, all connected components which do not belong to the largest component are removed. Second, holes within the mask are closed. For computing connected components in 3D image data, we use the Hoshen-Kopelman algorithm [29].

Before segmenting the active material in the previously determined mask, an anisotropic diffusion filter [30] is applied, which reduces noise in the image while maintaining edges.¹

¹For the anisotropic diffusion filter, we choose the default parameters in Matlab 2023a. This means, that

Subsequently, global thresholding is performed such that the resulting volume fractions of active material coincide with the experimentally determined values. Finally, we segment the CBD. Since the CBD is nanoporous as in [31, 32, 33], it is not possible to classify individual voxels either as CBD or pore. Thus, based on grayscale values and the experimentally determined porosity, we assign a value between 0 and 1 to each voxel indicating its nanoporosity. For this purpose, we perform a soft clustering with two classes using a Gaussian mixture model, see Sections 6.8 and 13.2 in [34]. We assume that the distribution of grayscale values is a mixture of two distributions, one coming from only porous voxels and one coming from voxels that also contain CBD. Using the Gaussian mixture model, we can assign a probability to each voxel to which class it belongs to. We interpret the probability of the CBD class to be proportional to the amount of CBD that is contained in this voxel. Finally, we define the amount of CBD within one voxel by the probability that the voxel belongs to the CBD class multiplied by some constant c , which is chosen such that the experimentally determined porosity is reproduced. The resulting image segmentation is visualized in Figure 3.

2.6. Effective bulk properties for the nanoporous active material particles

To allow for a homogenized view of the nanoporous NVP/C agglomerates within the battery model (see Section 2.8), we determine volume fractions, specific surface area and effective transport parameters from segmented image data. The corresponding code is openly available in the Python package *Taufactor* [35, 36]. The volume fraction of phase α (either active material, carbon or solid), denoted by ε_α is determined by the voxel-count method, see Section 6.4.2 in [11]. The specific surface area of a phase α denoted by a_α is defined as the ratio of the surface area A_α over the domain volume V , i.e. $a_\alpha = A_\alpha/V$. We estimate a_α using a surface representation based on the phase-field method introduced in [37] as this method significantly reduces grid anisotropy artifacts on voxel-based data. A diffuse representation via the continuous indicator field ϕ is obtained by smoothing the labeled image with a Gaussian kernel. The diffuse interface area is then defined by regions of $|\nabla\phi| \neq 0$. The specific surface area is then given as

$$a_\alpha = \frac{1}{V} \int_V |\nabla\phi| dV. \quad (1)$$

Note that a_α has unit 1/m.

The effective conductivity or diffusivity within the nanoporous and multiphase NVP/C particles is determined from simulations, where we assume that the bulk transport properties of single phases are known. Both steady-state diffusion and electrical conduction are described by the partial differential equation

$$\nabla \cdot (\Gamma \nabla u) = 0 \quad (2)$$

5 iterations are performed and the 26-connectivity is used on the voxel grid.

where Γ is either the bulk diffusivity $D_{\alpha,0}$ or the bulk electrical conductivity $\sigma_{\alpha,0}$ of the respective phase. The effective transport coefficient of a single phase α can be expressed as

$$D_{\alpha}^{\text{eff}} = \frac{\varepsilon_{\alpha}}{\tau_{\alpha}} D_{\alpha,0} \quad \text{and} \quad \sigma_{\alpha}^{\text{eff}} = \frac{\varepsilon_{\alpha}}{\tau_{\alpha}} \sigma_{\alpha,0}, \quad (3)$$

see [38, 39]. Here ε_{α} denotes the volume fraction which can be computed from direct image analysis and τ_{α} the tortuosity factor τ_{α} , which accounts for microstructure effects such as constrictions and tortuous pathways. It is computed by solving the physical equation Equation (2) and differs from the notion of mean geodesic tortuosity considered in Section 2.7. The code for computing a_{α} and τ_{α} are available in [36].

2.7. Statistical image analysis on electrode scale

Based on segmented 3D image data, as described in Section 2.5, morphological descriptors of the electrode structure are computed based on methods from spatial statistics. These descriptors serve as a quantitative characterization of the morphology, see Section 3.3, which allows for a better interpretation of the results obtained from electrochemical simulations in Section 3.5. These descriptors comprise both, global and local volume fractions of different phases in the electrode structure, as well as a continuous phase size distribution [40]. In particular, we analyze the volume fraction of CBD depending on the distance to the closest NVP/C particles. Another parameter is the mean geodesic tortuosity, see Section 2.5.3 in [41], measuring the windedness of shortest transportation pathways. For further information on these morphological descriptors, we refer to Appendix S1.1.

2.8. Models for electrochemical simulations

In this section, we describe the multi-scale electrochemical model which we use in the virtual electrochemical characterization of the NVP/C electrodes. The model specifically considers the hierarchical structure of the electrodes enabling identification of limiting factors for the cell performance on all scales. Figure S1 shows a schematic of the simulation setup starting at the cell level. The structural details on secondary and primary particle level are captured in respective submodels explained below.

The half-cell model comprises from negative to positive electrode: aluminum current collector, a sodium metal counter electrode, a porous separator, the NVP/C cathode and aluminum current collector. A detailed description in terms of mathematical equations can be found in Section S1.2. The sodium metal counter electrode is sufficient in size to be considered as an infinite reservoir of sodium. At the interface to the electrolyte, mass and charge transfer is described using a kinetic expression in the form of a Butler-Volmer equation. The separator is modeled as an effective medium consisting of electrolyte and separator material which obstructs transport processes resulting in reduced effective transport parameters in the electrolyte phase.

The focus of the modeling approach is on the hierarchically structured NVP/C cathode. The 3D segmented microstructure of the electrode as described in Section 2.5 is embedded

directly as computational grid at the cathode. Within the electrode, there are three domains described by different equations: Electrolyte, CBD, and nanoporous NVP/C particles. In the electrolyte we use the isothermal equations as derived in [42]. In nanoporous CBD, these equations are homogenized to consider subgrid effects as in [43]. The transport processes in the nanoporous NVP/C particles similarly occur below the resolution of the synchrotron image data acting as the cell level computational grid. Therefore, they are modeled by a homogenization approach in analogy to the well-known Doyle-Fuller-Newman (DFN) or P2D models [44]. The transport equations incorporate the effective transport parameters determined by the methods described in Section 2.6. Finally, on the scale of the primary particles we model intercalation on the surface and diffusional transport within idealized spherical particles. The chemical diffusion coefficient has been determined by the MD simulations described in Section 2.3. A detailed description and derivation of the model can be found in [45]. Note that NVP is a phase separation material (see [6, 46, 47]). This type of materials is typically described using a phase-field model (e.g. [48, 49]). In our approach, we simplify these processes by modeling Fickian diffusion to reduce computational complexity.

A summary of all model equations and boundary conditions is provided in the supporting information Section S1.2. More details on the parametrization of the models, particularly the material parameters of the electrolyte and the kinetic parameters of the sodium metal anode and NVP/C are provided in Section S1.3.

To reduce computational burden, we reduce the size of the simulation domain to an area of $25.2\text{ }\mu\text{m} \times 25.2\text{ }\mu\text{m}$ but keep the full electrode thickness. For improved statistics, we run simulations for each scenario on all four different virtual reconstructions of 3D electrode data for both, highly and mildly calendered electrodes, respectively (see Sections 2.4 and 2.5).

3. Results and discussion

In this section, we present results of the virtual characterization and optimization of hierarchically structured NVP/C electrodes using the multi-scale digital representation of the cells presented in the previous section. We start by discussing individually the key results of the complementary methods from material to electrode level. The discussion supports the analysis of limiting factors on cell level enabling virtual optimization of the particle design.

3.1. NVP diffusion coefficient

The calculated diffusion coefficients from AIMD simulations as described in Section 2.3 are summarized in Table 2 for various sodium concentrations and temperatures. In general, the diffusivity increases with temperature, as expected from a thermally activated hopping process. At room temperature the crystal configuration for $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ is so stable, that not enough hopping events are observed to compute D_{NVP} within feasible computational time. Therefore, diffusion coefficients at low temperatures and Na stoichiometry are expected to have a higher uncertainty.

Table 2: Diffusivity ($\text{cm}^2 \text{s}^{-1}$) results for different sodium concentrations and temperatures obtained from AIMD simulations. First column contains values of x in $\text{Na}_x\text{V}_2(\text{PO}_4)_3$

x	300 K	400 K	600 K	800 K	1000 K	1200 K
1.0	-	3.90×10^{-8}	1.03×10^{-7}	7.56×10^{-8}	9.74×10^{-8}	3.54×10^{-8}
1.5	2.55×10^{-14}	1.18×10^{-9}	1.18×10^{-6}	2.89×10^{-6}	7.73×10^{-6}	1.77×10^{-5}
2.0	2.52×10^{-13}	3.06×10^{-9}	1.72×10^{-6}	4.56×10^{-6}	4.00×10^{-6}	1.16×10^{-5}
2.5	5.97×10^{-13}	5.62×10^{-7}	2.01×10^{-6}	9.00×10^{-6}	7.70×10^{-6}	2.83×10^{-5}
3.0	2.11×10^{-12}	2.28×10^{-8}	5.66×10^{-6}	1.35×10^{-5}	2.66×10^{-5}	1.56×10^{-5}

Still, the range of values determined by [50] using GITT measurements during charge and discharge matches well with the results of our AIMD simulations. A one-to-one comparison between data sets is challenging since the experimental data is reported as a function of cell voltage. To reduce computational complexity of the electro-chemical simulations, we use a constant diffusion coefficient of $D_{\text{NVP}} = 2 \times 10^{-14} \text{cm}^2 \text{s}^{-1}$ in all simulations. The value represents the majority of experimental and theoretical data.

3.2. Structural analysis of secondary particles

Figure 2a shows the segmented 3D FIB-SEM image data of a NVP/C particle. At the cut the interior structure of the nanoporous NVP/C particle is clearly visible. The effective properties of nanoporous agglomerates are determined from the virtual structures which have been stochastically reconstructed in [10] based on segmented FIB-SEM and HR-SEM image data of the particle interior. From synthesis and subsequent characterization, the NVP/C particles are determined to consist of 55.6% NVP, 12.6% carbon-binder matrix and 31.8% nanopores, respectively, while image segmentation resulted in 51.5% NVP, 33.7% carbon-binder matrix and a nanoporosity of 14.8% [10]. The deviation has been explained with tiny nanopores that are within the areas labeled as carbon. These tiny nanopores can be visualized by means of transmission electron microscopy (TEM), but are below the resolution limit of HR-SEM, see Figure S2 in the supplementary information of [10]. By comparing the respective fractions of carbon and pore from experiment and image segmentation, we conclude that only 40.8% of the *carbon-labelled* regions are actually carbon. Therefore, we assume a homogenization of the electronic and ionic conductivity as well as the electrolyte sodium-ion diffusion in the carbon-labelled areas following the simple mixture rule $\hat{\Gamma} = 0.408 \Gamma_{\text{C}} + 0.592 \Gamma_{\text{pore}}$ which is relevant for the electronic transport as well as the sodium ion transport in pores wetted by electrolyte. All values reported in Table 3 and the remainder of this section are determined from a virtual 3D structure generated in [10].

The pairwise surface areas can be computed from the individual specific surface areas [51]. These computations yield $a_{\text{NVP-C}} = 0.01130 \text{nm}^{-1}$, $a_{\text{NVP-pore}} = 0.00447 \text{nm}^{-1}$ and $a_{\text{C-pore}} = 0.00910 \text{nm}^{-1}$. The sodium ion diffusion occurs in the electrolyte which fills the pore phase of the nanoporous secondary particles and the nanopores within the carbon-labeled domains.

Table 3: Phase-specific properties in nanoporous agglomerate

	NVP	<i>carbon-labelled</i>	pore
volume fraction ε_α [-]	0.515	0.324	0.160
specific surface a_α [nm ⁻¹]	0.01577	0.02040	0.01358
tortuosity factor τ_α [-]	2.053	4.289	-

Computing the effective diffusivity as described in Section 2.6 for this mixed transport yields a value of $D_{\text{Na}^+}^{\text{eff}} = 0.1527 D_{\text{Na}^+}$ (corresponding to $\tau_{\text{Na}^+} = 2.307$). Electrons are transported mainly through the carbon scaffolding within the nanoporous structure while the NVP phase can conduct electrons to some extent as well. The electrical conductivity of pure NVP has been measured to be as low as $3 \times 10^{-8} \text{ S/cm}$ [52]. The conductivity of carbon ranges e.g. for carbon black $\sigma = 0.1, \dots, 100 \text{ S/cm}$ [53]. Assuming that the conductivity of the carbon scaffolding is comparable to that of carbon black at a packing fraction of 40 % (conservative assumption), the electrical conductivity equals $\sigma_C = 0.1 \text{ S cm}^{-1}$. As the conductivity of the NVP phase is at least 6 orders of magnitude smaller, the contribution to electronic transport is negligible. The tortuosity factor for electronic transport in the carbon-labeled phase is computed as $\tau_{e-} = 4.289$ and, therefore, $\sigma_{e-}^{\text{eff}} = 0.00318 \text{ S cm}^{-1}$.

3.3. Electrode morphology

From SEM images taken in [26] we get a qualitative impression of the electrode structure. The images can be found in Figure 2. For the mildly calendered electrodes the image indicates that the inner structure of the NVP/C particles is not affected by the calendering process. Binder and conductive additives can be clearly distinguished from the secondary particles and pore space. The density of the electrode is moderate making it unlikely that ion transport is limiting the performance of the electrode. In contrast, the connections between CBD and NVP/C particles as well as the contact between different NVP/C particles are only weakly established.

The image of the strongly calendered electrode shows typical features of the compaction process. The density of the electrode and also the compaction of the CBD is visibly higher. This indicates improved electron transport on the electrode level due to improved contact among the solid phase components. However, we observe several broken secondary particles in the cross-cut. On the one hand, these cracks compromise electron transport on particle level, potentially even causing loss of NVP/C. On the other hand, cracks facilitate wetting of the internal pore structure with the liquid electrolyte.

For a quantitative analysis of the electrode structure, we consider 3D images acquired by X-ray tomography which are segmented as described in Section 2.5. The segmentation leads to 3D images, in which each voxel is either classified as solid voxel, as pore voxel or as CBD voxel. For the latter, we specify the amount of CBD, that is contained within this voxel, since the nanopores within CBD are below the voxel size of $0.36 \mu\text{m}$. The result of the

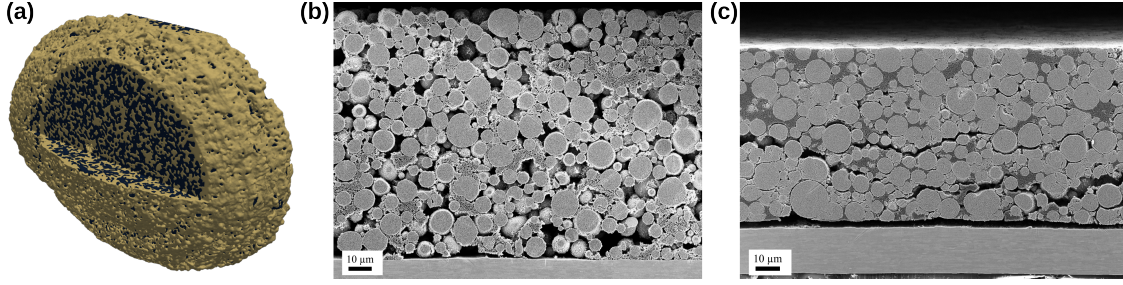


Figure 2: (a): 3D rendering of a FIB-SEM image acquired as described in [10] showing the outer shell with a cut to the inner structure of an NVP/C particle. Beige shows NVP, blue indicates interior pore and carbon phase which can not be distinguished in this image. SEM images [26] of the mildly (b) and strongly (c) calendered electrode. Stronger calendering leads to improved contact between particles and CBD but also to particle cracking.

segmentation is visualized in Figure 3. The segmented images show the compaction after calendering. The strongly calendered electrode (Figure 3d-f) is thinner with a higher volume fraction of NVP/C. Moreover, the NVP/C particles are pressed together such that voids between pairs of NVP/C particles are less pronounced. Note that the resolution in the X-ray tomography data is not sufficient to detect particle cracking as described above.

We computed the volume fraction of NVP/C for the image data, which is 0.477 for the mildly and 0.635 for the strongly calendered electrode. The resulting values are in good agreement with the experimentally determined volume fraction of NVP/C particles (including their nanopores) of 0.475 for the mildly and 0.633 for the strongly calendered electrode, respectively [26]. The most important morphological descriptors from Section 2.7 are shown in Figure 4. In Figure 4a the local volume fraction of CBD is shown. In general, we observe higher average local CBD volume fraction close to the NVP/C surface which can be interpreted as accumulation of CBD around NVP/C particles. After calendering, this effect is more pronounced. Furthermore, the strongly calendered electrode shows an increasing share of CBD with high solid volume fraction as indicated in Figure 4b. This confirms a formation of dense CBD in the calendering process, particularly close to the particle surface. Figure 4c shows the mean geodesic tortuosity. In our analysis, we vary the threshold of CBD volume fraction above which the CBD becomes blocking for ion transport. This result aligns with [54], where similar structured electrodes are studied. This threshold is shown on the x -axis of Figure 4c and the tortuosity consistently decreases by deactivating an increasing share of transport pathways when going from 0 to a 100 %. In all cases, the tortuosity of the strongly calendered electrode is higher compared to the mildly calendered electrode. Therefore, the impact of ion transport limitations and corresponding capacity loss at high rates is expected to be more significant in the strongly calendered electrode, which however performs better in the experimental tests, making electrolyte transport limitations on electrode scale an unlikely reason for the difference in cell performance. Finally, Figure 4d shows the continuous phase size distribution of the NVP/C phase indicating two interesting effects. First, calendering

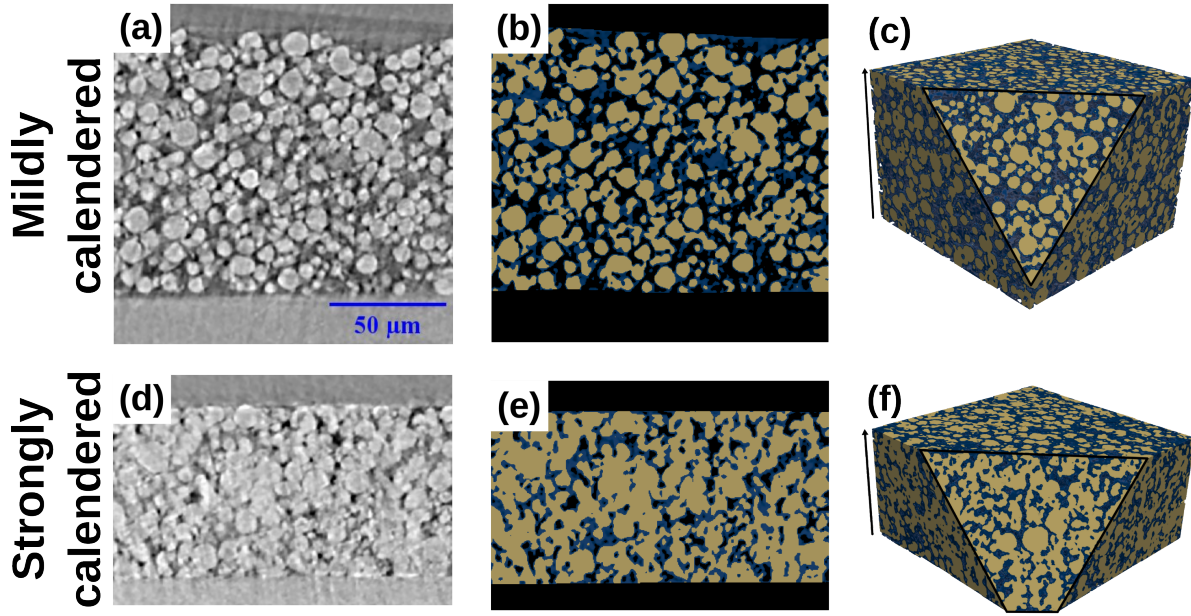


Figure 3: 2D cross-sections of grayscale images obtained by synchrotron X-ray tomography (a,d), the corresponding segmented images (b,e) and 3D render of resulting electrode structure (c,f). Sample with target microporosity of 60 % (mild calendering) shown in the top row (a,b,c) and 40 % (strong calendering) after calendering in the bottom row (d,e,f). In the segmented image, the NVP/C is labeled in beige, pores in black and the CBD phase is shown in blue. Arrows in 3D images (c,f) indicate thickness.

leads to the formation of NVP/C clusters, generally resulting in slightly higher values of the phase size distribution at high radius. As an effect a slightly improved network for electron conduction across the NVP/C network is expected. Second, after calendering the increase towards low radius is much steeper indicating that the particle shapes is less spherical and thus the continuous phase size distribution is generally smaller. This is indicative of particle breakage during calendering and the continuous phase size distribution suggests that this can become a dominating effect for macroscopically observable differences between the two electrodes.

3.4. Electrochemical characterization of the electrodes

In this section, we present the results of the electrochemical characterization of the NVP/C cathodes. In the discussion, we focus on the discharge data at C-rates between C/5 and 3C where we present complementary virtual characterization data in Section 3.5. The discharge curves are plotted in Figure 5. Data at higher C-rates is included in the supplementary information. Particularly, the discharge curves of the mildly calendered electrode showed inconsistent behavior for the rates 5C and 10C. Therefore, we neglect these data in our analysis. However, the electrodes show no signs of significant degradation during subsequent 90 cycles at 1C rate Figure S5. Therefore, we assume no major irreversible degradation

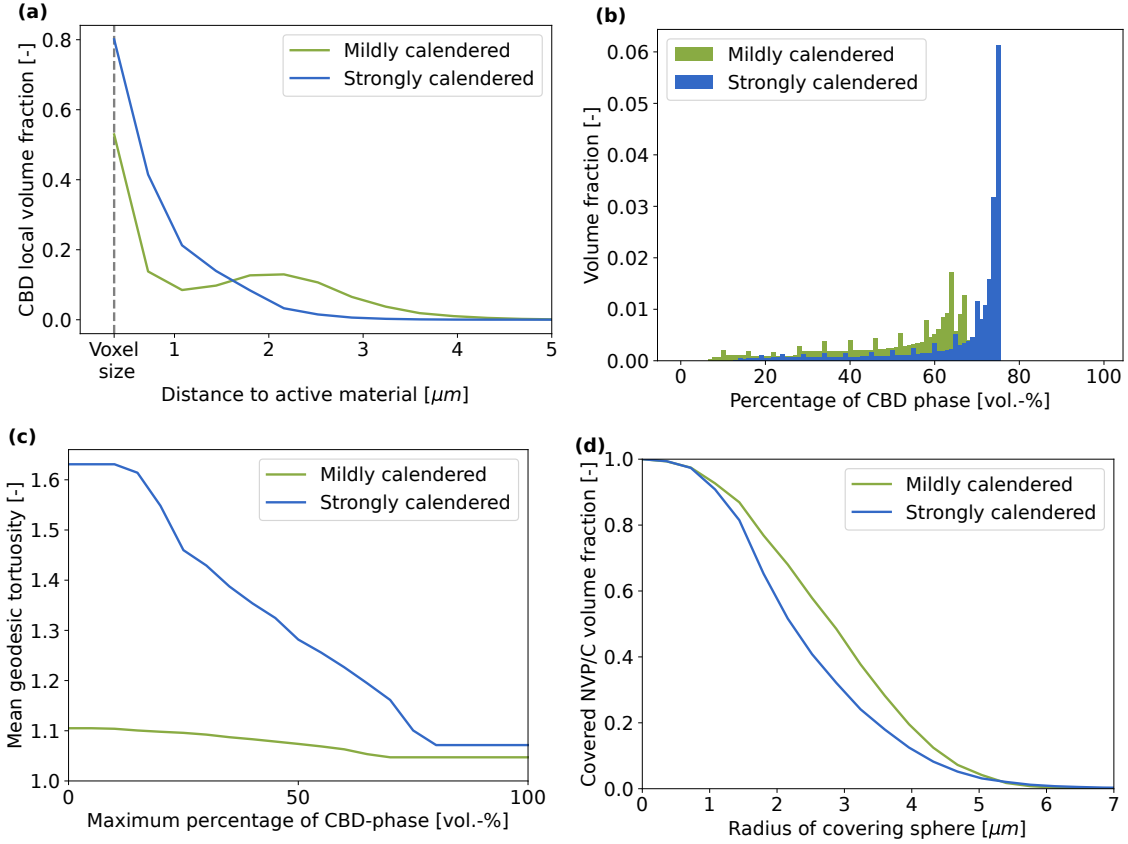


Figure 4: Morphological descriptors on the electrode scale: Volume fraction of the CBD versus distance to NVP/C (a), carbon density distribution of CBD phase (b) and mean geodesic tortuosity of the phase consisting of all voxels with less amount of CBD than a predefined maximum percentage (c). In (d) the continuous phase size distribution of the NVP/C particles is plotted.

processes are taking place during the rate test.

The C-rate test of the mildly calendered electrode is shown in Figure 5 a). At the lowest C-rate of C/5 the discharge curve shows the typical features of NVP material. At low capacity, we observe a steep drop in cell voltage before reaching a stable plateau at around 3.4 V. Only at the end of the sodiation process the cell voltage drops rapidly before reaching the lower cut-off voltage of 2.5 V. Both the capacity and the voltage plateau measured in this work at C/20 are close to the values of the open circuit voltage curve reported in the literature [6]. This confirms that up to C/5 rate we observe negligible kinetic losses and overpotentials in the electrode. Very similar behavior is observed for the strongly calendered electrode providing consistent results between both cell designs. At elevated rates the discharge curve of the highly calendered electrode shows only a moderate decrease in cell voltage and capacity indicating very good rate capability of the hierarchically structured NVP/C electrode concept.

This confirms that interior electrolyte channels within secondary particles provide sufficiently fast pathways for sodium transport. Additionally, the good rate performance of the dense electrode structure indicates that sodium ion transport in the electrolyte on electrode scale is not limiting cell performance. Despite better transport pathways in the electrolyte on electrode scale, we observe significant overpotentials and capacity loss of the mildly calendered electrode at high rates. At 3C the plateau phase is more than a 100 mV lower compared to the strongly calendered electrode and the discharge capacity drops to less than 90 mAh g^{-1} . We will investigate the origin of performance bottlenecks by utilizing by electrochemical simulations utilizing the digital twin of the NVP/C electrodes in the subsequent paragraphs.

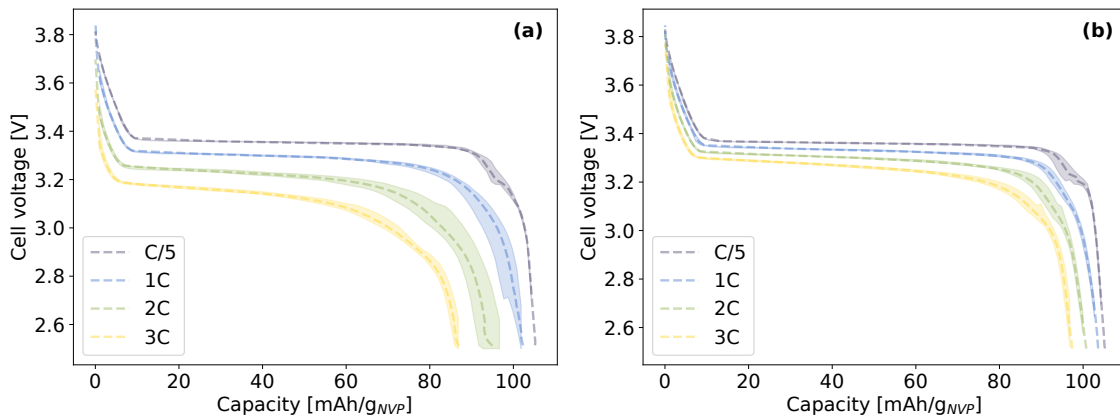


Figure 5: Discharge data for the mildly (a) and strongly (b) calendered electrode. The dashed line plots the mean value over all cycles of the same rate, the filled area indicates the minimal/maximal range of the values.

3.5. Electrochemical simulations

The digital representation of the NVP/C half-cell is based on the electrochemical model described in Section 2.8, 3D image data (Section 3.3) and material parameters (Section S1.3). Thereby, we fuse the different data sets into a predictive digital representation allowing for virtual characterization and analysis of cell properties. We start by validating the performance predictions of the digital representation by comparing it to the experimental data (Figure 7) before using the simulation results for analysis and optimization of the NVP/C electrode.

3.5.1. Model validation

Based on the digital representation of the NVP/C half-cell we perform virtual rate tests under the experimentally applied conditions (see Section 3.4). Therefore, we perform simulations on 3D data sets (see 3.3) using parameters obtained from lower scales and separate measurements (Table S3). The resulting simulated discharge curves for the mildly and strongly calendered electrodes are presented in Figure 6 a) and b), respectively. For the

simulated discharge curves of the strongly calendered electrode shown in Figure 6 b) the main voltage plateau and the final capacity are in good agreement with the experimental data. This confirms that the parametrization of the NVP/C material, electrolyte, and sodium anode is suitable. The standard deviation between simulations performed on different cutouts is negligible compared to the experimental data confirming that the size of the cutouts is sufficient to yield statistically representative electrode structures. We can conclude that the virtual representations of this half-cell are suitable approximations of their physical counterparts. However, the simulated discharge curves of the mildly calendered electrode differ significantly from the experimental data and can explain neither the lower voltage plateau nor the low capacity at high rates.

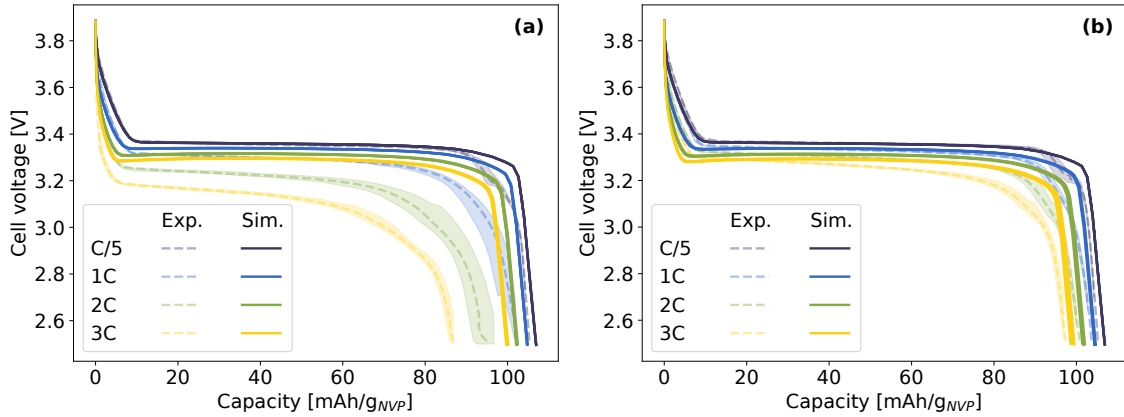


Figure 6: Discharge simulation with parameters from Table S3 for the mildly (a) and strongly (b) calendered electrode. The deviation between different cutouts is below the resolution of the diagram, causing all four cutouts to appear as the same result.

The large deviation from the experimental data indicates loss processes in the real electrodes which are not captured by the electrochemical model. We conclude that the differences in electrode performance between experiment and simulation observed in the mildly calendered electrodes are a result of the electrode processing. Strong calendering has a positive effect on the rate performance of the NVP/C electrodes. This can be assigned to structural properties of the electrode or secondary particles since we do not expect changes of material properties. Possible causes for the voltage drop of the plateau and the low capacity at high rates within the mildly calendered electrodes are discussed in the following Section.

3.5.2. Analysis of limiting effects in mildly calendered electrodes

Calendering can impact transport networks for both ions and electrons on electrode and secondary particle scale. Ionic transport is known to be the major performance bottleneck in conventional electrode designs [55, 56]. However, ionic transport limitations are expected to be more pronounced in calendered electrodes which contradicts the trend observed in Figure 5.

Further possible performance limitations in hierarchically structured electrodes include the electronic conductivity within secondary particles or loss of active material due to particle cracking. Both do not apply here, since the carbon additive in NVP/C electrodes was found to be very effective in improving electric conductivity on particle scale and we observe close to theoretical capacity at low C-rates. These considerations leave two probable candidates for the origin of the performance losses in mildly calendered electrodes. These are: i) Low electric conductivity on the electrode scale originating from resistive interfaces between solid components at low compaction. ii) Slow ion transport within secondary particles due to insufficient electrolyte wetting of the internal pore structure originating from low accessibility of the dense morphology of the secondary particles. In the sections below, we will investigate these effects in more detail.

Low electronic conductivity simulations. As discussed in Sections 3.3 and 3.5.1 and in [26, 54], calendering improves electronic transport paths on the electrode scale. In case of the mildly calendered electrode limited compaction can give rise to contact resistances between NVP/C particles with both neighboring particles and the CBD phase. This effect will result in low effective conductivity on electrode scale.

This reduction in contact points between solid components in the mildly calendered electrode compared to the strongly calendered sample can also be observed in SEM images in Figure 2. Additionally, reduced contact to the CBD is supported by the synchrotron image analysis, which shows a higher distance of the CBD to the NVP/C material (see Figure 4). This could point to additional contact resistances between NVP/C particles, as well as between NVP/C particles and CBD that is not yet captured in the model. Figure 7 shows results of simulations where we take both effects into account. The contact resistance is tuned such that the simulated voltage plateau at elevated C-rates matches the experimental results. However, the low electronic conductivity cannot explain the low capacity at high rates. Technical details related to the simulations including contact resistances can be found in Section S2.3. Our simulation results indicate that insufficient electron transport is a possible cause of for the low voltage plateau. However, it is not the origin of the capacity loss. Therefore, we turn our attention to the second hypothesis.

Reduced ionic transport within secondary particles. In the electrochemical model, we assume a homogeneous internal structure of secondary particles and perfect wetting of the internal nanoporosity with liquid electrolyte. However, electrolyte wetting depends on both, wetting properties and particle morphology [57]. Figure 2a shows a magnification of the 3D FIB-SEM stack [10] of a pristine and representative NVP/C particle. It shows a dense morphology on the particle surface and a homogeneously distributed nanoporosity in the interior. However, the dense surface could be a source of very inhomogeneous wetting of the internal particle nanoporosity. As a consequence the tortuosity of electrolyte transport pathways will increase significantly. Although sodium transport by diffusion is slow in the NVP bulk phase, it provides additional pathways to connect all primary NVP particles.

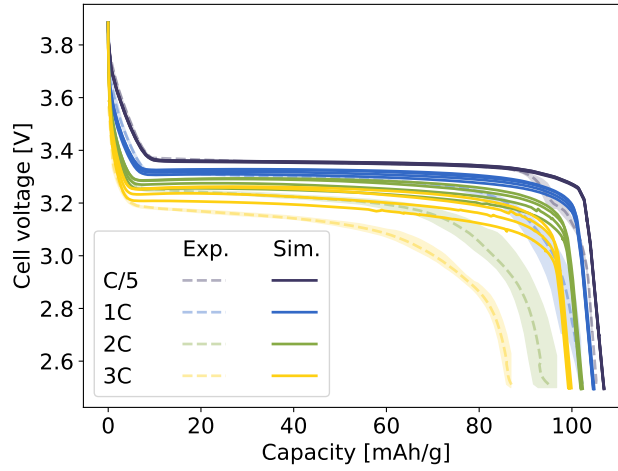


Figure 7: Simulation results for the mildly calendered electrode with additional inter particle contact resistance. The different lines for the simulation results belong to different cutouts of the electrode geometry.

As discussed above, strong calendering induces significant changes in the electrode microstructure. In addition, we observe cracks in a number of particles in strongly calendered electrode Figure 2, while secondary particles in the mildly calendered electrode mostly remain intact. Therefore, we hypothesize that strong calendering introduces cracks in the particles and particularly in the dense surface film. These cracks promote invasion of the interior nanoporosity with liquid electrolyte and, thus, improved wetting of the secondary particles. As a consequence the strongly calendered electrodes should show improved rate performance as predicted by the idealized digital representations.

To test our hypothesis we modify the effective structural model parameters of the secondary particles accordingly. An incomplete electrolyte filling results in a change of many parameters such as specific surface area, effective transport length in primary particles, and effective parameters of the nanoporous electrolyte network. To avoid overfitting by adjusting all these parameters, we only vary the effective transport parameter of the electrolyte network. Setting the tortuosity of the pore space of the particles to $\tau^{-1} = 1.5 \times 10^{-4}$ (value for ideal wetting $\tau^{-1} = 0.433$) results in a significant lower capacity at high rates without affecting the voltage plateau (see Section S2.4). This indicates that slow ionic transport processes in the secondary particles in the particle contribute to capacity loss in the rate tests. Numerical details about these simulations can be found in Section S1.4.

Simulation results for the mildly calendered electrode including both the effect of incomplete particle wetting and an increase in contact resistance between solid components yield very similar behavior compared to the experimental data in the virtual C-rate test (see Figure 8).

Deconvolution and quantification of the effects in the current experimental data is not feasible. In particular, the effect of electrolyte wetting of polycrystalline and cracked cathode

active materials is not well studied and requires additional research. Note that we expect that strong calendering causes cracks and improved wetting only in a fraction of the NVP/C particles.

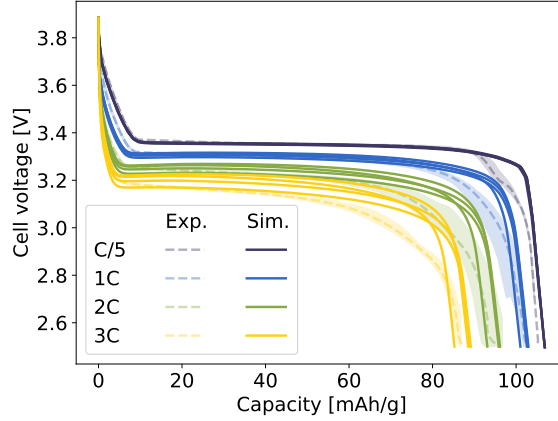


Figure 8: Discharge simulations with the combined effect of additional contact resistances and reduced ionic transport in the secondary particle network for the mildly calendered electrode.

3.5.3. Identification of critical transport processes

In the previous sections we presented model configurations that reproduce the main features of the experimental data. The virtual characterization indicates that the electrolyte transport in the secondary particles is a decisive factor for the electrode performance. The digital representation allows to study the 3D distribution of potentials and concentrations within the NVP/C cathode on both the electrode and secondary particle level.

For the strongly calendered electrode we can see a relatively homogeneous sodiation behavior for all discharge rates and only slight gradients in the electrostatic potential as well as in the electrolyte concentration across the electrode structure (cf. Figure S9a). However, the primary particles show a sodiation gradient in the radial direction, indicating that the transport within the primary particles is a critical factor (cf. Figure S9b).

For the mildly calendered electrode, we found two limiting factors affecting different parts of the electrode performance. The additional contact resistances between NVP/C particles and the CBD result in a lower voltage plateau. The slow ion transport within the secondary particles is the dominant factor for the low capacity at higher discharge rates leading to poorly sodiated primary particles in the center of the secondary particles (cf. Figure 9). This effect is more pronounced for larger particles due to the longer ionic transport pathways. This also indicates that cracking of only a few large particles can lead to significant capacity gain for this electrode.

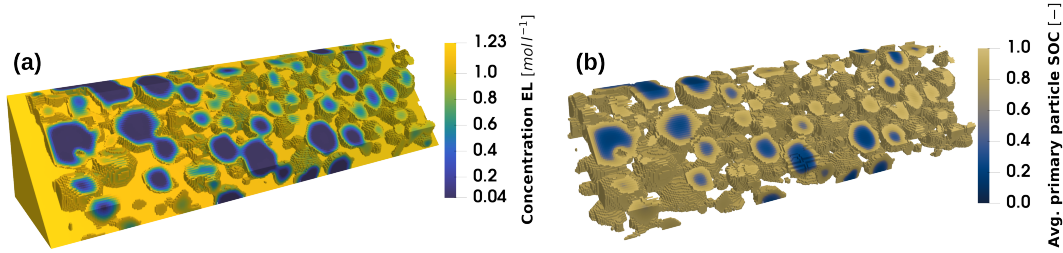


Figure 9: Visualization of locally resolved electrochemical simulation for the mildly calendered electrode at the end of discharge at 3C. In (a): The sodium concentration in the electrolyte is plotted in all electrolyte containing domains. A strong gradient in salt concentration within the secondary particles can be observed. In (b): Same electrode domain as in (a) but only the secondary particle structure is visualized. The color scale represents the average normalized concentration of sodium in the primary particles. For large secondary particles the inner primary particles are poorly utilized.

3.6. Virtual optimization of electrode design

In the previous section, we identified the electrolyte network on the secondary particle scale as the main limiting factor for rate performance. In the case of homogeneous particles without outer shell the internal particle nanoporosity improves the rate capability. However, at the same time we sacrifice volumetric energy density of the composite materials. The goal is to find the internal nanoporosity providing the optimal trade-off between power and energy density. Therefore, in this section, we study the effect of increasing NVP/C volume fraction in secondary particles on the energy density at 3C and 5C rate.

The virtual characterization data does not show significant sodium concentration gradients in the electrolyte across the electrode. Therefore, we reduce computational complexity by simulating single representative particles. The setup is illustrated in Figure S3. The volume fraction of carbon within the secondary particle is identical to the study on real electrode structures presented above and is constant at 0.133 throughout the study. Note, that this carbon content corresponds to the percolation threshold identified in [10] which is required for good conductive networks. The volume fraction of NVP is then increased, while reducing the porosity of the secondary particle accordingly, until we find an optimum in relative energy density of the particles.

The effective transport parameters are modeled by the functional dependencies reported in Figure S3. The most relevant parameter is the tortuosity of the electrolyte network. Here we use the relation given in [58], which has an upper limit. Outside this limit we assume a standard Bruggeman relation with coefficient 1.5.

The results of the optimization study are presented in Figure 10. Starting from the particle design employed in the digital representations above and presented in the previous sections, we see a constant increase in relative energy density for both rates. Interestingly, the increase is proportional to the NVP volume fraction for both C-rates down to a nanoporosity of only

3-5%. The linear increase demonstrates negligible transport limitations in the electrolyte. However, above the optimal NVP volume fraction the utilization and energy density drop rapidly. Overall, the study demonstrates that there is a high potential to further increase energy density in this hierarchical structure without compromising performance. A mandatory prerequisite is a well connected electrolyte network. Note that due to the loss in connectivity, due to fluctuations in particle synthesis at least 5-8% nanoporosity should be targeted to avoid the regime of rapidly dropping capacity utilization. A key step in the material development targeting such low porosity values is maintaining a well connected network with open pores.

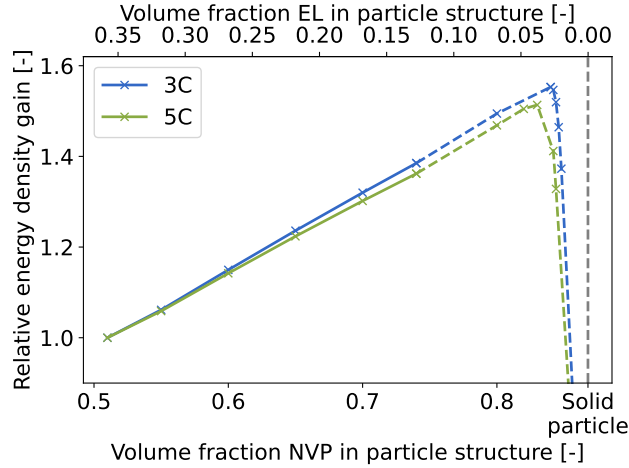


Figure 10: Gain in volumetric energy density relative to the initial particle parameter. Solid lines indicate simulations using the correlation provided in [10]. The dashed line indicates the simulations that use the Bruggeman approximation extending the range of effective parameters. The vertical gray line indicates where the particle is solid and contains only carbon and NVP.

4. Conclusion

We presented a multi-scale workflow for the analysis and optimization of hierarchically structured electrodes linking various modeling and experimental techniques. This includes methods, from atomistic simulations, stochastic and virtual structural analysis on particle and electrode level up to cell scale simulations to capture the effect of the hierarchical structure of these electrodes. Combination of the approaches provides digital representations of the battery cells, which are studied in virtual experiments.

We demonstrate the approach by studying hierarchically structured NVP/C electrodes which is a promising cathode material for SIBs. The digital representations were used to analyze experimental data and allowed us to identify the electrolyte network within secondary particles as decisive property for electrodes with high rate performance. In our optimization study, we could demonstrate excellent rate performance for secondary particle nanoporosities

as low as 10% of the particle volume. This offers the chance for significant improvements in terms of energy density while maintaining good rate capability at high rates.

Our work demonstrates the potential of nanoporous NVP/C materials as cathode active material in SIBs. Future work should try to improve the homogeneity of the nanoporous secondary particles, which was identified as a performance bottleneck in mildly calendered electrodes. For this the usage of sinter additives during the material synthesis are a promising way. To further improve the fidelity of the multi-scale digital representations the phase separating characteristics of NVP material should be modeled on the primary particle level. Still, our study demonstrates the predictive power of collaborative workflows for concerted material and electrode development allowing to reduce the time to market of promising new cell chemistries.

Declaration of competing interest

The authors declare that they have no conflict of interest. The funders had no influence on the design of the study, interpretation of data, on the writing of the manuscript or on the decision to publish results.

Data availability

The data used in this paper is either already publicly available or can be found under doi.org/10.5281/zenodo.22252004.

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