Modeling 3D-microbatteries based on carbon foams

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Porous electrodes are considered attractive for potential use as 3D current collectors in Li-ion microbatteries. Carbon foams, in particular, can be coated with a variety of active materials to prepare electrodes which can maximize energy and power density simultaneously. Modeling such electrodes will aid the selection of microstructural parameters (e.g. porosity) required to optimize their electrochemical performance. Here, experimentally-validated Finite Element Methodology (FEM) is used to simulate a 3D Li-ion microbattery featuring a carbon foam electrode coated by layers of LiFePO4 nanoparticles. The electrodes are cycled against Li-metal at various current densities, and the electrochemical data obtained are used to benchmark and parametrize the simulations. By systematic variation of the LiFePO4 coating thickness and homogeneity and the foam substrate, it is revealed that LiFePO4 exhibits a uniform delithiation process and that the electrochemical reactions favor particles closer to the carbon structure, which is due to the poor electrical conductivity of LiFePO4. Therefore, the cell capacity (mAh cm⁻²) per footprint area can be increased by using lower charging currents, smaller carbon macropore sizes and thicker LiFePO4 coatings. The porous carbon structure provides an excellent template for loadings of LiFePO4 material, which in turn allows using thicker coatings with improved cell performance.

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1. Introduction

An ever-increasing trend in miniaturization of devices for medical applications, sensing and telecommunications has recently intensified the development of suitable integrated power sources [1]. So far, Li-ion microbatteries (MB) represent one of the most promising energy-dense electrochemistry appropriate for these devices. To meet the demand for high energy and high power density (per footprint area of 1 mm²), MB based on 3-dimensional (3D) electrode architectures have emerged [2,3]. The key attributes of these electrodes are related to shorter Li-ion diffusion path lengths, increased working electrode surface area, and prolonged cell life due to limited mechanical stresses from Li⁺ insertion and removal [4]. To date, a variety of electrode architectures [5–8], novel electrode morphologies [9,10], active materials [11,12] and fabrication techniques [13–15] for 3D-MB-s have received considerable attention [16–19].

Among the fabrication techniques considered, photolithography of vertically-standing micropillars and the electrodeposition of arrays of nano-rods through porous membranes constitutes one of the first techniques to be explored [20]. Thin layers of active materials and electrolytes can be deposited onto the 3D structures when manufacturing electrodes for MB applications [3,21]. A more novel approach is to use foam-type electrodes, e.g. nickel foam as 3D electrode [22,23] or foam-type materials as 3D current collectors to be coated with various active materials [24]. For instance, Asfaw et al. [25] has reported the successful fabrication of a 3D composite cathode comprising LiFePO4 nanoparticles deposited conformally onto emulsion-templated carbon foams by sol-gel method.

Carbonaceous materials have long been used as negative active materials for rechargeable Li-ion batteries [26,27]. In recent years, there has been an increasing trend in the use of monolithic porous carbons as 3D electrodes or current collectors in Li-ion MB [28–30]. By virtue of its bicontinuous structure, a 3D electrode based on porous carbons promotes effective utilization of the active materials (e.g. LiFePO4 coating) as it provides both continuous electronic and ionic conduction pathways through the entire depth of the electrode. The mechanical stiffness associated with the electrodes helps reduce the risk of detachment of active materials during
battery operation, which thus improves the cycle life of the bat-teries [25,31]. Furthermore, as the porous electrodes provide high specific surface areas for coating with the active material and, possibly, with a solid electrolyte, they have low local current den-
sities and thus are well-suited for high rate cycling of active ma-
terials with minimal resistive losses.

The phospho-olvine LiFePO4 cathode material is widely used in
commercial products. It consists of plentiful constituents, is en-
vironmentally benign, abundant, low-cost, non-toxic and has a
competitive theoretical capacity of 170 mAh g⁻¹ [32]. The main
disadvantage associated with LiFePO4 is its poor electronic con-
ductivity (-5⋅10⁻² S m⁻¹) compared to other positive electrode
materials [33]. One strategy to overcome this obstacle is to down-
size the active material and to deposit it directly onto a surface of
a porous carbon network, which will serve as a support and 3D
current collector [25].

Various types of computational simulation methods have been
used to gain better understanding of the electrochemical behavior
and performance of electroactive materials in a rapid and cost-
effective manner [34,35]. Theoretical tools like Density Functional
Theory (DFT) calculations [36,37] and Molecular Dynamics (MD)
[38,39] simulations are frequently used to study material proper-
ties at the electronic and atomistic scale. However, Finite Element
Method (FEM) is the most successful approach when it comes to
solving equations that describe transport and kinetic processes and
hence is employed to simulate electrochemical devices at a cell
level [40–44]. So far, only a few groups have tried to represent the
electrochemical behavior of 3D-structured electrodes using 3D
models [45–50]. Although those works have provided helpful in-
sights into the non-uniformity of the electrochemical reactions
which occur due to the 3D-architectures and suggested different
strategies to mitigate these effects, it should be mentioned that
most of these studies use assumptions to approximate the 3D
electrodes using 1D transport models and have not used exper-
imental comparisons.

We focus on half-cells based on LiFePO4-coated 3D carbon foam
cathodes, employed using lithium foil counter and reference elec-
trodes [25]. An experimentally validated and parametrized model
is first constructed to benchmark the electrochemical performance
of the 3D-electrodes. Thereafter, we describe the effects of chang-
ing the geometrical parameters of the electrodes (i.e., the carbon
foam macropore size, the LiFePO4 coating thickness and the coating
homogeneity), followed by studies where the current density is
varied. These parametric simulations helps to suggest which 3D
carbon geometrical parameters should improve battery perfor-
mance. The voltage-charge capacity profiles and cell capacity, cur-
rent distribution, Li-ion concentration gradient in the electrolyte,
and material utilization in the electrodes are analyzed.

2. Materials and methods

2.1. Geometrical model and material parameters

In this work, a cell MB where a thin film of nanosized LiFePO4
particles are coated onto the walls of a carbon foam, working as a
3D composite nanoporous electrode (cathode) against a lithium
metal foil electrode (anode), has been studied. The geometrical
model used in these simulations is based on experimental work
carried out by Asfaw et al. [25]. One cross-section image of the
hierarchically structured composite electrode with an approximate
thickness of 400 μm is shown in Fig. 1a. It was found that the mean
diameter of the macro-pores in the carbon foam was around 20 μm
(Fig. 1b), which is equivalent to 50 voids per a millimeter [25]. At
higher magnification, the SEM images reveal details of the rough-
ness of the walls of the LiFePO4-coated carbon foam, also displaying
the interconnectivities (Fig. 1d). The coating thickness was esti-
mated to be roughly 175 nm [25]. For comparison, the 3D visuali-
sation of the LiFePO4 coated carbon foam used in the computer
model is shown in Fig. 1c.

The length of the complete simulation cell of the reference
system was chosen to be 57.5 μm and is presented in Fig. 2. Grey
domains represent the carbon structure with a length of 52 μm,
which is roughly 1/8 of the electrode thicknesses used in the ex-
periments (400 μm) to compromise computational cost and accu-
ry [25]. The surface of the carbon foam is coated with a thin
(200 nm) layer of the LiFePO4 nanoparticles (blue) while the Li-
metal electrode (green) has a thickness of 0.5 μm. The remaining
volume of the cell is filled with a liquid electrolyte (1 M LiPF6 in
ethylene carbonate (EC): diethyl carbonate (DEC) in a 1:1 wt ratio)
as in the experiments. Since, separator usually have high and
constant ionic transportation parameters then no separator was
used in these half-cell simulations.

2.2. Mathematical model

The applied electrochemical battery model is based on the
concentrated solution and porous electrode theories, established
for Li-ion batteries and originally developed by Newman’s group
[51,52]. The mass transport in the electrolyte originates from
Stefan–Maxwell multicomponent diffusion equation where Brug-
geman’s relation was used for effective ionic diffusion coefficient
and ionic conductivity of the electrolyte in the electrode pores
[53,54]. Also mass transport in the porous LiFePO4 electrode,
coating on the carbon foam, is corrected with Bruggeman’s effec-
tive electronic conductivity while diffusion is based on Fick’s
diffusion law [54]. The electrochemical kinetics of the electrode
reactions are defined by the Butler-Volmer equation [53,55]:

\[ J = i_0 \left[ \exp \left( \frac{\alpha_0 F n}{RT} \right) - \exp \left( -\frac{\alpha_1 F n}{RT} \right) \right] \]

where \( J \) represents the total rate of ion exchange as current density
(A m⁻²), \( i_0 \) is exchange current density (A m⁻²), \( F \) is Faraday’s con-
stant (C mol⁻¹), \( R \) is the universal gas constant (J K⁻¹ mol⁻¹), \( T \) is
temperature (K), \( \alpha_0 = \alpha_1 = 0.5 \) are anodic and cathodic transfer
coefficients, respectively, and the surface overpotential \( \eta \) during
 discharge is described as:

\[ \eta = \phi_1 - \phi_2 - U_{OC} \]

where \( \phi_1 \) is the potential in the electrode, \( \phi_2 \) is the potential in
the electrolyte and the open circuit potential \( U_{OC} \) of the electrode is a
fitted function obtained from literature [56,57]. The exchange cur-
rent density in Eq. (1) can be calculated according to:

\[ i_0 = F (k_a)^{\alpha_1} (k_c)^{\alpha_0} (c_{1, max} - c_1)^{d_1} (c)^{a_x} \]

Where \( k_a \) and \( k_c \) are anodic and cathodic rate constants (m s⁻¹), \( c_1 \)
and \( c \) are the Li-ion concentration in solid phase and in the
electrolyte, respectively. More detailed description of mathematical
model can be found in our previous studies of designing 3D-pillar
MB-s and thermal analysis of MB-s [46,48].

2.3. Model construction and validation

In the current study, in order to increase the computational
efficiency, the periodic nature in the spatial directions of the given
carbon foam was used and 1/8 of the experimental electrode
thickness was modeled. Since the foam electrode is highly porous
(defined as macropores in these simulation cells) then it is assumed
that electrolyte have good access in the foam and likewise a high electrochemical interaction interface due to the high surface area. Also, since the carbon electrical conductivity and diffusion coefficient of the LiFePO₄ are constant, the transportation limitations and resistance can be assumed to be a linear function in depth of the foam electrode. Accordingly, the applied current density \(0.37 \text{ mA cm}^{-2}\) in the simulations corresponds to 1/8 of the experimental values \(3 \text{ mA cm}^{-2}\). In each model, the current density \(0.37 \text{ mA cm}^{-2}\) was applied to the surface area (2.045 \(\times \) 10\(^11\) m\(^2\) in the reference system) of the carbon structure which is actually in contact with the current collector, shown in red in Fig. 2. The opposing current collector at the lithium metal side was grounded. The average size for majority of the LiFePO₄ particles (above 80%) was measured to be below 70 nm, and therefore an average particle diameter of 20 nm was used in the simulations. The LiFePO₄ volume fraction, the electrolyte volume fraction and the double layer capacitance were measured or calculated from experimental data and are presented in Table 1. The electrolyte ionic conductivity \((\text{S m}^{-1})\) is represented by a concentration-dependent function based on the experimental data [58].

Fine-tuning of the mathematical model involves the setup of the charge voltage profile. This is achieved by determining the Li-metal...
anodic and cathodic reaction rate constants by comparing experimental and simulation voltage profiles using least square fitting method [59].

$$\left( \frac{1}{n} \sum_{i=1}^{n} \left[ \text{experiment}(x_i) - \text{simulation}(x_i) \right]^2 \right) < 5\%$$

A lower electronic conductivity of the LiFePO₄ for the delithiated phase (FePO₄) has also been reported in previous studies [60]. Therefore, the LiFePO₄ electrical conductivity was set to decrease linearly from the value of 1 × 10⁻⁶ S m⁻¹ in the lithiated LiFePO₄ phase down to the value of 1 × 10⁻⁷ S m⁻¹ in the delithiated FePO₄ phase while charging the cell. The coated carbon foam electrode soaked in liquid electrolyte has a volume fraction around ~0.30. The porous LiFePO₄ layer coated on the walls of carbon foam has a fixed 0.65/0.35 electrode/electrolyte fraction in all the simulations, and Bruggeman’s approximation is used specifically for this layer. All other physical constants and parameters (electrolyte salt diffusion coefficient, electrolyte transport number, Li-ion diffusion coefficient in LiFePO₄, LiFePO₄ maximum species concentration, transfer coefficients, Li-metal electrical conductivity and carbon electrical conductivity) were found from literature and are presented in Table 1 with references.

The electrochemical behavior of this simulated material has been modeled using COMSOL Multiphysics 5.0. Applied model is based on the assumption that the salt in the electrolyte is completely dissociated. Initially, the electrolyte salt concentration was set to 1000 mol m⁻³ and the final LiFePO₄ lithiation level was 99% in each simulation. In addition, the temperature was kept constant at 293.15 K and lithium insertion into carbon and other possible side reactions were neglected. In these time-dependent studies, a segregated non-linear calculation method and the linear MUMPS solver was used. Mesh consists of ~100 000—200 000 tetrahedral elements with additional elements between thin surfaces to catch the boundary effects.

### 2.4. Simulated systems

A total of 16 cell models were built. The first galvanostatic charge curves of these systems were simulated and studied in the potential range from 3 V to 4 V vs. Li⁺/Li. In the first set, a parametric current density study was performed for 3 experimentally validated models, corresponding to the current densities 0.1, 1 and 3 mA cm⁻². A second set of simulations was carried out to investigate the effect of varying the LiFePO₄ coating thickness from 100 to 500 nm with increments of 100 nm. In addition, one simulated system with a non-uniform LiFePO₄ coating thickness varying from 200 nm to 600 nm was investigated to evaluate the insights of the homogeneity of the coating on the electrochemical performance of the electrode. Since the average size of the LiFePO₄ particles are less than 70 nm then particles with average diameter of 5, 10, 15, 20 and 40 nm were studied in the third part of the simulations to shed light on the role of particle size during cycling these 3D foam electrodes. Finally, two systems with different carbon voids (i.e., the macropore shown in Fig. 2), 5 and 10 µm radii-sized macropores, were simulated to collect the data about the influence of the foam structure on the cell performance. Throughout the studies, only one parameter was changed in each system of the comparative set. Each parametric set also includes the reference system (with values presented in Table 1) for comparison.

### 3. Results and discussion

#### 3.1. Charge characteristics of the simulated 3D half-cell and benchmarking towards experiments

The first single electrode system constructed and defined according to the experiment characteristics was named ‘reference system’, for which a current density of 3 mA cm⁻² was used. The complete current density study includes 0.1, 1 and 3 mA cm⁻², which would roughly correspond to 0.06, 0.69 and 2.44 C-rates, respectively. The simulated voltage-capacity curves (Fig. 3) are in close agreement with the experimental data, which in turn indicates that the model can accurately simulate the mass and charge transport phenomena in these cells, and can hence be used to obtain reliable insights into the electrochemical behavior of the MB with the 3D foam type of electrode architecture.

The voltage-charge capacity curve recorded at the current density of 0.1 mA cm⁻² exhibit a distinct plateau around 3.45 V, which is characteristic of cells containing LiFePO₄ active material [60,64,65]. Lower current densities surely provide lower local currents in the LiFePO₄-coated electrodes and thus a smoother and deeper delithiation, which accordingly increase the gravimetric capacity (mAh g⁻¹) per gram of LiFePO₄. For example, when decreasing the current density from 3 mA cm⁻² down to 0.1 mA cm⁻², the cell capacity increases from 118 mAh g⁻¹ to 160 mAh g⁻¹, i.e. 36% and forms 94% of the LiFePO₄ theoretical capacity (170 mAh g⁻¹). This effect is directly related to the fact that increased current densities cause higher voltage drops and kinetic overpotentials which limits the working voltage window, and thus
limit the accessibility of the active materials during cycling (as also discussed below).

Another interesting observation is that the simulated potential profiles appears to have more linear features at the beginning and end of charging, as compared to experimental data (Fig. 3). This effect might be caused by the simplistic and perfectly homogenous LiFePO4-coating of the carbon foam structure (Fig. 1c) used in these simulations, as compared to the experimental materials (Fig. 1b and d). Since the simulations do not capture any roughness of the electrode surface, this indicate that imperfections might be present in the experimental system.

When comparing the depth of delithiation (Fig. 3) for different current densities, there is a tendency that a lower level of delithiation (Li0.3FePO4) is achieved for lower C-rates (0.06 C). The highest C-rate (2.44 C) provides only delithiation to Li0.2FePO4 at the end of the charge. Therefore, lower C-rates lead to a deeper delithiation, which in turn gives higher capacity. This is likely due to the sufficient diffusion in the electrolyte phase to maintain a uniform charging at all depths of the porous electrode only at low charge/discharge rates. If the charging rate is high, however, the electrolyte becomes polarized at the largest distance from the anode, which results in the impeded charging so that only the parts near the separator can participate fully in the charging process [66]. Moreover, the results obtained here are very similar to the SOC curves of LiFePO4 [60, 64], where a delithiation level Li0.2FePO4 was achieved using a C/10 rate.

3.2. Current density distribution and concentration gradients in the cell

In Fig. 4a, the current density (A m⁻²) distribution in the carbon foam part of the simulated structure is presented, together with the Li-metal electrode. This particular snapshot is taken at the end of the charging, but is representative for the entire charging process since the applied current density is constant. The oxidation reaction in LiFePO4 during charging progress as the material is delithiated (i.e., LiFePO4 and x = 1 → 0) and can be expressed as:

\[
\text{LiFePO}_4 \rightarrow \text{FePO}_4 + \text{Li}^+ + e^-
\]  

Here a two-phase model (LiFePO4 as lithiated and FePO4 as delithiated phase) with non-stoichiometric compositions is used, which represents the average phase for certain region or the entire electrode. In the course of the above reaction, all electrons are transferred to the electronically well-conductive (100 S m⁻¹, which is several orders of magnitude higher than the electronic conductivity of LiFePO4) carbon structure where they continue moving towards the current collector.

Fig. 4a shows the situation where the highest C-rate (2.44), which corresponds to the current density of 3.7 A m⁻² used in the reference cell. However, the highest current density (~19 A m⁻²) that the carbon foam structure has to support is located in the narrow regions near the current collector. The electrons released into the carbon from LiFePO4 migrate towards the current collector, and the narrow carbon structure regions in its vicinity are therefore exposed to high currents and thus high current densities. This can give rise to the local overheating of these regions of the battery, and is an inherent effect of the highly porous structure of the carbon foam composite electrode [4].

In Fig. 4b, the Li-ion concentration gradient (mol m⁻³) in the electrolyte at the end of the charging process is presented. It can be noticed that the concentration gradient in the liquid electrolyte is higher in regions closer to the counter electrode (Li-metal). This effect is equivalent to a higher rate of changing Li-ion concentration in these regions. In addition, the black arrows in Fig. 4b represents the direction of the diffusive flux of Li-ions, thereby showing the direction of decreasing concentration. The length of the arrows proportionally displays the changes in the concentration gradient. At constant charging current, there is a constant flux of Li-ions from the LiFePO4 into the electrolyte. When the Li-ions are inserted into the Li-metal electrode, this causes a small deficit of Li-ions and a somewhat lower concentration near this surface, and the Li-ions are migrating towards these lower concentration regions. This effect of a higher gradient closer to the Li-metal remains almost unchanged during the entire charging process, as the current
density (3.7 A cm$^{-2}$) is constant and the delithiation of the LiFePO$_4$ layer is highly uniform (also discussed in section 3.3).

3.3. LiFePO$_4$ delithiation and coating homogeneity

In this part of the study, the phase evolution of a non-uniform LiFePO$_4$-coated carbon foam electrode is analyzed, for coating thicknesses varying from 600 to 200 nm. In Fig. 5, the depth of delithiation in the LiFePO$_4$ electrode (x in Li$_x$FePO$_4$) after 1500 s of charging at 2.44 C-rate is shown. It can be noticed that the electrochemical delithiation reaction (LiFePO$_4$ $\rightarrow$ FePO$_4$ + Li$^+$ + e$^-$) occurs preferentially in the particles that are closer to the carbon structure than in particles closer to the electrolyte. After 1500 s of charging, these regions are almost entirely delithiated and are seen as blue in Fig. 5.

The development of the delithiated phase is seen in better detail in Fig. 6. These cross-section snapshots of the electrode illustrate the progress of the delithiation as a function of time intervals during cell charging from 3 V to 4 V. The non-uniform LiFePO$_4$ coating on the carbon foam structure presents different coating consistencies and thicknesses: (a) a thin (200 nm) homogeneous coating, (b) a coating where edges and tips of the LiFePO$_4$ layer are somewhat thicker, (c) a coating where one side of the carbon has thicker coating than the other, and (d) a thick (600 nm) homogeneous coating. It is clearly seen that the LiFePO$_4$ particles near the carbon foam, in the bottom of the coating layer, are delithiated first while the chemical reaction progresses in the LiFePO$_4$ bulk layer within the time interval between 2000 and 4000 s for all investigated systems. At later charging stages (i.e., at 6000 s), it can be seen that regions with thinner LiFePO$_4$ coatings are fully delithiated but that the thicker regions (the edges on row b and the surfaces on c and d) remain lithiated. The major limiting factor for the electrochemical process in this system is the significantly lower electrical conductivity of the LiFePO$_4$ phase (~5 $\times$ 10$^{-7}$ S m$^{-1}$) compared to carbon foam. When Li-ions and electrons are extracted from the LiFePO$_4$ particles during delithiation, the carbon foam structure acts as a supportive highway for the released electrons to move towards the current collector, thereby favoring reactions in the LiFePO$_4$ particles in the coating near the carbon structure. This effect also has been reported by Strobridge et al. [67] who observed a preference for reactivity in LiFePO$_4$ particles closer to the current collector, which was explained by better wiring in this electrode region. Additionally, a lower and constant charging rate in the vicinity of a current collector generate a constant chemical reaction rate in the LiFePO$_4$, rendering a mostly homogeneous delithiated phase.

It can also be seen in Fig. 5 that depth of delithiation in the LiFePO$_4$ is very similar in the regions near the Li-metal and near the regions where current is applied, indicating that the delithiation is rather homogeneous throughout the porous electrode. This is in contrast to Liu et al. [66] and Strobridge et al. [67] who studied the delithiation processes of LiFePO$_4$ composite electrodes using energy-dispersive X-ray diffraction (EDXRD) methodology, and found that the delithiation of LiFePO$_4$ starts in particles which are closer to the separator (Li-metal side) than in parts which are closer to the current collector. This inhomogeneity of the electrochemical reaction in the electrode suggests Li-diffusion limited kinetics in the electrolyte across the electrode thickness [58]. On the other hand, the present study comprises a highly electrically conductive carbon foam as a 3D support and a liquid electrolyte with high ionic conductivity. Moreover, the simulated electrode has a thickness of only 52 μm, as compared to the approximately 285 μm thick electrode studied by Strobridge et al. Therefore, any effect of inhomogeneous delithiation of the electrode is less likely to occur in these present studies. In conclusion, the surprisingly highly homogeneous delithiation observed in the simulations is most likely caused by the high electrical conduction (100 S m$^{-1}$) of the carbon foam, the large macropores filled with electrolyte, the high enough ionic diffusivity (3 $\times$ 10$^{-10}$ m$^2$ s$^{-1}$) of the electrolyte, and the low charging rates (C-rate 2.44).

3.4. Variation of the LiFePO$_4$ coating thickness

To investigate how the cell capacity and electrochemical performance in these 3D-foam electrodes depend on the thickness of the LiFePO$_4$ coating, five different homogeneously LiFePO$_4$-coated electrodes with thicknesses of 100–500 nm were simulated. The voltage-capacity profiles of the charging process in these systems are shown in Fig. 7a and b for the areal capacity and gravimetric capacity, respectively. As expected from the different mass loadings, the gravimetric capacity (mAh g$^{-1}$) per gram of LiFePO$_4$ varies less than capacity per footprint area for the different coating thicknesses (Fig. 7b). Fig. 7a shows clearly that thicker coatings will increase the cell performance, simply because more active electrode material is available. Therefore, a footprint area capacity of 3.09 mAh cm$^{-2}$ is achieved for the thicker coating (500 nm) as compared to 0.59 mAh cm$^{-2}$ for the 100 nm LiFePO$_4$ coating (Fig. 7a and Table 2). On the other hand, when the volume of the LiFePO$_4$ was increased by 479% when using thicker coating, the footprint area capacity increased by 424%. Thus, the cell capacity per footprint area is significantly improved throughout the investigated range, although slightly less is gained when increasing the thickness from 400 nm to 500 nm coating as compared to increasing thinner layers. In conclusion, thicker coatings are preferable in this system, provided that these are possible to achieve using the current carbon foam macropore sizes and by the current synthesis techniques. It can be possible that very thick coating at some point decreases the cell capacity due to the increased diffusion pathways and clogged pores. The coating thickness of 500 nm is still not limiting the performance of the cell.
Upon closer examination of Fig. 7a, it can be seen that thinner coatings (100 nm and 200 nm) provide higher gravimetric capacity (119 and 118 mAh g$^{-1}$, respectively) than thicker (500 nm) coatings, which give 106 mAh g$^{-1}$. This tendency to a minor
decrease in gravimetric capacity per gram of LiFePO₄ is likely caused by the low electronic conductivity of LiFePO₄. Furthermore, this low conductivity possibly causes a faster potential rise in systems where a thicker coating was used. This rise of the ohmic polarization primarily originates from the resistance of the electrode material and the linear Ohm’s law relationship between current and cell potential [69]. Hence, the thicker the coating of the LiFePO₄, the longer is the diffusion pathway from the lithium-rich particles to the electrolyte, and the active material delithiation thereby becomes limiting and the capacity decreases. These phenomena were also discussed previously in section 3.3. Therefore, increasing the electrical conductivity of the electrode material (e.g. coating the LiFePO₄ particles with highly conductive material), should hypothetically allow usage of thicker LiFePO₄ electrode films which would increase the cell capacity and allow applying higher charge/discharge rates.

3.5. Variation of the LiFePO₄ particle size

Furthermore, the influence of LiFePO₄ particle size (diameter of 5, 10, 15, 20 and 40 nm) on the cell electrochemical behavior was studied. In the porous electrode theory developed by Newman and Tiedemann [52,58], the electrode is treated as a one-dimensional continuous superposition of solid active material and liquid electrolyte phases, where the transport properties are corrected by the Bruggeman expressions [70]. In the following simulations the coating thickness (200 nm) and charging current density (3 mA cm⁻²) were kept unchanged in all systems. Calculated gravimetric capacities for different electrode material particle sizes are presented in Fig. 8a. Since a relatively thin material coating (200 nm) was modeled, the particle size variation only resulted in minor capacity differences. However, it can be seen that smaller LiFePO₄ particles provided somewhat higher cell capacities. After the implementation of the porosity in the model, the decreased particle size effectively increases the electrode material volume ratio, and thereby the capacity increases. Moreover, Orvananos et al. [71] found that smaller particles provide a better rate performance compared to the larger particles due to their larger surface-to-volume ratio and smaller diffusion lengths for both ionic transport and electrical conduction [65]. In the delithiation process, Li-ions are more easily extracted from smaller particles rather than the larger particles, due to the length of the diffusion pathways and hence a lower overpotential is required. In addition, Li et al. [72] observed that since the Li-ion conduction channels within LiFePO₄ particles are one-dimensional, the diffusivity is mainly governed by the concentration of anti-site defects in these channels [73]. Therefore, smaller particles reduce ion diffusivity and electronic conductivity of the material. The simulations here display similar effects being in a good agreement with several previous studies on the cell capacity dependency on the LiFePO₄ particle size [60,74,75].

3.6. Variation of the carbon foam macropore size

Clearly, the size of the macropores in the LiFePO₄-coated carbon foam (Fig. 1a and b) plays an important role in the performance of the electrochemical cell in which the 3D electrodes are used. In this section, a cathode with a macropores radius of 5 μm (Fig. 8b) is simulated and the results are compared with the reference system with macropore radius of 10 μm (Fig. 8c). A smaller macropore size will lead to an increased amount of carbon per identical volume of the simulation cell. This means that a larger coating area is available, and thereby LiFePO₄ electrode loading is higher. Direct comparisons of the electrochemical performances are thus difficult to make, although the contact areas between the current collector and the foam structure are equivalent in both systems.

The simulations showed that the increased (116%) LiFePO₄ loading volume resulted in an increase in capacity per footprint area (111%; from 1.23 up to 2.59 mAh cm⁻²) when the radius of the

![Fig. 8.](image-url)
macropores was reduced (Table 3). This capacity gain per footprint area stemming from the increased volume of the LiFePO₄ seems reasonable in the context of the results in section 3.4, and it can be concluded that using carbon foam with smaller macropores is the key for improving the battery performance when other parameters of the materials and the cell geometry remain unchanged. Also, the gravimetric capacity of these cells remains largely unchanged. The carbon framework in the foam with smaller macropore size (Fig. 8b) has thinner and tight carbon regions than carbon foam structure with larger pores (Fig. 8c) to support locally high currents. Nevertheless, the simulations showed comparable current densities for carbon foam system with smaller macropore size (~19.1 A m⁻²) and the reference system (18.9 A m⁻², corresponding to the red colored regions in Fig. 4a), because the cross-section area of the carbon is similar in both systems.

The Li-ion concentration gradient occurrence in the electrolyte and the delithiation distribution in the LiFePO₄ layer was similar in both smaller and larger macropore size systems. Accordingly, like in the reference system, the Li-ion concentration gradient in the electrolyte was observed to be higher in the regions near the Li-metal side. In addition, the delithiation of the LiFePO₄ was homogeneous in these systems and favorable in particles situated closer to the carbon structure, as discussed in section 3.3.

Only a small fraction of the material can be simulated by direct modeling of the 3D architecture simulation cell due to computational limitations. Since the two systems studied only showed minor limiting effects, however, also 10 times smaller macropores are likely to show similar results.

4. Conclusions

An experimentally-validated half-cell electrochemical system comprising a nano-sized LiFePO₄-coated carbon foam electrode was simulated first time, and parametric studies were successfully carried out. These calibrated models reveal insights into mass and ionic transport phenomena and suggest optimal electrode geometrical parameters to increase 3D MB capacity. Applying lower current density of 0.1 mA cm⁻² provided smoother and deeper delithiation with about 36% increased cell gravimetric capacity (mAh g⁻¹) per gram of LiFePO₄ as compared to the higher current density 3 mA cm⁻². The simulations showed that the Li-ion concentration gradient is higher in the regions near the separator, but that the current density in the carbon foam is higher in the regions closer to the current collector. Both effects are associated with the higher ionic and electronic transports, respectively, observed in these regions. It is interesting to note that LiFePO₄ delithiation occurs homogeneously throughout the porous structure with the electrochemical reactions taking place preferably in the particles near the carbon foam due to the very low electrical conductivity (~1 × 10⁻⁷ S m⁻¹) of the LiFePO₄ coating. A certain suggestion for experimentalist is that carbon foam where exist smaller macropores, with increased available coating area and thicker coatings of the LiFePO₄ lead to an increased mass of available active material and thus enhanced cell capacity per footprint area. This shows that the porous carbon structure provides an excellent template for loadings of LiFePO₄ material in terms of current and electrolyte distribution, and any system limitations are hardly observed even for rather thick loadings. Therefore, this novel foam type electrodes can be a good candidate for improving the performance of 3D MB used in micromechanical systems.

Generally, the rate performance of a practical battery, and the reaction mechanism, are not merely a function of the size and morphology of the active materials, but as these studies demonstrate also depend strongly on the structure of the composite electrode and the resulting global electronic and ionic conductivities. Although the present study clearly shows that improvements in the cell performance can be achieved when lower current densities are used, carbon foam have smaller macropores and thicker coatings are applied, it is probably important to note that experimental capability to fabricate these composite electrodes with thick, homogeneous coatings may be a limiting factor.

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References
