Hessisches Kompetenzzentrum für Hochleistungsrechnen

Chemo-Mechanical Analysis of Inverse Opal Structures as Cathode for Lithium-Ion Batteries

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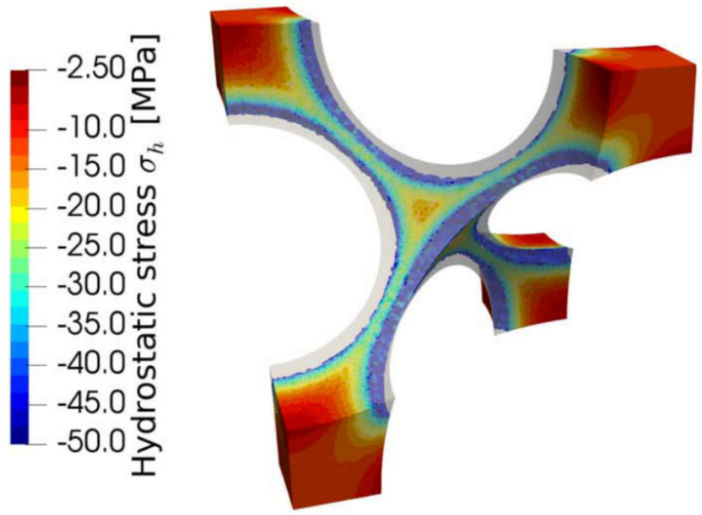
Clusters
Lichtenberg Cluster Darmstadt

Additional Software
NETGEN, FEAP

Institute
FG Mechanik Funktionelle Materialien

University
Technische Universität Darmstadt



Introduction

Lithium-ion batteries are the fundamental technology of energy storage for all kind of mobile devices. The never decreasing demand for high charge rates and high-power density warrants research into new materials for energy storage or into novel microstructures that allow to overcome the limitations of known materials. One of these microstructures of interest are inverse opal structures which shall be used for cathodes of Lithium-ion batteries. These structures essentially maximize the exposed surface area to the batteries' electrolyte while providing short diffusion paths due to their slender geometric features. Their electrochemical properties have been studied for instance by Chalker et al. [1], who have observed increased charge rates and an enhanced effective diffusion coefficient of the microstructure dependent on the size of the internal pores. In this study, we aim to model the mechanically coupled diffusion process appearing in inverse opal microstructures. Thereby, mechanical contributions to the system's free energy are regarded, which introduces additional driving forces into the diffusion process. Further, surface stresses and electrochemical surface reactions are introduced into the model to allow the investigation of size effects and chemo-mechanical interaction. To solve the corresponding equation systems of multiple parameter studies within a reasonable amount of time, we required access to the HPC.

Methods

In this project various parameters and their influence on the state of charge are investigated in a finite element study. Therefore, different geometries were generated via CSG modelling with the open-source software NETGEN. Afterwards, a previously evolved user element for the finite element software FEAP was used to analyze the lithiation process of the generated inverse opal microstructures. The user element is able to consider stress-coupled diffusion, mechanically modulated surface reactions and surface-stress-induced bulk stresses.

Results

The small feature sizes of inverse opal structures lie on a length scale where surface stresses gain significant influence on the materials' behavior. These stresses induce a non-uniform pressure field in the active material, which reduces the accessible capacity of the active material under insertion. The pressure, however, facilitates the extraction of ions from the electrode. The magnitude of these changes in accessible capacity is similar to that appearing in an equivalent freestanding spherical particle. To due to large surface area exposed to electrolyte of inverse opal structures the insertion/extraction reactions can proceed in parallel at many intercalation sites. As a consequence, the (dis)charge rates of an inverse opal structure unit cell exceeds that of an equivalent spherical particle by a factor of circa 1.8. The relative density of the considered inverse opal structures appear to be independent of the pore radius. However, every increase in charge rate due to reduced pore sizes is bought by a loss in accessible capacity of the active material. An optimal electrode pore radius can be determined from balancing the requirements of high charge rates against surface-stress- induced losses in the accessible capacity, which leads, for the samples considered in this study, to a structure with pore radius of 250 nm.

Discussion

Due to their large surface area, inverse opal structures are more sensitive to the formation of a solid-electrolyte interface. This inactive surface layer induces some losses in usable lithium for energy storage and contributes additional mechanical restraints against chemical swelling. Its influence on the chemo-mechanical behavior of inverse opal structures is unknown and deserves further attention. As well as our assumption that the structure contains only active electrode material. It appears to be more economical to use a coat of active material, which also considers the effect of delamination of the active layer from the underlying structure due to inhomogeneous deformation. This leads to further loss of cell capacity. Also, the local pressure maxima in the inverse opal ligaments highlight the danger of structural stability losses in the microstructure through buckling, which would cause local fragmentation of the active material. In addition, till now we only considered a unit cell of the electrode structure under approximated electrochemical conditions. The impact of geometric inverse opal features on the performance of a battery cell has, so far, not been investigated.

Figures

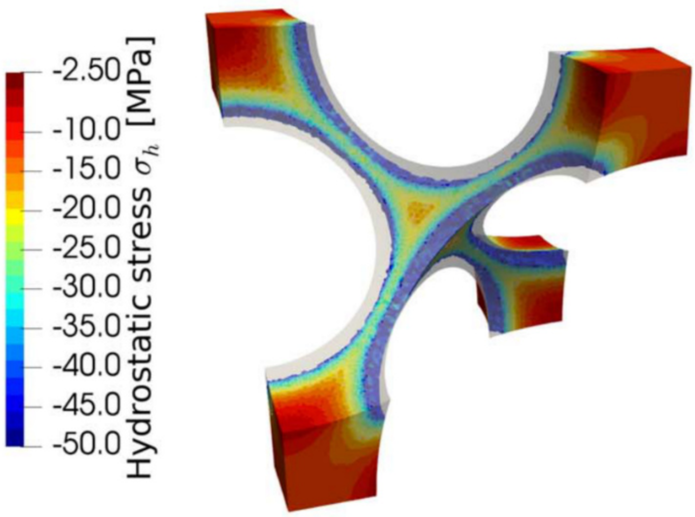


Figure 1: Distribution of hydrostatic stress σ_h due to surface stress within an inverse opal unit cell.

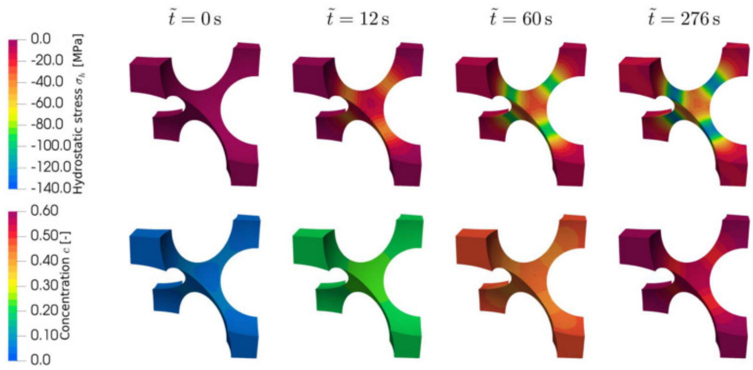


Figure 2: Evolution of the hydrostatic stress (top row) and the normalized concentration field (bottom row) in the inverse opal unit cell (no surface stress) over time. [2]

Publications

Stein, P.; Wissel, S; Xu, B.-X. The influence of surface stress on the chemo-mechanical behaviour of inverse-opal-structured electrodes for lithium-ion batteries. Journal of The Electrochemical Society 167.1: 013529 (2019) http://dx.doi.org/10.1149/2.0292001JES

Reference

[1] Chalker, C. et al. Fabrication and Electrochemical Performance of Structured Mesoscale Open Shell V2O5 Networks. Langmuir 33, 24, 5975–5981 (2017) https://doi.org/10.1021/acs.langmuir.6b04163

[2] Stein, P.; Wissel, S; Xu, B.-X. The influence of surface stress on the chemo-mechanical behaviour of inverse-opal-structured electrodes for lithium-ion batteries. Journal of The Electrochemical Society 167.1: 013529 (2019) http://dx.doi.org/10.1149/2.0292001JES

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