The energy density of the current generation of Li-ion batteries (LIBs) is only about 1% of that of gasoline. Improving the energy density of the rechargeable battery is critical for vehicle electrification. Employing high capacity electrode materials is a key factor in this endeavor. Silicon (Si) is one of the high capacity anode materials for LIBs. However, Si experiences large volume variation (up to 300%) during battery cycling, which affects the structural integrity of the battery and results in rapid capacity fading. It has been shown that the cycle life of Si anode can be improved significantly through various novel electrode designs. So far, such work is conducted through experiments. Numerical simulations have the potentials for design optimization of LIBs, as demonstrated in multiphysics models for LIBs with graphite anode. This research extends a previously developed microstructure-resolved multiphysics (MRM) battery model to LIBs with a-Si anode. The MRM model considers the electrochemical reactions, Li transport in electrodes and electrolyte, Li insertion induced volume change, mechanical strains and stresses, material property evolution with lithiation, and the chemo-mechanical coupling. The model is solved using finite element package COMSOL Multiphysics.

The major challenges in this work are the large deformation of the Si, and the uncertainty in parameters and the coupling relation. To simulate the large deformation of Si, a large strain based formulation for the concentration induced volume expansion was used. The electrolyte was modeled as fluid. A method to simulate the galvanostatic charge/discharge of an electrode with varying surface area was developed.

Important model parameters were determined one by one by correlating the simulation to appropriate experiments. For example, the Li diffusivity in Si reported in literature varies from $10^{-13}$ to $10^{-19}$ m$^2$/s. To estimate this parameter, the experiment of two-phase lithiation of a-Si nanospheres in-situ in a transmission electron microscope was simulated. The diffusivity was found at the order of $10^{-17}$ m$^2$/s for the lithium poor phase in first lithiation and $10^{-15}$ m$^2$/s for lithium rich...
phase and in subsequent cycles. The reaction rate constant and the apparent transfer coefficient are determined in a similar way using different experiments.

In literature, different forms of chemo-mechanical coupling theories have been proposed for Li diffusion in Si. The coupling relationship and parameters were often derived based on one type of experiment even though the process is highly coupled. In this work, the chemo-mechanical coupling was investigated by simulations of two geometries: a thin film and a sphere. A strong asymmetric rate behavior between lithiation and delithiation has been observed in thin film a-Si anode but not in other geometries. The results reveal that the rate behavior is affected by the geometry and the constraint of the electrode, the chemo-mechanical coupling, and the prior process. A substrate-constrained film has a relatively low surface/volume ratio and a constant surface area. Its lithiation has a great tendency to be hindered by surface limitation. The chemo-mechanical coupling plays an important role in the specific rate behavior of a geometry.

Finally, a MRM model was built for a half cell with a-Si nanowalls as anode. The specific and volumetric capacities of the cell as a function of size, length/size ratio, spacing of the nanostructure, and the Li\(^+\) concentration in electrolyte were investigated. The results show that the factors reducing the concentration polarization can enhance the maximum achievable SOC of the cell. However the cell with the highest SOC does not necessarily lead to the highest capacity.

Persons with disabilities please contact the Mechanical Engineering office at 517-355-5131 to request accommodations.

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