Phase field modeling of diffusion and fracture of silicon electrodes in lithium-ion batteries

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ABSTRACT

Lithium-ion batteries are important energy storage devices, which are widely used in portable electronics. To meet the emerging requirement from the electric vehicle industry, lithium-ion batteries with higher energy storage density and longer cycle life are needed. Silicon (Si) is one of the most promising anode material with a high theoretical specific energy of 4200mAh/g, compared with 372mAh/g for graphite used in current commercial lithium-ion batteries. However, the undergoing large volume changes (~300% at full lithiation) during the charge and discharge process causes fracture of electrodes, which leads to mechanical failure, chemical degradation, capacity loss and shortened cycle life. Substantial research on diffusion processes, electrochemical reactions, volume changes, stress evolution, and mechanical failure has been performed in the past through experiments and numerical simulations.

During the initial lithiation process of Si, it has been found that a two-phase diffusion process happens for both crystalline Si (c-Si) and amorphous Si (a-Si), where the newly formed amorphous Li-Si alloy (a-Li_xSi) and the remaining Si forms an evident reaction front. The reaction front is observed to have a nanoscale thickness with a high Li concentration gradient for c-Si. During the lithiation of Si nanoparticle electrodes, the reaction front is found to slow down as it progresses towards the core and to move linearly with time for a-Si.

A thorough understanding of the complicated electro-chemo-mechanical problem involved in the (de)lithiation process of Si is needed to improve the performance of lithium-ion batteries. In this work, a reaction-controlled diffusion model will be presented firstly to capture the two-phase diffusion mechanism involved in the initial lithiation process of a-Si and c-Si electrodes. Next, instead of using sharp discontinuties [1-5], a diffusive phase field model [6] coupled with this new reaction-controlled diffusion model will be used to investigate the diffusion induced elasto-plastic deformation and fracture involved in pherical c-Si electrodes at large deformations. The importance of the hydrostatic pressure in the diffusion and fracture process is studied. We also investigate the size effect and lithiation concentration on the fracture behavior of silicon anodes. Finally, our numerical simulation results are compared with existing experimental data.

REFERENCES

[1] C. Linder and F. Armero, "Finite elements with embedded strong discontinuities for the modeling of failure in solids", *Int. J. Numer. Meth. Engng*, **72**, 1391-1433 (2007).

[2] C. Linder, D. Rosato and C. Miehe, "New finite elements with embedded strong discontinuities for the modeling of failure in electromechanical coupled solids", *Comput. Meth. Appl. Mech. Eng.*, **200**, 141-161 (2011).

[3] C. Linder and A. Raina, "A strong discontinuity approach on multiple levels to model solids at failure", *Comput. Meth. Appl. Mech. Eng.*, **253**, 558-583 (2013).

[4] C. Linder and X. Zhang, "A marching cubes based failure surface propagation concept for three-dimensional finite elements with non-planar embedded strong discontinuities of higher-order kinematics", *Int. J. Numer. Meth. Engng*, **96**, 339-372 (2013).

[5] C. Linder and X. Zhang, "Three-dimensional finite elements with embedded strong discontinuities to model failure in electromechanical coupled materials", *Comput. Meth. Appl. Mech. Eng.*, **273**, 143-160 (2014).

[6] C. Miehe and L. Schänzel, "Phase field modeling of fracture in rubbery polymers. Part I: Finite elasticity coupled with brittle failure", *J. Mech. Phys. Solids*, **65**, 93-113 (2014).