11th World Congress on Computational Mechanics (WCCM XI)
5th European Conference on Computational Mechanics (ECCM V)
6th European Conference on Computational Fluid Dynamics (ECFD VI)
July 20 - 25, 2014, Barcelona, Spain

# PLASTICITY IN SILICON ANODES TOWARDS THE DESIGN OF LITHIUM ION BATTERIES

**S. Mostafa Khosrownejad[1]*, William A. Curtin[2]**

[1] École polytechnique fédérale de Lausanne, Switzerland, mostafa.khosrownejad@epfl.ch
[2] École polytechnique fédérale de Lausanne, Switzerland, william.curtin@epfl.ch

**Key Words:** *Lthiumi-ion battery, Silicon anode, Plasticity.*

Lithium–ion batteries are characterized by high specific energy capacity, high operating voltage, low self-discharge energy storage and long life [1]. Silicon has the highest known theoretical specific charge capacity to be utilized in lithium–ion batteries [2]. In spite of the promising electrochemical properties of silicon based lithium alloys, they cannot be easily used in lithium cells. The main issue is the existence of a large volume expansion–contraction which occurs during the charge–discharge processes. These volume changes induce mechanical stresses, which result in disintegration of the electrode with consequent failure after a modest number of charge–discharge cycles [1, 3].

Although many models have been developed for understanding the precise mechanisms of lithium insertion–extraction [4, 5], lithiated silicon expansion–contraction [6] and failure mechanisms, these models are still far from being quantitative and not ready for design applications. A major challenge in the modeling of electrode swelling is the interplay between diffusion of lithium into silicon anode and mechanical properties of amorphous lithiated silicon [7]. Ref. [8] developed the concept of “reactive flow” in solids for lithium–ion battery electrodes to address the effect of diffusion on plastic behavior of these systems. In their view, an electrode in a lithium–ion battery may undergo inelastic processes of two types: flow and reaction. Flow changes the shape of the electrode, preserves its composition and volume, and is driven by the deviatoric stress. By contrast, reaction changes the composition and volume of the electrode, and is driven by a combination of the mean stress and the chemical potential of lithium in the environment. Consequently, the yield surface is assumed to be dependent on both stress and chemical potential. Although, this model has a well-structured mathematical framework, it does not predict certain essential physical behavior of the material. For instance, the shape of yield surface remains unaddressed. Furthermore, chemical potential is an equilibrium thermodynamic property and might not have a well-defined value during the nonequilibrium charge–discharge processes.

In this work a mechanistically-based constitutive model for amorphous Li–Si alloys is proposed which describes the effect of diffusion on plastic behavior of the alloy. We presented a modeling concept based on the existing amorphous metal constitutive laws. As a tool we focused on a specific theory for explanation of plasticity in amorphous metals called “free volume theory” [9]. We added appropriate pieces to the free volume theory in order to obtain physics based description of the material behavior.

The yield stress of Li–Si alloy with a specified concentration of lithium is defined as a function of a history variable. The history variable characterizes structural disorder in the amorphous alloy or equivalently, it is a measure for reduction in barrier energies for plastic events. Moreover, the history variable has a direct relationship with the charge–discharge rate. Thus higher charge–discharge rates in the electrical loading history end up with lower yield stresses which is in agreement with results in Ref. [8]. However, our model predicts yield stresses as a function of well-defined material parameters and loading conditions.

Finally, as an example application of the proposed model, a series of molecular dynamics cells for simulating Li–Si alloy discharging process have been created. The material yield stress has been calculated for all simulation cells and the model parameters were calibrated. Due to the fact that molecular dynamic simulation method is limited to small time intervals, we are only capable of performing simulation of discharging at limiting rate values. The model predicts yield stresses for limiting values of discharging rate with a very good agreement with simulation results. Furthermore, it can be used to calculate yield stresses at modest rates (close to experimental conditions) which are not possible to be computed using the conventional molecular dynamics simulation techniques.

## REFERENCES

[1] B. Scrosati and J. Garche, Lithium batteries: Status, prospects and future, *J. Power Sources*, Vol. **195**, pp. 2419–2430, 2010.

[2] K. Kang, H.-S. Lee, D.-W. Han, G.-S. Kim, D. Lee, G. Lee, Y.-M. Kang, and M.-H. Jo, Maximum li storage in si nanowires for the high capacity three-dimensional li-ion battery, *Appl. Phys. Lett.*, Vol. **96**, pp. 053110–053116, 2010.

[3] M. Winter and J. O. Besenhard, Electrochemical lithiation of tin and tin-based intermetallics and composites, *Electrochem. Acta*, Vol. **45**, pp. 31–50, Sept. 1999.

[4] Y.-M. Kang, S.-B. Suh, and Y.-S. Kim, First-principle calculation-assisted structural study on the nanoscale phase transition of si for li-ion secondary batteries, *Inorganic Chem.*, Vol. **48**, pp. 11631–11635, 2009.

[5] M. K. Y. Chan, C. Wolverton, and J. P. Greeley, First principles simulations of the electrochemical lithiation and delithiation of faceted crystalline silicon, *J. Am. Chem. Soc.*, Vol. **134**, pp. 14362–14374, 2012.

[6] V. Shenoy, P. Johari, and Y. Qi, Elastic softening of amorphous and crystalline li-si phases with increasing li concentration: A first-principles study, *J. Power Sources*, Vol. **195**, pp. 6825–6830, 2010.

[7] K. Zhao, W. L. Wang, J. Gregoire, M. Pharr, Z. Suo, J. J. Vlassak, and E. Kaxiras, Lithium-assisted plastic deformation of silicon electrodes in lithium-ion batteries: A first-principles theoretical study, *Nano Lett.*, Vol. **11**, pp. 2962–2967, 2011.

[8] L. Brassart and Z. Suo, Reactive flow in large-deformation electrodes of lithium-ion batteries, *Int. J. Appl. Mechanics*, Vol. **04**, pp. 1250023–1250037, 2012.

[9] F. Spaepen, A microscopic mechanism for steady state inhomogeneous flow in metallic glasses, *Acta Metallurgica*, Vol. **25**, pp. 407–415, 1977.