Effect of Stresses with Different Triaxiality Ratios on the Electrochemical Response of Silicon Electrodes

Anh Tuan Le*[1], Xavier Bruant[2,3], François Ozanam[4], Michel Rosso[3], and Laurent Guin[5,6]

[1]Laboratoire de Mécanique des Solides – Ecole Polytechnique – France

[2]Laboratoire de mécanique des solides – Ecole Polytechnique, Centre National de la Recherche Scientifique, Institut Polytechnique de Paris – France

[3]Laboratoire de physique de la matière condensée – Centre National de la Recherche Scientifique, Ecole Polytechnique – France

[4]Département de Chimie de l'Ecole Polytechnique (X-DEP-CHIMIE) – Ecole Polytechnique – École polytechnique, 91128 Palaiseau Cedex, France

[5]LMS - Ecole polytechnique (LMS - EP) – CNRS : UMR7649 – Palaiseau, France

[6]ETH Zurich (ETH) – Leonhardstr. 21, 8092 Zurich, Switzerland

Abstract

Silicon as a material for the negative electrode of lithium-ion batteries has ten times the capacity of the traditionally used graphite. Lithiation (resp. delithiation) refers to the mechanism of inserting of lithium into (resp. extracting from) silicon, two processes inherent to the functioning of a battery. With a volume expansion of 300% when fully lithiated, the integration of silicon into commercial batteries is still a challenge. During lithiation and delithiation, silicon experiences large stresses that in turn affect its electrode potential and as a result the voltage of the battery. This study investigates the effect of stresses of different triaxiality ratios on the electrochemical response of silicon electrodes using experimental and modeling approaches. A 50-nm thick amorphous silicon (a-Si) layer is deposited on a stainless steel substrate as the positive electrode, with lithium metal as the counter electrode. The stainless steel substrate is subjected to *operando* uniaxial and equibiaxial tensile loading, while the silicon thin film is subjected to galvanostatic lithiation and delithiation cycles. Since this study focuses on low-strain conditions and the a-Si exhibits strong adhesion to the stainless-steel substrate, the strain in the a-Si thin film is equal to that of the stainless steel during tensile loading. From the experimental results of the coupled lithiation-tensile tests, the electrical potential undergoes changes of the order of 2 mV when subjected to uniaxial strain of ϵ_xx = 2.2× 10^(-3) and changes of _~ 4 mV for equibiaxial strain of ϵ_xx=ϵ_yy=1.5×10^(-3).
These experimental results of stress-induced changes in electrode potential are rationalized using a chemomechanical model that describes the interplay between species diffusion and mechanics. The model is based on irreversible continuum thermodynamics, the Larché-Cahn theory (1), and in particular its extensions to inelastic materials (2), describing the lithium-silicon alloy as a viscoplastic material. We also show how our coupled experiments allow an indirect quantification of the mechanical properties of the lithium-silicon alloy, which are otherwise difficult to measure. On the one hand, the stress-induced changes in electrical

*Speaker

potential measured during tensile tests allow us to determine the Young's modulus and the viscoplastic properties of the lithium-silicon alloy. On the other hand, similar measurements under different states of biaxial stress conditions allow us to determine its Poisson ratio as a function of lithium content, a parameter that has not been previously accessible to measurement. 1. F. Larché, J.W. Cahn, A linear theory of thermochemical equilibrium of solids under stress, Acta metallurgica, 21(8), 1051-1063, 1973.
2. L. Anand, A Cahn–Hilliard-type theory for species diffusion coupled with large elastic–plastic deformations, Journal of the Mechanics and Physics of Solids, 60(12), 1983-2002, 2012.