Chemo-mechanical coupling problems in mechanics of solids

Alexander Freidin*†[1]

[1]Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences – Russia

Abstract

Highlights

- Due to the competition of chemistry and mechanics, there are chemical reactions that are affected by stresses and chemical reactions that are caused by stresses.
- There is principal difference between chemical reaction with elastic and viscoelastic reaction products. In the case of viscoelastic reaction product, unlike an elastic case, stress relaxation can protect the reaction from blocking. Two regimes of the front propagation in the case of viscoelastic product are possible: kinetic regime and quasi-equilibrium propagation regime.
- Various diffusion patterns are described depending on diffusion coefficients for the diffusion through the initial and transformed solid constituents. A phase field model has been developed aimed at a unified description of localized and volumetric reactions and related to the chemical affinity tensor. Chemical affinity tensor is a proper tool for describing chemical reactions in solids.

Introduction

Chemo-mechanical coupling remains one of the mainstreams of modern multiphysics. Lithiation of silicon in Lithium-ion batteries (charge–discharge cycles of the batteries), oxidation of silicon in integrated circuits and semiconductor technologies, formation of intermetallic phases in lead-free solders, oxidation and fracture of polycrystalline silicon microscale parts of MEMS are among important examples of reactions between solid and diffusing reactants accompanied by the transformation strain (volumetric expansion, for example up to 300% in the case of silicon lithiation), which generates stresses which, in turn, affect the reaction rate, see e.g., (1,2,3,4) or reviews (5,6). So, the appearance of stresses due to the transformation strain and the effect of stresses on the rate of a chemical reaction up to its blocking are well-documented facts.

Initial-boundary value problem of chemo-mechanics

In the present paper, we start by considering the reactions localized at the reaction front (a sharp interface). The system of equations includes:

*Speaker

†Corresponding author: alexander.freidin@gmail.com

- diffusion equation with a boundary condition and the condition at the reaction front (mass balance) with a sink defined by the reaction rate which depends on the concentration of the diffusing constituent and mechanical stresses;
- mechanical equilibrium equation with boundary conditions and conditions across the interface.
- to close the system, one needs constitutive equations for the diffusion flux, for mechanical behaviour of solid constituents and an equation defining the dependence of the reaction rate on the concentration and mechanical stresses.

Thus, like a phase transition problem, we have a coupled problem with propagating unknown interface the velocity of which depends on stresses and concentration, while the stresses and concentration depend on the interface position.

Kinetics of the propagation of the chemical reaction front in elastic and viscoelastic frameworks

The kinetics of the front propagation is described in the framework of an approach in which stresses affect the reaction rate through a chemical affinity tensor A scalar chemical affinity is one of the basic notions of physical chemistry (7). Tensorial nature of the chemical affinity in the case of deformable solids follows form the consideration of the reaction not just in points but at oriented area elements. (There is an analogy with the stress tensor defining tractions at oriented area elements.) The concept of the chemical affinity tensor was developed earlier (8) (see also (9)). The expression of the chemical affinity tensor was derived from fundamental balances and entropy inequality, and a number of boundary value problems were solved, which demonstrated how mechanical stresses can retard and block the reaction (see, e.g., (10,11) and reference therein), including stability analysis (12).

In the present considerations, after the general formulation of the initial boundary value problem "diffusion -chemistry-mechanics", we focus on the following aspects of the problem:

(i) There are stress-affected and stress-induced chemical reactions, reflecting the competition between pure chemistry and mechanics (there is an analogy with stress-induced phase transitions in nonlinear elastic materials with non-convex energy) (12).

(ii) The influence of the relationships of elastic moduli of solid constituent on strains and stresses which block and unblock the chemical reaction (13).

(iii) The effects of changing the rheology of the material due to the reaction. Our first results on chemical reactions in an elastic–viscoelastic mechanical framework were presented in (13) where the propagation of a plane reaction front was considered at zero stress in the direction perpendicular to the interface. Now, considering a chemical reaction front propagation under uniaxial deformation, we focus on studying the kinetics of the reaction front in dependence on external strains, including cyclic deformation, and emphasize the differences with the elastic case. Unlike in the case of solid elastic components, in the viscoelastic case, the stresses relax, which protects the reaction from blocking and leads to the coupling of the kinetics of the reaction front and the stress relaxation process.

A special attention is paid to unlocking the previously blocked reaction due to the stress relaxation. Possibility of two regimes of the front propagation in the case of viscoelastic constituent is discussed: "kinetic regime" of the front propagation controlled by the chemical affinity tensor defining the corresponding configurational force, and quasi-equilibrium propagation of the front when chemical equilibrium is maintained at the front during propagation.

(iv) Various diffusion patterns and conditions at the reaction front for the diffusion problem (see also (11)). Two different problem formulations are examined for which:

- Diffusion through the untransformed material does not occur, as it is, for example, in the case of lithiation of crystalline silicon (14).
- Diffusion is possible through both transformed and untransformed materials, and the diffusing constituent located ahead of the reaction front in the untransformed material affects the velocity of the front as well as from the side of the transformed material.

Comparison of quasi-steady-state and non-steady-state diffusion approaches is also made. Within the framework of the developed approach, the propagation of the reaction front, controlled by the reaction rate or the diffusion rate, is discussed.

Volumetric reactions

Finally, we present a modification of the model in the spirit of the phase field approach aimed at a unified description of localized and volumetric reactions. A special attention is paid to the definition of a reaction extent in the case of finite strains, since it acts as a phase field parameter. It is shown how the configurational force driving the volumetric reaction is related to the chemical affinity tensor (15). The time evolution of space distributions of reaction extent and the concentration of the diffusing constituent is studied in dependence of the diffusion and reaction rate parameters. It is demonstrated how the pattern changes depending on whether mechanical stresses are taken into account or not.

References

(1) McDowell M.T., Lee S.W., Nix W.D., Cui Y. 25th anniversary article: Understanding the lithiation of silicon and other alloying anodes for lithium-ion batteries. Advanced Materials **25**(36): 4966–4984, 2013.

(2) Heidemeyer H., Single C., Zhou F., Prins F.E., Kern D., Plies E. Self-limiting and pattern dependent oxidation of silicon dots fabricated on silicon-on-insulator material. Journal of Applied Physics **87**: 4580–4585, 2000.

(3) Buttner C.C., Zacharias M. Retarded oxidation of Si nanowires. Appllied Phys. Lett. **89**: 263106, 2006.

(4) Muhlstein C.L., Ritchie R.O. High-cycle fatigue of micron-scale polycrystalline silicon films: Fracture mechanics analyses of the role of the silica/silicon interface. International Journal of Fracture **119**(4-2): 449–474, 2003.

(5) Fang X., Li Y., Yue M. *et al.* Chemo-mechanical coupling effect on high temperature oxidation: A review. Sci. China Technol. Sci. **62**: 1297–1321, 2019.

(6) Tian J., Chen Z, Zhao Y. Review on modeling for chemo-mechanical behavior at interfaces of all-solid-state lithium-ion batteries and beyond. ACS Omega **7**: 6455–6462, 2022.

(7) Prigogine I., Defay R. Chemical Thermodynamics. Longmans, Green, London. 1954.

(8) Freidin, A.B. Chemical affinity tensor and stress-assist chemical reactions front propagation in solids. In: ASME International Mechanical Engineering Congress and Exposition, Volume 9: Mechanics of Solids, Structures and Fluids, p. V009T10A10, 2013.

(9) Freidin A., Vilchevskaya E. Chemical affinity tensor in coupled problems of mechanochemistry. In: H. Altenbach, A. Öchsner (eds.) Encyclopedia of Continuum Mechanics. Springer, Berlin, Heidelberg, 2020.

(10) Poluektov M., Freidin A.B., Figiel Ł. Modelling stress-affected chemical reactions in non-linear viscoelastic solids with application to lithiation reaction in spherical Si particles. Int. J. Eng. Sci. **128**: 44–62, 2018.

(11) Freidin A. B., Rublev I. A., Korolev I. K. Initial-boundary value problem for the propagating chemical reaction front. Acta Mechanica **235**: 4289–4310, 2024.

(12) Morozov A., Freidin A., Müller W. On stress-affected propagation and stability of chemical reaction fronts in solids. International Journal of Engineering Science **189**: 103876, 2023.

(13) Petrenko S., Freidin A.B., Charkaluk E. On chemical reaction planar fronts in an elastic – viscoelastic mechanical framework. Continuum Mech. Thermodyn. **34**: 137–163, 2022.

(14) Liu X.H., Wang J.W., Huang S., Fan F., Huang X., Liu Y., Krylyuk S., Yoo J., Dayeh S.A., Davydov A.V., Mao S.X., Picraux S.T., Zhang S., Li J., Zhu T., Huang J.Y. In situ atomic-scale imaging of electrochemical lithiation in silicon. Nature Nanotechnology **7**: 749–756, 2012.

(15) Poluektov M., Freidin A.B. Localisation of stress-affected chemical reactions in solids described by coupled mechanics-diffusion-reaction models. Int. J. Engineering Science **196**: 104006, 2024.