Modeling and Simulation of Silicon Swelling in Battmo

1 Introduction

As the demand for batteries is and will sharply increase, modeling their behavior and improving their capacity has been a central research topic in recent years. At the moment, almost all the batteries in the electric vehicles or electronic devices are based on the Li-ion technology, with a graphite anode. This type of battery is based on a liquid electrolyte in which Li^+ ions carry the current and undergo a red-ox reaction at the electrodes surface. The, if we consider for example a battery being charged, an electron will react with a Li^+ at the negative electrode interface and produce a Li atom which will then diffuse into the graphite electrode. The opposite reaction occurs at the positive electrode : a lithium ion as well as an electron are produced. If graphite is at the moment almost the unique negative electrode material to be used because of its high capacity and its stability, the ten times higher specific capacity of silicon ($3590\,\mathrm{mA\,h\,g^{-1}}$, [1]) compared to graphite ($372\,\mathrm{mA\,h\,g^{-1}}$, [1]) has always tempted the battery manufacturers. Still, it is well known that silicon based electrodes suffer from poor cyclability due to the extremely important swelling of silicon (up to $380\,\%$ of absolute change) occurring during lithium insertion and diffusion in the electrode.

In fact the expansion of silicon particles under lithiation generates stresses which can lead to fractures. The fractures isolate Silicon active material who looses electrical contact with the current collector and therefore with the electrical circuit. In addition to this loss of Silicon, a second major issue induced by the expansion is that the SEI layer of the particles (thin insulating layer due to a parasitic reaction of lithium ions at the surface of the active material particles) is continuously destroyed and reformed, thus consuming a great amount of lithium ions which are lost in the SEI and then no more used for electrical transport. One can then understand the interest of modeling such electrodes for trying to limit the rapid decrease of the extremely high specific capacity of $Li_{15}Si_4$ after a few charge/discharge cycles.

2 Literature overview

Literature about silicon expansion is quite abundant but the initial hypothesis as well as the angle of attack taken by the authors can be very different. To summarize very roughly the different type of papers we read, we divide them into the three following categories.

2.1 Experimental approach

In the great majority of the cases, silicon swelling was studied through experiments and observations. These papers give some crucial experimental data, such as the open-circuit potential curves [2], the capacity of the materials, the reaction rates coefficient, the diffusion coefficients [3]. A subcategory of these papers would be the ones which intend to find techniques to minimize or even suppress the porosity changes, by using techniques such as elastic binders or highly porous materials. We can also cite some papers [4] which focus on giving a charge strategy that mitigates the stresses.

2.2 Purely mechanical approach

As explained previously, stress has to be computed and understood if one aims at predicting the fractures in the active material and the resulting ohmic contact losses. However, w these approaches were purely mechanical and did not take into consideration any electrochemical aspects. We can cite the hard sphere model used in [5] or the elastic layer model presented in [6]. As the idea was to implement the model in *BattMo* which has only experimental support for solid mechanics, these approaches were not retained.

2.3 Electrochemical Approach

The last and finally selected category of papers is detailing an electrochemical model giving laws for the variation of silicon particles radius and the porosity as a function of reaction rates. These papers used for their model composite silicon-graphite electrode and nano-sized particles in order to limit the mechanical stresses and fractures issues. Choosing such particles however increases the electrolyte/electrode interface and thus increases the SEI formations/destructions during the charge and discharge cycles. The focus was made on the porosity changes which directly impacts the behavior of the battery as well as the apparition of convective flux in the electrolyte and in the particle as the silicon swells. This approach is particularly interesting because at the moment, it is the strategy used by many battery manufacturers : a tiny amount of silicon is introduced into graphite electrodes in order to enhance a little their capacity but without massive and and problematic swelling. The reference paper used for this work is [1]. The papers [7] and [8] have also largely been used for completing and comparing models.

3 Model equations

The expansion of silicon particles could be modeled under two different assumptions. Either we assume a constant global casing volume with a varying porosity or a constant porosity with a varying global casing volume, see Figure 3. We choose the first option.

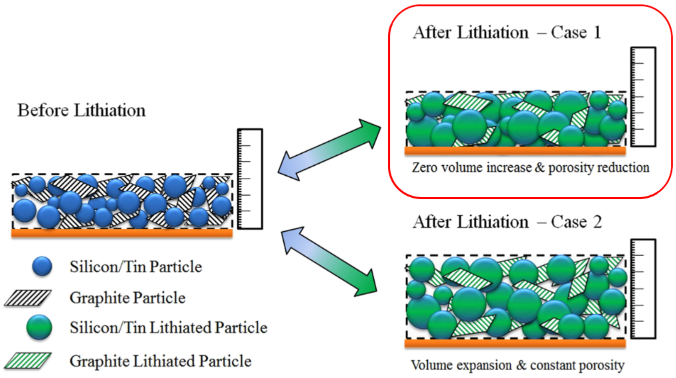

Figure 1: Constant versus expanding casing modeling hypothesis *Source: Design-Considerations regarding Silicon/Graphite and Tin/Graphite Composite Electrodes for Lithium-Ion Batteries - Scientific Figure on ResearchGate.*

3.1 Particle Radius, Volume Fraction and Convective Flux

Let $\langle x \rangle$ denote the Lithium *fill-in level* in Silicon, which by definition has a value between 0 and 1. For the molar volume of lithiated Silicon, we use the following expression [8],

$$\tilde{V}_{\mathrm{LiSi}_{4/15}} = \frac{4}{15}\left(\tilde{V}_{\mathrm{Si}} + \frac{15}{4}\langle x \rangle \tilde{V}_{\mathrm{Li}}\right) \tag{1}$$

where $\tilde{V}_{\mathrm{Si}}$ and $\tilde{V}_{\mathrm{Li}}$ are the molar volume of Silicon and Lithium, respectively. For the underlying spherical particle, the radius is given by

$$R = R_0 \left(1 + \zeta \langle x \rangle\right)^{1/3} \tag{2}$$

where $\zeta = \frac{\frac{15}{4}\tilde{V}_{\mathrm{Li}}}{\tilde{V}_{\mathrm{Si}}}$. For the volume fraction of the Lithiated Silicon, denoted ε_s, we have

$$\frac{\varepsilon_s}{4/3\pi R^3} = \frac{\varepsilon_{s,0}}{4/3\pi R_0^3}, \tag{3}$$

From (3), we obtain an expression of the volume fraction as a function of the particle filling level,

$$\varepsilon_s = (1 + \zeta \langle x \rangle)\varepsilon_{s,0}.$$

We can compute the fill-in level, which we denote $\langle x\rangle$, as a function of stoichiometry. By definition, we have

$$\langle x\rangle = \frac{\varepsilon_s c_{\text{aver}}}{\varepsilon_{s,\text{max}} c_{\text{aver},max}} \tag{4}$$

where c_{aver} is the average concentration in the particle, see (10) below. The stoichiometry coefficient for Lithium is defined as

$$\theta = \frac{c_{\text{aver}}}{c_{\text{aver,max}}}.$$

After some simplification, we get the following relationship between the stoichiometry coefficient and the fill-in level,

$$\langle x\rangle = \frac{\theta}{1+\zeta(1-\theta)}.$$

In [1], the following expression for the evolution of the porosity, denoted ε, is given

$$\frac{\partial\varepsilon}{\partial t} = \frac{\gamma}{nF} i_n \tilde{V}_{\text{Li}}, \tag{5}$$

where

γ : volumetric surface area ($\text{m}^2\,\text{m}^{-3}$)
F : Faraday constant ($96\,487\,\text{C}\,\text{mol}^{-1}$)
i_n : Reaction rate at the surface of the electrode computed through the Butler-Volmer equation.

Using (11), which is introduced below, we can check that this expression is equivalent to (1).

Another important feature is the apparition of a convective flux in the electrolyte $c_{\text{elyte}} v^{avg}$ induced by the swelling of the particles. This flux has to be computed and added in the electrolyte mass conservation equation. The convective flux becomes important compared to diffusive flux mainly at high rates, as detailed in [8]. This flux is given according to [7] (equation 16) by

$$v^{avg} = \frac{1}{nF}\left(\tilde{V}_{\text{LiSi}} - \tilde{V}_{\text{Si}}\right) i_{\text{elyte}}$$

see also Appendix for definition of i_{elyte}. The value of $\tilde{V}_{\text{LiSi}}$ depends of the fill-in level. We have, from [7] (equation 17),

$$\tilde{V}_{\text{LiSi}} = \frac{4}{15}\left(\tilde{V}_{\text{Si}} + 3.75\,\langle x\rangle\,\tilde{V}_{\text{Li}}\right).$$

3.2 Solid Diffusion Equation in Particle with Varying Radius

The lithium diffusion equation into the silicon electrode particles has to be modified to account for the moving boundaries as the particle swells. This issue is not explicitly detailed in the papers mentioned above (some of them neglected the swelling in the diffusion equations, some others gave a simple but imprecise corrective term for the mass source term). We detail here the derivation of the diffusion equation. We introduce a time dependent radius $r(t)$ and let the particle geometry evolve as

$$x = \frac{r(t)}{r_0}\hat{x}. \tag{6}$$

It means that a point in the solid particle which is initially located at a point $\hat{x}$ will follow the trajectory $x(t, x_0) = \delta(t)\hat{x}$, where $\delta = \frac{r}{r_0}$, as the particle starts deforming. We assume therefore that the particle grows uniformly in the radial direction. The governing equation for the concentration in the moving frame is the combination of the diffusion process and of the convection due to the particle swelling,

$$\frac{\partial c}{\partial t} + \nabla_x \cdot (-D\nabla_x c + cv) = 0 \tag{7}$$

where $v(t, x)$ is the velocity of the point in the particle. This velocity is obtained by differentiating (6),

$$v(t, x) = \frac{\dot{\delta}}{\delta}x$$

We want to rewrite (7) in the fixed frame given by $\hat{x}$. Let $\hat{t} = t$ and $\hat{c}(\hat{t}, \hat{x}) = c(t, x)$. The change of coordinate for the operators are

$$\frac{\partial}{\partial \hat{t}} = \frac{\partial}{\partial t} + \dot{\delta}\hat{x} \cdot \nabla_x \quad \text{and} \quad \nabla_{\hat{x}} = \delta\nabla_x.$$

We use these operators in (7) and get

$$\frac{\partial \hat{c}}{\partial \hat{t}} - \frac{\dot{\delta}}{\delta}\nabla_{\hat{x}}\hat{c} = \frac{1}{\delta}\nabla_{\hat{x}} \cdot (D\frac{1}{\delta}\nabla_{\hat{x}}\hat{c} - \hat{x}\dot{\delta}\hat{c}).$$

The expression can be simplified to

$$\frac{\partial \hat{c}}{\partial \hat{t}} + 3\frac{\dot{\delta}}{\delta}\hat{c} = \frac{1}{\delta}\nabla_{\hat{x}} \cdot (D\frac{1}{\delta}\nabla_{\hat{x}}\hat{c}).$$

where we have used $\nabla_{\hat{x}} \cdot \hat{x} = 3$ in 3D. We can simplify further this expression and obtain the governing equation for the rescaled concentration $\hat{c}$ in the particle.

$$\frac{1}{\delta}\frac{\partial}{\partial \hat{t}}(\delta^3\hat{c}) = \nabla_{\hat{x}} \cdot (D\nabla_{\hat{x}}\hat{c}). \tag{8}$$

We use the P2D assumption where the particle is spherical. We have to the set the boundary condition which is given by the incoming flux in the particle in the reference frame, given by

$$f_{\text{bc}} = 4\pi r_0^2 D\frac{\partial \hat{c}}{\partial \hat{r}}. \tag{9}$$

Let c_{aver} be the average concentration in the particle. We need to differentiate now between the particle coordinate, which we have denoted by x or $\hat{x}$ in the reference frame, and the spatial coordinate. To avoid the confusion, we denote the later by ξ. We have

$$c_{\text{aver}}(t,\xi) = \frac{\int_{B(r)} c(t,\xi,x)\,dx}{\frac{4}{3}\pi r^3}. \tag{10}$$

The reaction rate in $\mathrm{mol\,m^{-3}\,s^{-1}}$ is given by $\frac{\gamma}{F} i_n$, see in the appendix, where we have collected all the equations. We have therefore the identity

$$\frac{\partial}{\partial t}(\varepsilon_s c_{\text{aver}}) = -\frac{\gamma}{F} i_n, \tag{11}$$

where ε_s denotes the volume fraction of the electrode. The minus sign comes from the convention on the direction of the reaction. Let us use this expression to determine the value of the flux f_{bc} we have to impose at the boundary. We have, after changing variable

$$\varepsilon_s c_{\text{aver}} = \varepsilon_s \frac{\int_{B(r_0)} \delta^3 \hat{c}(t,\xi,\hat{x})\,d\hat{x}}{\frac{4}{3}\pi r^3} = \frac{\varepsilon_{s,0}}{\frac{4}{3}\pi r_0^3} \int_{B(r_0)} \delta^3 \hat{c}(t,\xi,\hat{x})\,d\hat{x}.$$

Hence, using (8), we get

$$\frac{\partial}{\partial t}(\varepsilon_s c_{\text{aver}}) = \delta \frac{\varepsilon_{s,0}}{\frac{4}{3}\pi r_0^3} f_{\text{bc}}.$$

Hence,

$$f_{\text{bc}} = -\frac{1}{\delta^2}\frac{\gamma_0}{F}\frac{\frac{4}{3}\pi r_0^3}{\varepsilon_{s,0}} i_n$$

where we have used that the dependence of the volumetric surface area on δ is given by

$$\gamma = \frac{\gamma_0}{\delta}.$$

3.3 Transport effective parameters

The change in porosity modifies the effective transport parameters. In the electrolyte, we have the effective diffusion coefficient,

$$D_{\text{elyte,eff}} = D_{Li^+}\varepsilon^b$$

and the effective conductivity

$$\kappa_{\text{elyte,eff}} = \kappa_{\text{elyte}}\varepsilon^b.$$

Here, b is the Bruggeman coefficient. In the electrode, we have the effective conductivity

$$\kappa_{\text{elde,eff}} = \kappa_{\text{elde}}\varepsilon^b.$$

4 Mechanical Stress

4.1 Different mechanical stresses and their impact

We can distinguish between two types of stresses:

Diffusion induced stresses: The diffusion of lithium into an isolated particle generates a stress in the particle, which is known as diffusion-induced stress (DIS). This stress is due to a lithium concentration gradient in the hosting particle which induce modifications of the atomic arrangement as well as lattice structure distortions. According to the work of Cheng and Verbrugge in [9], the diffusion induced hydrostatic stress at the surface of the particle can be expressed as

$$\sigma_h = \frac{2E\Omega}{9(1-\nu)}\left(c_{av} - c_{surf}\right)$$

where Ω is the partial molar volume of the electrode

Mechanical induced stresses: The silicon particles are not isolated in the electrode. The expansion of particles then directly impact the stress of the other particles as particles which were not in contact in the unlithiated case can push each other when they swell. Furthermore, as the global casing is kept to a constant volume, this can also also become a stress source. In order to limit this phenomenon, using binder that limits particle interactions but ensure electrical connectivity is a very common option. This mechanical stress is also the reason why at the moment, just a very small amount of silicon is used in graphite-silicon composite electrodes. It enable to enhance the battery capacity while the silicon amount is kept sufficiently low so that its swelling has no impact on the overall battery behavior.

These stresses can have two major impacts on the battery behavior:

Modification of the electrochemical reactions kinetics: The central kinetic equation of the *BattMo* model is the Butler-Volmer equation which gives the interface reaction rate for each electrode. In a graphite-anode battery, the stresses are considered sufficiently low to be neglected. Still, a high stress density modifies the kinetics, which is perfectly understandable as one could expect that a particle under high compressive stresses will tend to be less incline to accept lithium than a one without stress. Hence, a modified form for the Butler-Volmer equation is proposed in [10]

$$i_n = i_0\left(\exp\left(\beta\frac{F\eta - \Omega\sigma_h}{RT}\right) - \exp\left(-(1-\beta)\frac{F\eta - \Omega\sigma_h}{RT}\right)\right).$$

Cracks and fractures: This contribution is crucial but is also definitely the more complex to handle. In fact, predicting the stresses as well as deducing from them the cracks and thus the ohmic losses and silicon active material losses for such a problem is a very demanding solid mechanics problem.

4.2 A few more words on external mechanical stresses and fractures

As *BattMo* is not primarily a solid mechanics software, we do not cover the creation of mechanical fractures and pulverization into the silicon. The choice was made to consider nanometric particles used in sufficiently low quantity so that the stress effects were negligible. Yet, as already explained, this phenomenon keeps the major drawback and hinder to silicon-based batteries commercialization because of their very quick capacity decrease.

As a complete mechanical model could be lately developed for pure silicon electrodes, here is a brief summary of a few different approaches and theoretical model found in the literature:

Experimental based approximations: In [1] the impact of the fractures on the silicon electrode behavior included by modifying the diffusion coefficients into the particle into $D_{WithStress} = D_{WithoutStress}(1 - f_{bb})^{\gamma}$ where the density of crack f_{bb} and the exponent γ are given according to the work of Barai et al in [11]. However, in this work, the bulk diffusion coefficient D_{Si} is taken as a fitting parameter to fit the experimental data.

Solid spheres approach: Another approach common to several papers such as in [5, 12]is to model the situation as a solid sphere problem where the stresses are computed as a function of strains (radial expansion). Different contact laws between the particles can be considered, as the below schematic Hertz-Mindlin contact law:

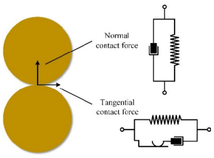

Figure 2: Schema of a Hertz-Mindlin contact

Figure 3: *

Source: Local Scour Mechanism of Offshore Wind Power Pile Foundation Based on CFD-DEM by Zhang and Zhao

Elastic layer: Another approach simple approach adopted in the paper [6] is to divide the electrode into layers and then to express the strain the ratio of lithiated and unlithiated volumes and then to adopt a simplistic linear elastic model which directly gives the stress. Still, this approach as well as the solid sphere approach allows to get the stresses but fractures and pulverization effects from this stress are not included in the model.

5 Appendix A

Electrolyte mass conservation	$\frac{\partial \varepsilon c_{\text{elyte}}}{\partial t} + \nabla N_+ = \frac{\gamma i_n}{F}$ with $N_+ = -D_{\text{elyte,eff}} \nabla (c_{\text{elyte}}) + \frac{i_{\text{elyte}} t_+}{z_+ \nu + F} + v^{avg} c_{\text{elyte}}$
Electrolyte charge conservation	$\nabla \cdot i_{\text{elyte}} = \gamma i_n$ with $i_{\text{elyte}} = -\kappa_{\text{eff,elyte}} \nabla \phi_{\text{elyte}} - \left(\frac{\partial \mu}{\partial c_{\text{elyte}}} \right) \frac{\kappa_{\text{eff,elyte}} (1 - t_+)}{F z_+}$
Electrode charge conservation	$\nabla \cdot i_{\text{elde}} = -\gamma i_n$ with $\quad i_{\text{elde}} = -\sigma_{\text{elde,eff}} \nabla \phi_{\text{elde}}$
Electrode surface reaction	$4 \pi R^2 D \frac{\partial c}{\partial r} = \frac{a i_n}{F}$
Electrode mass conservation	$\frac{\partial c_{\text{elde}}}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \left(-D_{\text{elde}} \frac{\partial c_{\text{elde}}}{\partial r} \right) \right) = 0$
EI equation	$I = i_{\text{elde}} + i_{\text{elyte}}$
EI control	Ohm laws for a real circuit, fixed par the user in our case (constant current, constant voltage)

Surface Reaction rate	$i_n = i_0 \left(e^{\frac{\beta F \eta}{RT}} - e^{-\frac{(1-\beta) F \eta}{RT}} \right)$
Surface reaction rate coefficient	$i_0 = Fkc_{\text{elyte}}^{\beta}(c_{max} - c_{\text{elde,surf}})^{\beta} c_{\text{elde,surf}}^{1-\beta}$
Overpotential	$\eta = \phi_{\text{elde}} - \phi_{\text{elyte}} - OCP(c_{\text{elde,surf}})$

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