Influence of interface-mediated elastic relaxation of lithiation precipitates in aluminium electrodes

Numerical models for atomistic simulations

Felix Wilms

Supervisors: Dr. Claas Hüter, Prof. Dr. Benjamin Stamm

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1 Introduction

We consider the thermodynamic preferential lithiation of aliminium electrodes subject to formation stresses. A continuum model is described to account for the elastic contributions from a thermodynamic perspective of lithium precipitation during the charging half cycle. The influence of the elastic effects mainly depends on the relative elastic stiffness of electrolyte and electrode material and the presence of a stiff interfacial film. Specifically, we refer two experimental findings which show either interface-dominated precipitation or bulk lithiation in the Aluminium electrode. Our findings suggest that in spite of the kinetic nature of the charging process, thermodynamic aspects can explain a substantial part of the precipiation.

2 Analytical description

In this chapter we first derive the solubility limit of lithium into an aluminum anode in the low temperature regime. We do so by first deriving the phase coexistence between a phase with low concentration - which we will call phase a - and a highly lithiated phase - which we will call phase b - using a regular solution modell for both phases and taking into account elastic coherency effects inside an infinite host lattice of metal atoms.
The model is based on the Gibbs free energy, which is of the form [1]

$$\mathcal{G} = \mathcal{G}_a + \mathcal{G}_b + \mathcal{G}_{el}^{bulk}, \tag{1}$$

where the first two terms are given by the number of host atoms in phase a and b, respectively, and the Gibbs free energy density of the regular solution model for each phase, meaning that

$$\mathcal{G}_{a,b}(x_{a,b}, T) = N_M^{a,b} g^{RS}(x_{a,b}, T)$$
$$\text{where} \tag{2}$$
$$g_{a,b}^{RS}(x_{a,b}, T) = \alpha x_{a,b}(1 - x_{a,b}) + kT \left[x_{a,b} \, ln(x_{a,b}) + (1 - x_{a,b}) \, ln(1 - x_{a,b}) \right]$$

It depends on the temperature T and on the dimensionless, interstitial concentrations x_a and x_b, which are defined as the ratio between the number of lithium atoms and host particles in phase a and b respectively, meaning that they are defined as

$$x_a := \frac{N_{Li}^a}{N_M^a}; \qquad x_b := \frac{N_{Li}^b}{N_M^b} = \frac{N_{Li} - N_{Li}^a}{N_M - N_M^a}, \tag{3}$$

where N_M and N_{Li} are the total number of host and lithium particles, respectively. The factor α is the interaction parameter specific to the system and is calculated via Ab Initio calculations.

According to [1], the contribution to the Gibbs free energy by bulk coherent elastic stresses is given by

$$\mathcal{G}_{el}^{bulk} = \frac{\Omega_0}{N_0} V \frac{E\chi^2}{1-\nu} \, v(1-v) \, (x_b - x_a)^2. \tag{4}$$

Here, V denotes the volume of the system, Ω_0 and N_0 the volume and number of host atoms inside a unit cell, respectively, E, χ and ν the Young's modulus, Vegard coefficient and

Poinnson ratio and v is the volume fraction of the highly lithiated phase with respect to the entire system, which is given by

$$v := \frac{N_M^b}{N_M} = \frac{N_M - N_M^a}{N_M}. \tag{5}$$

If temperature, pressure and the total number of lithium and host particles are fixed, thermodynamic equilibrium is achieved by minimizing $\mathcal{G}$ with respect to N_{Li}^a and N_M^a:

$$\left(\frac{\partial \mathcal{G}}{\partial N_{Li}^a} \right)_{N_M, N_{Li}, N_M^a, T} \overset{!}{=} 0$$

$$\Rightarrow \left[\frac{\partial g_a}{\partial x_a} + 2 \frac{E\chi^2}{1-\nu} \frac{\Omega_0}{N_0} x_a \right] - \left[\frac{\partial g_b}{\partial x_b} + 2 \frac{E\chi^2}{1-\nu} \frac{\Omega_0}{N_0} x_b \right] \overset{!}{=} 0 \tag{6}$$

$$\left(\frac{\partial \mathcal{G}}{\partial N_M^a} \right)_{N_M, N_{Li}, N_{Li}^a, T} \overset{!}{=} 0$$

$$\Rightarrow g_a - x_a \frac{\partial g_a}{\partial x_a} - \frac{E\chi^2}{1-\nu} \frac{\Omega_0}{N_0} x_a^2 - \left(g_b - x_b \frac{\partial g_b}{\partial x_b} - \frac{E\chi^2}{1-\nu} \frac{\Omega_0}{N_0} x_b^2 \right) \overset{!}{=} 0 \tag{7}$$

By defining the auxilliary potentials

$$\bar{g}_{a,b}(x_{a,b}, T) := g_{a,b}(x_{a,b}, T) + \frac{E\chi^2}{1-\nu} \frac{\Omega_0}{N_0} x_{a,b}^2, \tag{8}$$

we can see that (6) and (7) are equivalent to

$$\bar{\mu}_a \overset{!}{=} \bar{\mu}_b$$
$$\bar{\omega}_a \overset{!}{=} \bar{\omega}_b, \tag{9}$$

where

$$\bar{\mu}_{a,b}(x_{a,b}, T) := \frac{\partial \bar{g}_{a,b}(x_{a,b}, T)}{\partial x_{a,b}}$$

and

$$\bar{\omega}_{a,b}(x_{a,b}, T) := \bar{g}_{x_{a,b}, T} - x_{a,b} \bar{\mu}_{a,b}(x_{a,b}, T) \tag{10}$$

are the chemical and grand canonical potential of the auxilliary potentials of phase a and b, respectively.

Before proceeding further, we will split the the modified energy densities into a regular and a secular part

$$\bar{g}_{a,b}(x_{a,b}, T) = \bar{g}_{a,b}^0(x_{a,b}) + g_{a,b}^c(x_{a,b}, T), \tag{11}$$

where

$$g_{a,b}^c(x_{a,b}, T) = kT \left[x_{a,b} \ln(x_{a,b}) + (1 - x_{a,b}) \ln(1 - x_{a,b}) \right]$$

is nothing but the entropic contribution to the regular solution model. We call this term secular in the sense that in the limit $x_{a,b} \to 0$ or $x_{a,b} \to 1$, $g_{a,b}^c \to 0$, but $\frac{\partial g_{a,b}^c}{\partial x_{a,b}}$ will diverge. On the other hand, both the regular part and its derivative will stay finite for all values of $x_{a,b}$.

Since the equilibrium conditions (6) and (7) can be interpreted as the equilibrium conditions for a double tangent construction (9) of the auxiliary energy densities $\overline{g}_a$ and $\overline{g}_b$, we can use exactly this procedure to describe the Gibbs free energy density of the heterogeneous system $\overline{g}_{het}$ at equilibrium.

Applying the common tangent construction to the modified energy density of phases a and b, using the lever rule, gives us

$$\overline{g}_{het}(x,T) = (1-v)\overline{g}_a(x_a, T) + v\overline{g}_b(x_b, T), \tag{12}$$

where

$$x = (1-v)x_a + vx_b \tag{13}$$

and v again is the volume fraction of the highly lithiated phase b with respect to the volume of the system.

We consider our system to have zero solubility in phase a for $T \to 0$, i.e. $x_a \to 0$. In the same limit, the concentration of the highly lithiated phase b has to go to 1 then. Therefore, using the lever rule (13), we know that the volume fraction of phase b is approximately given by

$$v \approx x \tag{14}$$

in the limit $T \to 0$.

Before we proceed, we will split the auxilliary Gibbs energy densities of phases a and b into a regular and a

By definition of the Maxwell construction, the chenical potential of the heterogenous system needs to be equal to the chemical potentials at the solubility limits. This means that given the two solubility limits $x_a^*(T)$ and $x_b^*(T)$, for which phase coexistence is only possible if $x_a^*(T) \leq x \leq x_b^*(T)$, it is true that

$$\frac{\partial \overline{g}_{het}(x,T)}{\partial x} = \left(\frac{\partial \overline{g}_a(x_a, T)}{\partial x_a}\right)_{x_a = x_a^*} = \left(\frac{\partial \overline{g}_b(x_b, T)}{\partial x_b}\right)_{x_b = x_b^*} \tag{15}$$

This relation even has to hold true if $x = x_a^*$ and $x = x_b^*$. As was mentioned before, in the limit $T \to 0$ we have $x_a^* \to 0$ and $x_b^* \to 1$.

Since x_a and x_b are held fixed when taking the derivative of $\overline{g}_{het}$ with respect to x, the only dependence appears to the volumentric fraction v. Therefore, applying the $T \to 0$ limit to $\frac{\partial \overline{g}_{het}}{\partial x}$ gives

$$\left(\frac{\partial \overline{g}_{het}}{\partial x}\right)_{T, x_a, x_b} \approx \left[\overline{g}_b^0(1) - \overline{g}_a^0(0)\right] \tag{16}$$

In the same limit we have

$$\begin{aligned}
\left(\frac{\partial \overline{g}_a}{\partial x_a}\right)_T &\approx \overline{g}_a^{0'}(0) + kT ln(x_a) \\
\left(\frac{\partial \overline{g}_b}{\partial x_b}\right)_T &\approx \overline{g}_b^{0'}(1) - kT ln(1 - x_b),
\end{aligned} \tag{17}$$

where we have neglected the part of $\frac{\partial g_{a,b}^c}{\partial x_{a,b}}$ that does not diverge in the $T \to 0$ limit.

By considering the 'dillute limit' $x \to 0$, we can use $\frac{\partial \overline{g}_{het}(x,T)}{\partial x} = \left(\frac{\partial \overline{g}_a(x_a,T)}{\partial x_a}\right)_{x_a = x_a^*}$ from

equation (15) to give the low-concentration solubility limit as

$$x \approx \exp\left(-\frac{\Delta\mathcal{G} + \Delta\mathcal{G}_{el}^{bulk}}{kT}\right), \tag{18}$$

where

$$\Delta\mathcal{G} = g_a^{0'}(0) + g_a^0(0) - g_b^0(1) \tag{19}$$

is the energetic contribution from the regular solution model and

$$\Delta\mathcal{G}_{el}^{bulk} = -\frac{E\chi^2}{1-\nu}\frac{\Omega_0}{N_0} \tag{20}$$

is the contribution coming form coherent elastic stresses.

As was shown in [2] , in the situation where the inclusion is close to a surface, the elastic contribution to the Gibbs energy density changes according to

$$g_{el}^{bulk} \rightarrow g_{el} = (1-\gamma)g_{el}^{bulk}, \tag{21}$$

where $\gamma = \frac{\mathcal{G}_{el}}{\mathcal{G}_{el}^{bulk}} - 1$ depends on the specific structure of the inclusion, but apart from that is constant.
Therefore, one can apply (21) to the solubility limit (18) in order to approximate the solubility limit in the presence of a surface as

$$x \approx \exp\left(-\frac{\Delta\mathcal{G} + (1-\gamma)\Delta\mathcal{G}_{el}^{bulk}}{kT}\right) \tag{22}$$

2.1 Equilbirium at the Electrode-Electrolyte Interface

Besides the equilbirum of inclusion and electrode, we also need to consider the equilibrium of electrode and electrolyte. The relevant condition is the Nernst equilibrium, which now takes into account the modification of the Gibbs energy density due to the coherency stresses.

We begin by remembering that for a general chemical reaction

$$\sum_i s_i M_i^{z_i} \rightarrow ne^-,$$

where M_i are the chemical symbols, s_i stochiometric coefficients, z_i the charge numbers and n the number of transferred electrons, the system will be in equilibrium if the chemical potentials of both sides will be equal, that is if

$$\sum_i s_i \mu_i = n\mu_e, \tag{23}$$

where μ_e is the Fermi energy of the electrons.
The main reaction at the electrode-electrolyte interface is given by

$$Li - Li^+ \rightarrow e^-, \tag{24}$$

which means that our system will be in equilibrium if

$$\mu_{Li} - \mu_{Li^+} \stackrel{!}{=} \mu_e. \tag{25}$$

As a next step we will have to set up a macroscopic model for the Gibbs free energy densities in order to compute the chemical potentials for each of the constituents of the reaction above.

The model we choose consists of four contributions $g_i = g_i^0 + g_i^c + g_i^{el} + g_i^{\phi_i}$, which will be explained in the following.
g_i^0 describes the density of the mixing enthalpy, which is of the form

$$g_i^0(x_i) = \alpha_i x_i (1 - x_i) \tag{26}$$

for each constituent i in our simplified model.
Together with the the configurational entropy g_i^c, which is of the form

$$g_i^c(x_i, T) = kT \left[x_i \, ln(x_i) + (1 - x_i) \, ln(1 - x_i) \right], \tag{27}$$

it forms what is known as a regular solution model.
g_i^{el} describes the elastic effects due to coherence stresses in the continuum limit. Therefore, it can be seen as the macroscopic analogon to the elastic contribution (21). However, we will assume that it only plays a role in the behavior of the aotmic lithium inside the electrode. The reason for that is that the classical radius of the electron is at least five orders of magnitude smaller than the lattice constant of the host matrix and will therefore not give rise to any elastic deformations. Furthermore, we neglect g^{el} for the ionic lithium inside the electrolyte, since we assume that it is homogenously dissolved and will therefore not form an inclusion. It was suggested by Cahn [3], that in the case of linear, isotrpic elasticity, the Gibbs energy density can be modeled as

$$g_{Li}^{el} = (1 - \gamma) \frac{E\chi^2}{1 - \nu} \frac{\Omega_0}{N_0} x_{Li}^2, \tag{28}$$

where the elastic constants E, χ and ν describe the bulk modulus, Vegard coefficient and Poisson ratio as before and we have included the factor $(1 - \gamma)$ to account for the influence of a surface on the elastic energy of an inclusion.
Finally, the term $g_i^{\phi_i}$ describes the energy density coming from an electrostatic potential, which therefore is of the form

$$g_i^{\phi_i}(x_i) = z_i e \phi_i x_i. \tag{29}$$

Since the atomic lithium is not electrically charged, it has on electrostatic contribution to its energy density. By taking the derivative of g_i with respect to the concentration x_i, we can calculate the chemical potential of each component of the reaction, which therefore is of the form

$$\mu_{Li} = \mu_{Li}^{\Theta} + kT ln \left(\frac{x_{Li}}{1 - x_{Li}} \right) + (1 - \gamma) \frac{2E\chi^2}{1 - \nu} \frac{\Omega_0}{N_0} x_{Li,0}$$

$$\mu_{Li^+} = \mu_{Li^+}^{\Theta} + kT ln \left(\frac{x_{Li^+}}{1 - x_{Li^+}} \right) + e \phi_{Li^+} \tag{30}$$

$$\mu_e = \mu_e^{\Theta} + kT ln \left(\frac{x_e}{1 - x_e} \right) - e \phi_e.$$

Here we have defined μ_i^Θ as the so-called 'standard state', and have used $x_{Li,0}$ as the lithium concentration in equilibrium. Since we want to calculate the maximum shift in the electrostatic potential due to the influence of coherent surface stresses, we will set $x_{Li,0} = 1$ from now on. By defining

$$a_i = \frac{x_i}{1 - x_i} \tag{31}$$

as the chemical activity of component i, the condition for thermodynamic equilibrium (25) reads:

$$\left(\mu_{Li}^\Theta - \mu_{Li^+}^\Theta\right) + kTln\left(\frac{a_{Li}}{a_{Li^+}}\right) + (1-\gamma)\frac{2E\chi^2}{1-\nu}\frac{\Omega_0}{N_0} - e\phi_{Li^+} = \mu_e^\Theta + kTln(a_e) - e\phi_e. \tag{32}$$

After rearranging the terms, we find the Nernst potential $\Delta\phi = \phi_e - \phi_{Li^+}$ to be

$$\Delta\phi = \Delta\phi^\Theta + \frac{kT}{e}ln\left(\frac{a_{Li^+} a_e}{a_{Li}}\right) - \frac{(1-\gamma)}{e}\frac{2E\chi^2}{1-\nu}\frac{\Omega_0}{N_0}, \tag{33}$$

where

$$\Delta\phi^\Theta = \frac{\mu_e^\Theta - \left(\mu_{Li}^\Theta - \mu_{Li^+}^\Theta\right)}{e} \tag{34}$$

is the interfacial voltage when all reactants are in their standard states.

Therefore, we see that the consideration of coherent elastic stresses near a surface can decrease the voltage difference up to $\frac{(1-\gamma)}{e}\frac{2E\chi^2}{1-\nu}\frac{\Omega_0}{N_0}$.

3 Introduction to the model system

We consider a cylindric geometry for our halfcell model, which is representative of classical pouch cells and many other battery systems. The material mix we are interested in first is Al-Li as electrode material and LiPON as electrolyte. Concretely, we consider an electrode which, when fully charged, fully consists of βAlLi, i.e. equal atomic amounts of Al and Li. The model geometry includes only these two layers and an inclusion which forms upon lithiation, see Fig. 1. We assume coherency for all interfaces, which depend on the position of the inclusion. Thus, the position of the inclusion with respect to the electrode-electrolyte interface determines the form of the thermodynamic and mechanical equilibrium conditions. If the inclusion forms in the electrode bulk, all interfaces satisfy mechanical equilibirium. Furthermore, the electrode-electrolyte interface satisfies also electrochemical equilibrium, and the electrode-inclusion interface satisfies electrochemical and phase equilbirium. If the inclusion forms at the electrode-electrolyte interface in the electrode phase, the geometry exhibits triple points. The equilibrium conditions again include mechanical equilibrium at all interfaces, and, in this case, the inclusion and the electrolyte also create an interface, resulting in electrochemical equilibrium between inclusion and electrolyte in addition to electrochemical and phase equilbirium between electrode and inclusion and electrochemical equilibrium between electrode and electrolyte.

We begin with the scenario of an inclusion in the electrode bulk. To simplify the formal approach to the charging half cycle, we take advantage of the fact that AlLi electrodes during the discharge half cycle exhibit a stable βAlLi phase down to a delithiation of 40 % [4]. This allows us to assume identical lattice structures in the bulk matrix of the electrode and the inclusion, where only the reference concentrations of Li in the matrix phase and in the

inclusion phase differ. During the charge half cycle, the delithiated βAlLi phase is lithiated up to its maximal level, where, in a bulk phase, the ratio of Al atoms and Li atoms equals 1. First we consider the case that in a delithiated region of the electrode an inclusion with Li-saturated stochiometry forms. In this case, there are two sets of equilbirium conditions, one set for the inclusion-electrode interface, and one set for the electrode-electrolyte interface. At the electrode-inclusion interface, we assume that due to the high electronic conductance in the electrode, the electric contribution to the electrochemical and phase equilbirium are negligible. For the remaining elastochemical contributions, we introduce a type of regular solution model which includes the coherency contribution introduced by Cahn [3]. We only consider the charging half cycle, and the βAlLi phase shows a drastically extended regime of stability down to a delithiation which corresponds to a stochiometry $Al_1Li_{0.6}$. This allows us to approximate the matrix and inclusion lattice as identical.

4 Numerical setup

In order to calculate the elastic energy of the electrode-electrolyte system, we calculate the elastic energy density in the system, which, in the case of linear, isotropic elasticity, is of the form

$$\hat{g}_{el} = G \left[\epsilon_{i,j} - \chi x_{Li} \right]^2 + \frac{\lambda}{2} \left[\epsilon_{k,k} - 3\chi x_{Li} \right]^2. \tag{35}$$

Here, G, λ and χ are the shear modulus, Lamé coefficient and Vegard coefficient, respectively. The main task there is to calculate the displacement field $\mathbf{u}(\mathbf{r})$, which determines the strain tensor via

$$\epsilon_{i,j} = \frac{1}{2} \left(\nabla \mathbf{u}(\mathbf{r}) + [\nabla \mathbf{u}(\mathbf{r})]^T \right)_{ij}. \tag{36}$$

$\mathbf{u}(\mathbf{r})$ itself is calculated by solving the system of linear elastic equations

$$\frac{\partial \sigma_{i,j}}{\partial x_j} = 0, \tag{37}$$

with the stress tensor

$$\sigma_{i,j} = 2G \left[\epsilon_{i,j} - \delta_{i,j} \chi x_{Li} \right] + \lambda \delta_{i,j} \left[\epsilon_{k,k} - 3\chi x_{Li} \right]. \tag{38}$$

By making use of the cylindrical symmetry of the electrode mentioned in chapter 3, we can effectively reduce the problem to a two dimensional setup by demanding that the inclusion - which we will assume to be spherical - will form around the symmetry axis of the subvolume under consideration.

Therefore, in order to solve (37), we use the open-source finite element package 'FreeFEM'. Here, we load a rectangular geometry, as shown in figure 1 and account for the different materials in the system by setting the elastic constants at a given position accornding to the present material.
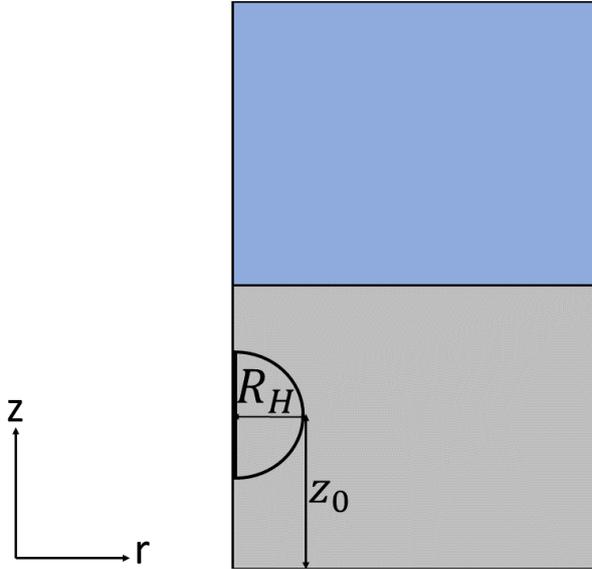
Figure 1: Simulation volume; grey: *AlLi*-phase; blue: Al_2O_3 or $LiPON$; at $z = 0$: free surface

Furthermore, in order to investigate the formation of a highly lithiated inclusion into a lithium-free region, we set the lithium concentration inside the inlcusion to 1 and 0 anywhere else.

As boundary conditions we use a rigid surface on the left boundary of the cylinder, as the rotational axis should not undergo any displacement. Furthermore, since we ensure that the cylinder is sufficiently large to approximate the volume as infinitely extended, we choose the upper and right boundary to be free surfaces. For the bottom surface we choose natural boundary conditions as well, as this represents the limit of a crack in the material appearing at the simulation boundary. However, we have to ensure that the distance of the free surface to the electrody-electrolyte interface is large enough to not have any influence on the inclusion formation near this area.

5 Discussion

As was shown in [5] and [4], there is a great influence of elastic effects on the thermodynamic behaviour of aluminum-lithium electrodes. Here it was shown in [5] that during the first charging cycle of an aluminum electrode, there appear elastic deformations that correspond to a voltage change of approximately $0.67\,V$, using a non-coherent model.

Furthermore it was shown in [4] that the $\beta AlLi$ after charging is stable up to delithiation depths of approximately 40%. However it should be noted that after the first charge-discharge cycle the electrode is expected to have a heterogenous lithium distribution throughout the system due to the formation of cracks and the existence of defects in the electrode material. Therefore, we will consider the formation of a highly lithiated, spherical inclusion inside a completely delithiated region of the $AlLi$ structure in the presence of a surface either made out of $LiPON$ or Al_2O_3. Since $\beta AlLi$ is an fcc lattice, the number of host atoms inside a unit cell is $N_0 = 4$ and the unit cell volume is given by $\Omega_0 = a_{AlLi}^3 = 255.81\,\mathring{A}^3$[6], where a_{AlLi} is the lattice parameter of $AlLi$.

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By comparing the Young's modulus, Poisson ratio and Vegard coefficient of $AlLi$, $LiPON$ and Al_2O_3 in table 1 we hypothesisze that forming an inclusion close to the interface will be energetically unfavourable to the formation inside the bulk in the case of an interface between $AlLi$ and Al_2O_3, due to the more than four times larger Young's modulus of Al_2O_3 compared to $AlLi$ or $LiPON$.

Material	$AlLi$	$LiPON$	Al_2O_3
E [GPa]	75.7	77	340
ν	0.24	0.25	≈ 0.25
χ	-0.0783	-0.0796	-0.3517

Table 1: Material parameters; Source: [7], [6], [8]; χ is approximated via $\chi_2 \approx \chi_1 \frac{E_2}{E_1}$

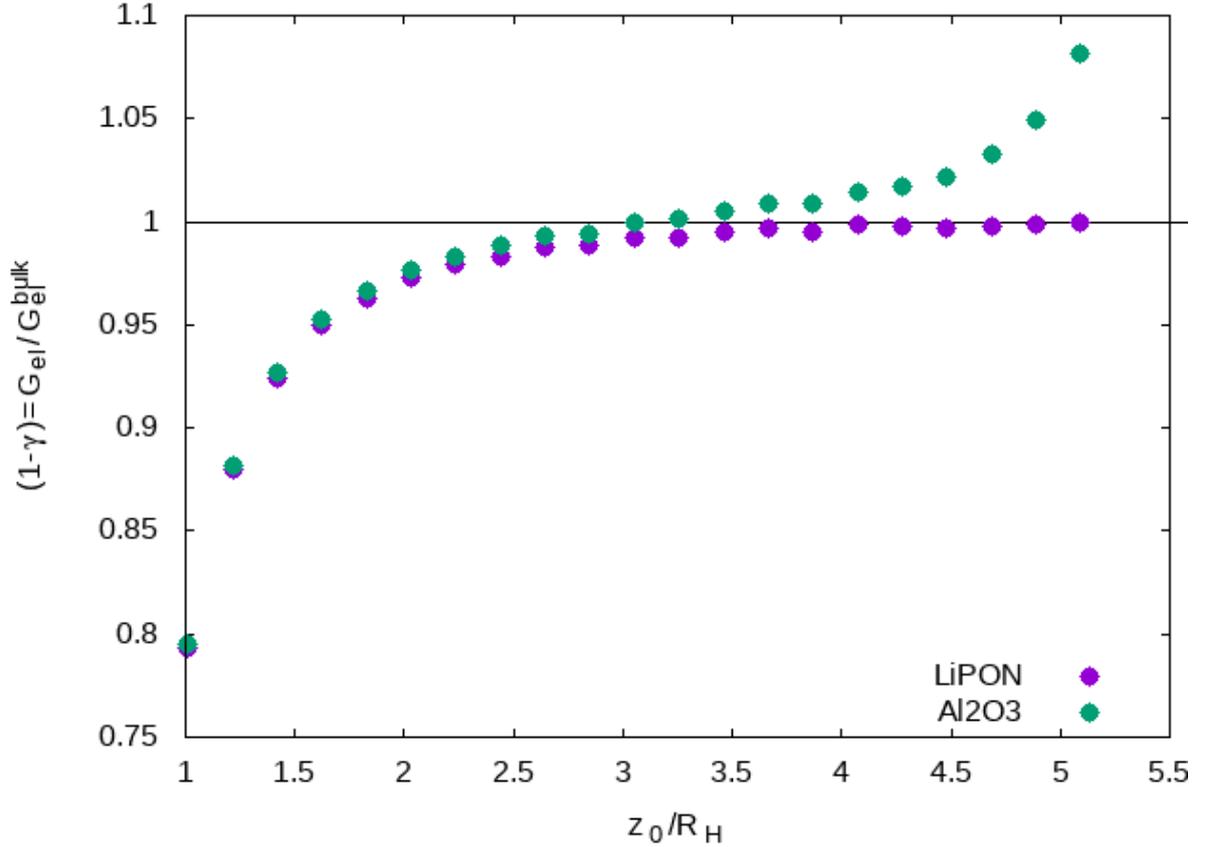This is indeed confirmed when inspecting figure 2.

Figure 2: Ratio of elastic to bulk-elastic energy

Here we can see that the formation energy of an inclusion close to Al_2O_3 is almost 1.1 times the amount of energy required for the formation of an inclusion inside the $AlLi$ bulk. On the other hand, forming an inclusion close to the $AlLi - LiPON$ interface requires almost the

same amount of energy as forming an inclusion inside the electrode bulk.

Using the results from figure 2 in order to calculate the solubility limit from equation (22), we obtain the curves depicted in figure 3 for $T = 293K$:
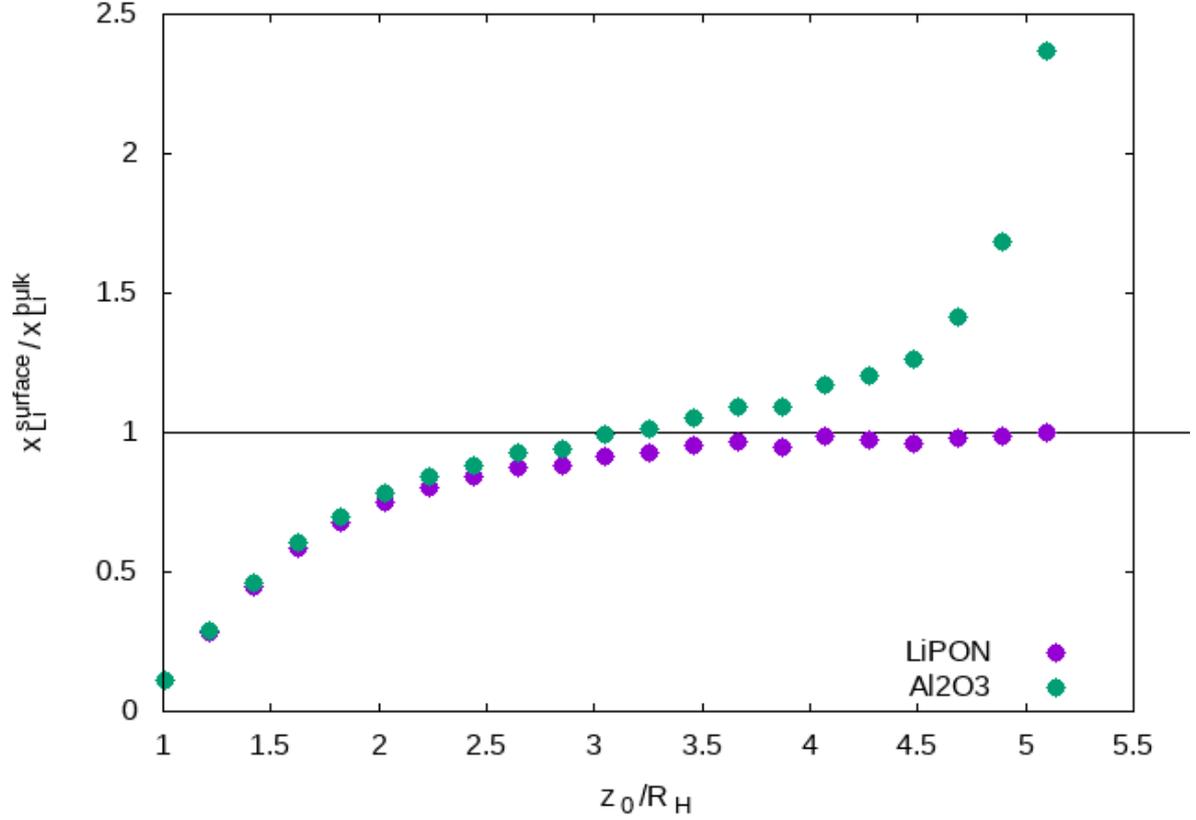

Figure 3: Solubility limit for $T = 293K$ for interface with $LiPON$ and Al_2O_3

Here we see that the solubility limit is greatly decreased if the inclusion forms close to the free surface, whereas in the case of a formation close to the $AlLi - Al_2O_3$ interface one can incorporate almost 2.5 times the amount of lithium into the electrode until the formation of a precipitate starts at room temperature.

When inserting the results from figure 2 together with the elastic constants of $AlLi$ that were used before into equation (33), we can see that in the case of the Al_2O_3 interface, the contribution due to coherent deformations can change the interface voltage even in the case of lattice stability at $x_{Li,0} = 0.6$ by an amount between $0.25\,\mathrm{V}$ and $0.35\,\mathrm{V}$, depending whether the inclusion is forming close to the free surface or the $AlLi - Al_2O_3$ interface.

All these results lead us to the conclusion that, although it was claimed in [9] that kinetic effects were dominant in the charge and discharge process of aluminum electrodes, the influence of thermodynamic effects can indeed play an important rule in the lithiation behaviour.

6 Summary

In this project we considered the influence of coherent elastic stresses on the lithiation behaviour of aluminum electrodes. In order to do so, we first introduced an analytical model for the conditions of phase coexistence inthermodynamic equilibrium when considering the effects of elastic coherent stresses that arise due to the formation of highly lithiated precipitates inside the electrode material. After this, we derived an approximate equation for the solubility of such systems in the limit of low temperatures and low concentrations. Futhermore we derived a simple model for the interface voltage between electrode and electrolyte that takes into account the influence of elastic coherent deformations as well. In both cases, we took special interest in the influence of interface boundaries on the formation of the precipitates, where we found that the solubility limit can be increased by almost a factor of 2.5 if the inclusion manifests close to an interface between $AlLi$ and Al_2O_3. Furthermore, we found that elastic effects have the potential to play a major role in determining the interface voltage required for the charging process of an aluminum electrode, which leads us to the conclusion that, despite the claim of [9] that the lithiation and delithiation process in aluminum electrodes is dominated by kinetic effects, the influence of thermodynamic processes shoudl not be discarded.

References

[1] R Spatschek, Giorgia Gobbi, Claas Hüter, Aurab Chakrabarty, Ugur Aydin, Steffen Brinckmann, and Jörg Neugebauer. Scale bridging description of coherent phase equilibria in the presence of surfaces and interfaces. *Physical Review B*, 94(13):134106, 2016.

[2] Robert W Balluffi. *Introduction to elasticity theory for crystal defects*. World Scientific Publishing Company, 2016.

[3] John W Cahn. Coherent fluctuations and nucleation in isotropic solids. *Acta Metallurgica*, 10(10):907–913, 1962.

[4] Y Hamon, T Brousse, F Jousse, P Topart, P Buvat, and DM Schleich. Aluminum negative electrode in lithium ion batteries. *Journal of Power Sources*, 97:185–187, 2001.

[5] Tetsu Ichitsubo, Shunsuke Yagi, Takayuki Doi, Shunsuke Yukitani, Kosuke Hirai, and Eiichiro Matsubara. Influence of mechanical strain on the electrochemical lithiation of aluminum-based electrode materials. *Journal of The Electrochemical Society*, 159(1):A14–A17, 2011.

[6] Rafael Sarmiento-Pérez, Tiago FT Cerqueira, Irais Valencia-Jaime, Maximilian Amsler, Stefan Goedecker, Aldo H Romero, Silvana Botti, and Miguel AL Marques. Novel phases of lithium-aluminum binaries from first-principles structural search. *The Journal of chemical physics*, 142(2):024710, 2015.

[7] https://www.azom.com/properties.aspx?ArticleID=52.

[8] Zhi Deng, Zhenbin Wang, Iek-Heng Chu, Jian Luo, and Shyue Ping Ong. Elastic properties of alkali superionic conductor electrolytes from first principles calculations. *Journal of The Electrochemical Society*, 163(2):A67–A74, 2016.

[9] Marina S Leite, Dmitry Ruzmetov, Zhipeng Li, Leonid A Bendersky, Norman C Bartelt, Andrei Kolmakov, and A Alec Talin. Insights into capacity loss mechanisms of all-solid-state li-ion batteries with al anodes. *Journal of Materials Chemistry A*, 2(48):20552–20559, 2014.