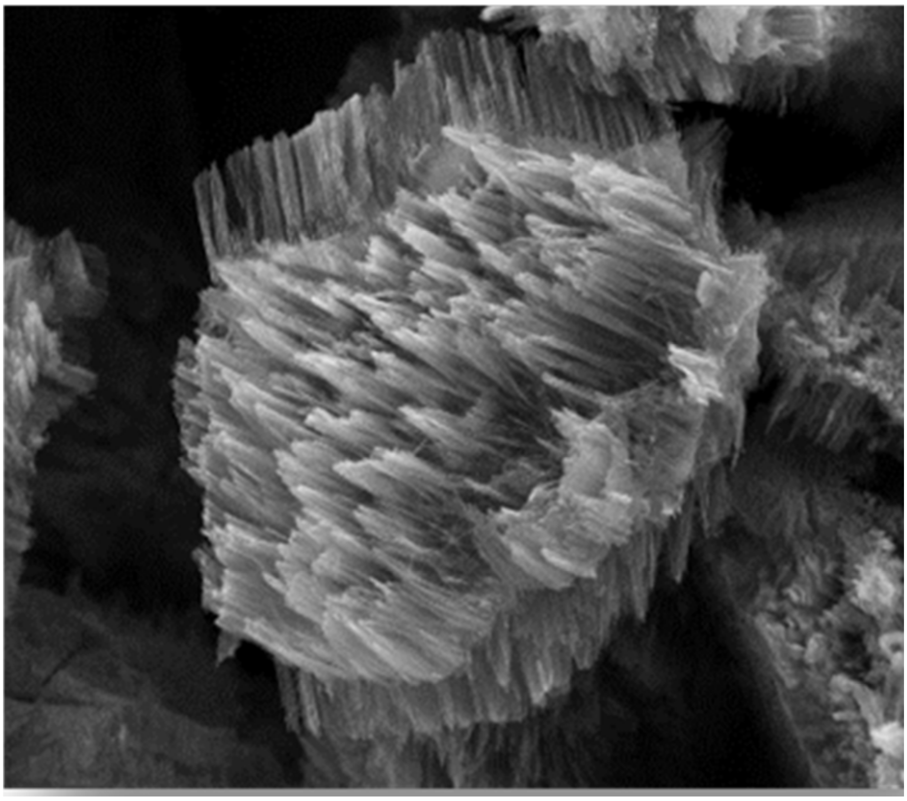
EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling



Stress Distributions in Silicon Electrodes During Lithiation

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1. Introduction

Lithium-ion batteries are used more and more in portable power applications, from laptops to mobile phones and, more recently, in electric vehicles. They are ideal for these applications due to their impressive energy density, power density and capacity. We show a schematic illustrating how lithium-ion batteries produce a current in figure 1. Lithium ions (Li^+) are stored in the anode at a high chemical potential. When a circuit is connected, the Li^+ ions are released into the electrolyte and move to the cathode where the Li^+ is stored at a lower chemical potential. Electrons are released when the lithium ionises into Li^+ and these flow around the connected circuit and induce a current. When the battery is being charged, an external voltage is applied to draw Li^+ ions from the cathode back into the anode.

Lithium-ion batteries are used in portable power applications such as mobile phones, laptops and electric vehicles.

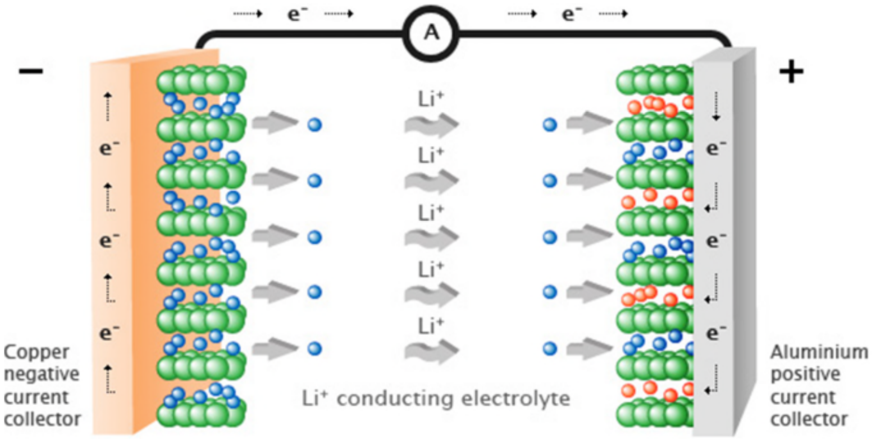

Figure 1: Schematic showing how a battery induces a current during discharge. In the anode the Li atoms split to Li^+ ions and electrons. The electrons flow round the circuit while the Li^+ ions flow through the electrolyte and they neutralise each other again to form Li atoms in the cathode.

The materials that are used for the cathode and anode materials significantly affect the performance of the battery. Currently, graphite is the most common anode material in production; however, the theoretical maximum energy storage (capacity) is believed to have been reached. As a result, some companies (including Nexeon) are exploring using silicon as a potential anode material due to its increased capacity for Li^+. When fully lithiated, silicon can accommodate 4.4 Li^+ ions per silicon atom whereas graphite can only accommodate 1 Li^+ ion per 6 carbon atom (0.167 Li^+ ions per carbon atom). Therefore, the same volume or mass of silicon can provide power for much longer than graphite before needing recharging, making it more suitable for portable power sources.

However, when silicon is fully lithiated the anode's volume swells by 300-400%. This makes the use of these batteries as portable power sources more difficult, causes large stresses in the anode, and can lead to pulverisation and fractures in the anode. Many techniques have been tried to overcome the expansion, mainly using nano-scale features to avoid large strains and exploiting the porosity to minimise the overall expansion of the anode. These techniques include nanowires, using nanoscale particles known as secondary particles, and using shells of Li^+-conducting materials that have a lower expansion, for example graphite, to cover the silicon to suppress the expansion. It is this expansion of an anode made up of microscale secondary particles that we attempt to mathematically model.

Silicon anodes have the best potential for high capacity batteries; however, large expansion after charging (300-400%) causes portability issues and damage to the anode.

In section 2, we introduce the project aims and define some key terms used and in section 3 we outline the mathematical problem and the techniques that we use to solve it. In section 4 we present some results of some example designs we have used to test the model, in section 5 we discuss the use of the model and the conclusions we can draw along with how it can be expanded, and finally, in section 6 we look at the potential impact of the results of the project for Nexeon and the lithium-ion battery industry

A 'secondary particle' is a microscale particle of anode material. These are agglomerated together to form the full anode.

2. Project Aims

In this project we model the expansion of a lithium-ion battery anode after lithiation, investigating the use of both silicon and graphite as the anode materials. We focus attention on the case where the anode is made from microscale secondary particles and we investigate the effect on the whole anode when the anode materials and the geometry of the secondary particle are changed. The overall expansion of the macroscale anode is the main measure of the 'success' of the secondary particle design. If the design produces low macroscale expansion, portability of the battery is easier and thus the design is suitable for lithium-ion battery applications.

Glossary of terms

- Stress: The internal forces which neighbouring internal particles exert on each other. Exerting a force on a body produces stress.
- Displacement: The distance in each axis that each particle has moved from its original 'reference position'. This is usually dependent on the original position of the particle and so a displacement field is present which relies on the Cartesian spatial variables x, y, z.
- Displacement Gradient: Used to represent the change in shape of an infinitesimally small volume within an object.
- Stiffness: The extent to which an object resists deformation in response to a given force or stress.
- Periodicity: A property such as geometry, displacement or stress is periodic if it repeats in each of the three Cartesian coordinates over a 'period'. The property must therefore be equal at either end of the period.

We model the expansion to be proportional to the concentration, c, of Li^+ in the anode and the material's elastic response to resist this expansion to be proportional to the stiffness of the material.

3. Mathematical Model

We now introduce the mathematical model we are going to use to describe the expansion of the anode after lithiation. We assume that the anode is made up of a periodic lattice of secondary particles as shown in figure 2, where the size of the anode is L and the size of the secondary particles is εL where $\varepsilon \ll 1$. The stress in the anode material $\boldsymbol{\sigma}$ is caused by the expansion due to the lithiation of the anode but is counteracted by the elasticity of the anode material – known as the elastic response. The expansion is proportional to the concentration of Li^+ in the anode and the elastic response is proportional to the displacement gradient (see glossary). Therefore the stress in the anode is given as:

$$\boldsymbol{\sigma} = \mathbb{C} : \nabla \boldsymbol{u} - \boldsymbol{\Psi} c, \qquad (1)$$

where $\mathbb{C}$ is the stiffness of the anode material which is derived from experiment, $\nabla \boldsymbol{u}$ is the displacement gradient and the colon denotes an alternative type of multiplication. $\boldsymbol{\Psi}$ is the expansion coefficient and c is the relative Li^+ concentration, which ranges from 0 (the anode has no Li^+) to 1 (a fully saturated anode). The stiffness $\mathbb{C}$ and the expansion coefficient $\boldsymbol{\Psi}$ are the constants of proportionality for the elastic response and the expansion due to lithiation, respectively. To find the expanded volume of the anode, we solve for the displacement $\boldsymbol{u}$ when the anode is in mechanical equilibrium ($\boldsymbol{\nabla} \cdot \boldsymbol{u} = 0$).

This problem is difficult to solve since it only holds in the anode (the electrolyte between the secondary particles does not get lithiated) and the geometry of the anode without the electrolyte is very complicated, as shown in figure 2. We exploit the periodicity in the lattice of secondary particles to simplify this problem using a technique called homogenisation. We assume that the displacement $\boldsymbol{u}$ varies periodically on the microscale but not periodically over the macroscale and so we can separate these two length scales. Therefore, we can solve a simpler problem to find the microscale displacement and then solve another simpler problem to find the macroscale displacement.

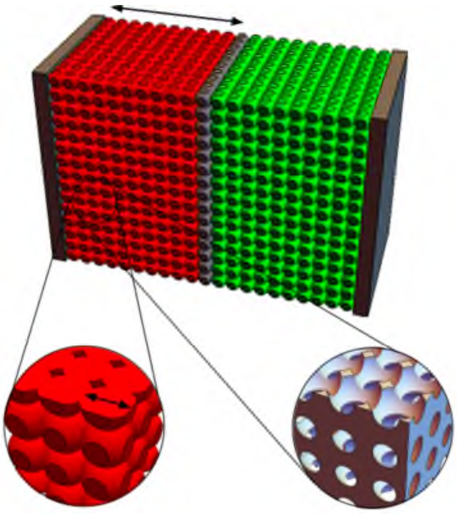

Figure 2: Geometry of full battery made up of secondary particles. Cuboids on the left and right represent current collectors, green units represent cathode secondary particles, grey units represent the separator and red units represent secondary particles of the anode. Close up circles show the fine structure of the secondary particles (left) and the surrounding electrolyte (right).

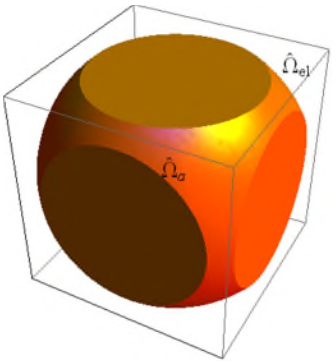

Figure 3: Geometry of unit cell made up of the anode material (red domain $\hat{\Omega}_a$) and the surrounding electrolyte (clear domain $\hat{\Omega}_{el}$). The geometry we use for the secondary particle is a truncated sphere.

We solve a problem on the repeating unit cell (shown in figure 3) to find effective parameters for the full anode.

The microscale problem is solved over the geometry that is repeated periodically over the anode; we call this geometry the unit as shown in figure 3. We solve the microscale problem over the unit cell to take the geometry and volume of both the anode and the electrolyte in the unit cell into account. We use the solutions to the unit cell problem to calculate an 'effective' stiffness and expansion coefficient of the whole anode, assuming it was made from one material, rather than a combination of anode material and electrolyte. We write the macroscale problem as:

$$\boldsymbol{\sigma}_{\text{eff}} = \mathbb{C}_{\text{eff}} : \nabla \boldsymbol{u} - \boldsymbol{\Psi}_{\text{eff}} c, \tag{2}$$

where $\boldsymbol{\sigma}_{\text{eff}}, \mathbb{C}_{\text{eff}}$ and $\boldsymbol{\Psi}_{\text{eff}}$ are the effective stress, the effective stiffness, and the effective expansion coefficients, respectively, that are calculated by solving the unit cell problem. This is essentially identical to equation (1) but now this can be solved on a simple cuboid instead of taking into account each microscale secondary particle.

Uniform Expansion

By considering a uniform concentration of Li^+ in an unconstrained secondary particle, we have shown that the effective expansion coefficient $\boldsymbol{\Psi}_{\text{eff}}$ is related to the effective stiffness $\mathbb{C}_{\text{eff}}$ by:

$$\boldsymbol{\Psi}_{\text{eff}} = \mathbb{C}_{\text{eff}} : \mathbf{I}, \tag{3}$$

It can be shown analytically that, for a constant Li^+ in the secondary particle, the full anode will expansion uniformly, independent of the geometry.

where $\mathbf{I}$ is the identity matrix. This means that, if there are no constraints on the anode expanding and the Li^+ concentration is uniform, then each secondary particle expands by a proportion of the original size and the whole anode will expand by the same proportion, independent of the geometry of the secondary particle. While this is a fairly trivial result, it helps to validate the model we have presented and tells us that, to control the expansion of the anode through using secondary particles, a non-constant Li^+ concentration needs to be used. This could be achieved by changing the concentration in time by, for example, diffusion or changing the concentration in space by using multiple materials in the secondary particle.

4. Results

We now discuss the measures of how ‘successful’ the secondary particle design is. We design the secondary particles with the objective to minimise the volume of the fully expanded anode. If we assume isotropic expansion (equal expansion in all directions) and that the full anode is in equilibrium ($\boldsymbol{\nabla} \cdot \boldsymbol{\sigma}_{\text{eff}} = 0$), we can calculate the fully expanded volume V, relative to the original volume V_0. Using the effective stress equation (2) and relating the displacement in each direction to the volume change, this can be thought of as:

$$\text{Relative expanded volume} \coloneqq \frac{V}{V_0} = \left(1 + \frac{\boldsymbol{\Psi}_{\text{eff}}}{\mathbb{C}_{\text{eff}}}\right)^3, \qquad (4)$$

where we have assumed the anode is saturated with Li$^+$ $(c = 1)$.

However, when we consider battery design, we must take into account the capacity of the resulting battery. For example, if we only wanted to minimise expansion, using a material that did not accommodate any Li$^+$ and did not expand at all would be ‘optimal’; however, this is obviously not a good choice for the anode material. Therefore, we take the amount of Li$^+$ a material can accommodate into account by using another measure given by:

$$\begin{matrix}\text{Relative expanded} \\ \text{volume per capacity}\end{matrix} \coloneqq \frac{V}{QV_0} = \left(\frac{V}{V_0}\right)\left(\frac{1}{\phi_{\text{Si}}\left(1 - \frac{c_{\text{max,C}}}{c_{\text{max,Si}}}\right) + \frac{c_{\text{max,C}}}{c_{\text{max,Si}}}}\right), \qquad (5)$$

where Q denotes the capacity of the anode, ϕ_{Si} denotes the fraction of the secondary particle that is made up of silicon (known as the volume fraction) and $\frac{c_{\text{max,C}}}{c_{\text{max,Si}}}$ is the ratio of the maximum concentration of Li$^+$ each material can accommodate which can be found through experiment. This calculates the expanded volume an anode would need to be to have the same capacity of a silicon secondary particle of unlithiated unit size (i.e. $V_0 = 1$). We only compare silicon and graphite and so these measures are written using only C and Si but they can be used for other materials as well.

Using these measures, we can see that an ideal anode design should have both V/V_0 and V/QV_0 as small as possible.

Silicon vs Graphite

First we compare unimaterial secondary particles solely made of silicon or graphite. We solve the unit cell problem for both a silicon secondary particle and a graphite secondary particle to find the effective parameters $\mathbb{C}_{\text{eff}}$ and $\boldsymbol{\Psi}_{\text{eff}}$ and therefore the success measures V/V_0 and V/QV_0. The results are given in table 1.

It can be seen that the expanded volumes, V/V_0, agree with experimental results: 350% and 10% volume increase for both silicon and graphite, respectively. This suggests that silicon is the worse material. However, the expanded volume per capacity V/QV_0 is much greater for a graphite secondary particle than for a silicon one. This is due to the larger starting volume of graphite that would be needed to match the capacity of the silicon secondary particle. Therefore, using this more appropriate measure, silicon is the better material.

We reproduce the experimental expanded volumes of silicon and graphite. If capacity is taken into account, V/QV_0 suggests that silicon is a better anode material.

Measure	Silicon	Graphite
V/V_0	4.5026	1.0999
V/QV_0	4.5026	20.910

Table 1: Mathematical results obtained using unimaterial secondary particles made solely of silicon or graphite.

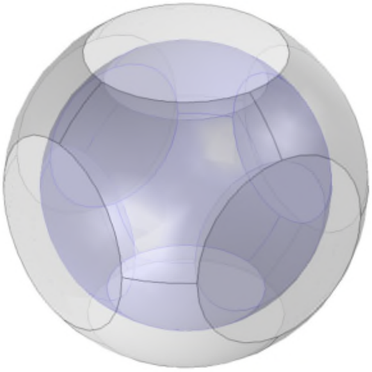

Figure 4: Geometry used in the graphite shell numerical experiment. The silicon core (blue) is a truncated sphere surrounded by a truncated sphere of graphite as a shell (grey).

Graphite Shell

We now consider using both graphite and silicon in the secondary particle. We investigate a geometry using a graphite shell around a silicon core as shown in figure 4. Both the silicon core and the carbon shell are truncated spheres as in the unimaterial case. We investigate the effect of varying the size of the silicon core (while keeping the full secondary particle size constant) on the measures V/V_0 and V/QV_0.

In figure 5 we plot V/V_0 and V/QV_0 against ϕ_{Si}. We see that V/V_0 linearly increases with ϕ_{Si} from the value for pure graphite (1.0999) to that for pure silicon (4.5026), given by the orange and blue lines, respectively. V/QV_0 drops rapidly as the volume of silicon used in the anode increases from 0 to 0.3 but increasing the volume fraction of silicon more than this has negligible effect. This shows that adding a small silicon core to graphite secondary particles can reduce the total expanded volume per capacity of a graphite anode.

We also compare these results to those obtained from the model currently used by Nexeon. This model assumes that the two materials are incompressible and so expand independently from one another, and predicts the expanded volume to be:

$$V/V_0 = 4.5026\phi_{\text{Si}} + 1.0999\phi_{\text{C}}. \tag{6}$$

Therefore this incompressible model also predicts a linear relationship between V/V_0 and ϕ_{Si}, as seen in figure 5 (left). This shows the incompressible model is sufficient to describe this graphite shell model. This is because the graphite has a lower stiffness than silicon (silicon is stronger than graphite) and so the graphite cannot actually constrain the expanding silicon very much. The materials therefore expand independent of one another.

The results we obtain for varying silicon core size match that of the incompressible model assuming independent expansion. This would not occur with a stronger shell material.

5. Conclusions and Further Work

We have developed a solid mechanics-based model to describe the macroscale expansion and stress of a lithium-ion battery anode for a given microscale structure of a secondary particle. The following conclusions can be drawn for the results here:

- If the Li^+ concentration is approximately uniform throughout the secondary particle, the whole anode will expand uniformly by the same amount as the secondary particle, independent of the geometry. This suggests that using porosity of anodes to control expansion will not be as effective as trying to control the concentration of Li^+.
- The model is able to predict the experimentally measured values of the expanded volumes of anodes made of solely silicon and solely graphite, which helps to validate the model.

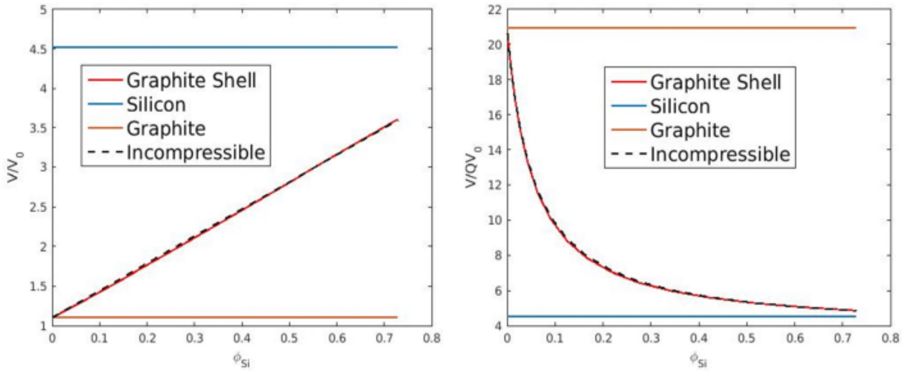

Figure 5: Results from investigating the effect on the expanded volume and the expanded volume per capacity of varying the size of the silicon core in a silicon-core, graphite shell geometry. On both plots, the values of V/V_0 and V/QV_0 for a secondary particle of pure graphite and pure silicon are provided for comparison as well as the results of using the incompressible model currently used by Nexeon.

- When capacity is taken into account, the expanded volume of a silicon anode that is required to hold a certain amount of Li^+ is much smaller than that of graphite due to the much lower capacity of graphite.
- For the graphite shell design, the expanded volume has a linear relationship with ϕ_{Si}, whereas the volume per capacity shows that even adding a small silicon core can greatly reduce the expanded volume for a given capacity.
- The results match the incompressible model used by Nexeon currently which assumes independent expansion of the two materials. This is due to graphite being much weaker than silicon and thus is unable to suppress the large expansion very well.
- For stronger 'shell' materials, this would not be the case and the expanded volume per capacity would be reduced compared to solely silicon secondary particle.

There are multiple extensions to the model presented here and further areas which could be explored. We only concentrate on reducing expansion here, whereas another concern of materials companies is the stresses inside the anode. Therefore, designing secondary particles to control the stresses should be investigated. Incorporating diffusion of the Li^+ ions through the secondary particles and the anode can cause the non-uniform Li^+ concentration that is required to control the expansion and so this physics should be incorporated into the model. Lastly, there are other mechanical phenomena that the anode materials may exhibit which should be incorporated into the model, for example nonlinear elasticity and plasticity.

According to the measures in the report, a solely silicon secondary particle gives the best expansion per capacity; however, adding a small core of silicon to a graphite secondary particle can greatly reduce the expanded volume without sacrificing the capacity.

6. Potential Impact

The work produced in this project provides Nexeon with a better understanding of the techniques and tactics they use to design the microstructures of the anodes they produce. Our model has the potential to save Nexeon money and time by producing theoretical predictions for new designs.

Bill Macklin (Nexeon) commented:

"*Through his insightful modelling work Ian has added another important dimension to the existing tools at Nexeon for designing better battery materials to meet the challenges of the massive Li-ion battery market. We look forward to now building on this output in the forthcoming exciting research project with Ian and his academic supervisors at the CDT.*"