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# A parameter study of intercalation of lithium into storage particles in a lithium-ion battery

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ABSTRACT

The effect of stress on storage particles within a lithium ion battery, while acknowledged, is not fully understood. In this study we identify three non-dimensional parameters which govern the stress response within a spherical storage particle, and we carry out numerical simulations to characterize the stresses that are developed. The non-dimensional parameters are developed using system properties such as the diffusion coefficient, particle radius, lithium partial molar volume and Young's modulus. Stress maps are generated for various values of these parameters for fixed rates of insertion, with boundary conditions applied to particles similar to those found in a battery. Stress and lithium concentration profiles for various values of these parameters show that the coupling between stress and concentration is magnified depending on the values of the parameters. The resulting maps can be used for different materials, depending on the value of the dimensionless parameters. Finally, the value of maximum stress generated is calculated for extraction of lithium from the particle and compared with those generated during insertion.

## 1. Introduction

As battery technologies are being applied to large scale portable devices e.g. automobiles, it is being realized that the ageing and subsequent failure of the battery are not very well understood. The US government has specified a list of requirements [1] for use in electric vehicles, one of which is an extended lifetime of 10–15 years. Ageing manifests primarily as decrease in capacity or capacity fade, power fade, increase in impedance and an overall decrease in performance [2–4].

In Fig. 1 we see a schematic of a lithium ion battery. There are two different electrodes, the anode and the cathode, which are each connected to a metal plate called the current collector. A dividing polymeric segment known as the separator lies in between the two electrodes. Within the electrodes themselves there are storage particles. For the cathode, these consist of layered materials or oxides, such as lithium manganate and lithium cobalt oxide. For the cathode the most conventional material in use is graphite, or some form of carbon. The storage particles are mixed along with a polymeric binder, e.g. PVDF, which is added to give the structure integrity, along with carbon particles which are added in order to boost the electronic conductivity. Finally the entire electrode and separator is filled with the electrolyte. This normally consists of a lithium-based ionic salt, e.g. $LiPF_6$, dissolved in an organic solvent.

During the discharge process, i.e. extraction of electrical energy from the battery, lithium stored in the anode is oxidized to its ionic form and moves through the electrolyte to the cathode. The electrons flow through the external circuit as they cannot pass through the electrolyte in the separator. The electrons flow into the storage particle in the cathode through the current collector. The lithium ions recombine with the electrons and remain in the storage particle in the cathode. During the charging process the reverse occurs, with lithium leaving storage particles in the cathode and moving into storage particles in the anode.

The process of removing or inserting lithium ions into the storage particles is known as intercalation. This can be formally defined as the insertion of a guest species into normally unoccupied interstitial sites in the crystal structure of an existing stable host material [2]. Though the chemical composition of the host phase initially present can be substantially modified, the basic crystal structure is preserved. The addition of interstitial species causes a change in volume: this leads to strain, and, when it is heterogeneous, stress in the system.

This shrinking and swelling of storage particles can lead to comminution of the particles. Depending on the material being used as

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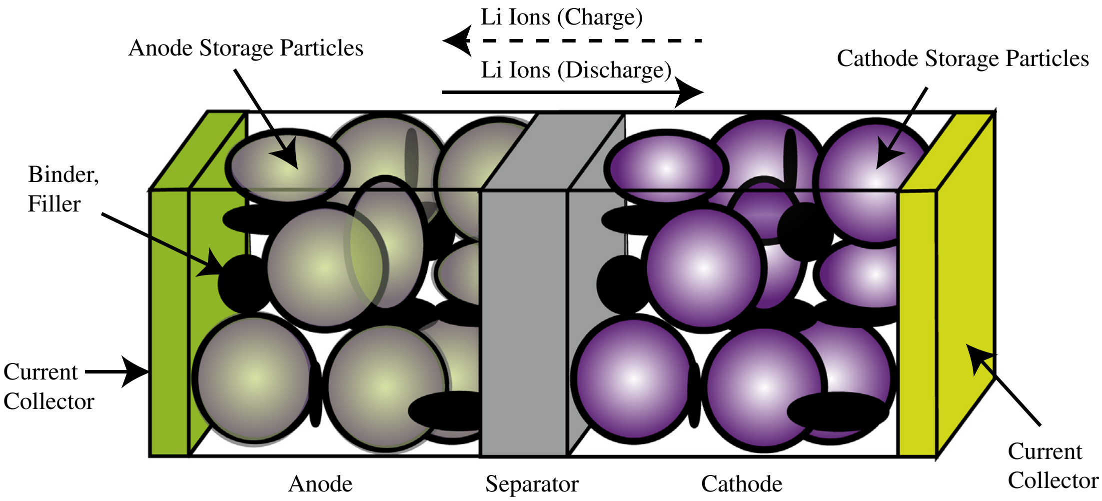

**Fig. 1.** A schematic of the structure of the lithium ion battery. The main components are the current collectors, the electrodes, the anode and cathode and the separator. The electrodes are made up of active storage particles, binder and filler. Electrolyte fills the pores of the structure, including both electrodes and the separator. The particles in an actual battery are not so regular in shape, but for the purposes of our simulation they are spherical. Lithium ions flow through the separator from the anode to the cathode during discharge and vice versa during the charging process.

much as 100% of the lithium can be extracted, which leads to significant shrinkage [5]. In $LiMn_2O_4$ it is observed that a depletion of around 60% of the original capacity leads to a volume reduction of 6.5% [6]. During charging, lithium in the cathode intercalates initially from the surface of the storage particle, leading to a high tensile hoop stress there as the outer layer shrinks. This can lead to comminution of the particle during charging [3], which is aggravated over repeated cycling of the battery. Graphite, an anode material, is observed to show an increase in volume by 8% when the number of lithium atoms per C ring is increased from 0 to 0.6 [6]. Of further concern are newer materials such as Si which can swell by almost 300% [4,7,8]. Such materials will therefore show significant stress and strain generation during cycling of the battery, and will hamper their use on a large scale.

Porous electrode theory [9] has been extensively used to represent the complex microstructure of the battery as a 1-d approximation [6,8,10–14]. This has lead to ‘pseudo-2D’ models, in which a single particle is coupled to a battery simulator based on porous electrode theory [15,16] and models have now been refined to include phase transformations as well. Garcia et al. [17,18] studied stresses within the electrode using a 2-D model, in which the entire electrochemistry of the battery was modeled including storage particles, binder and electrolyte pores. However, these results are highly dependent on the material data that is observed from experiments.

Single particle models have been used to examine what occurs within the particle in much more detail with stress and diffusion coupled. Christensen and Newman [6] developed a multi-component diffusion model for estimating the stress generated in $Li_xMn_2O_4$, where they included the volume change during phase change. The pressure term was used to account for the stress generated within the particle. Sastry and workers [19] developed a model based on a thermal analogy for stress, and also took into account the effect of different shapes of the particle as well as phase changes [20]. Verbrugge and Cheng [21,22] developed analytical models for stress within the particle for calculating the diffusion induced stresses (DIS) based on the concentration within the particle, i.e. the stress is coupled to the concentration but not vice versa. Bohn [23] developed a simulation for the diffusion within the particle based on a model for the Li chemical potential encompassing excess Gibbs free energy. As a result they are able to simulate the effect of phase change and staging in the storage particles.

Previous work has shown that the storage particles within the battery electrodes develop cracks over time and eventually comminute [24–27]. There have been several attempts at applying fracture mechanics to these problems in order to predict conditions conducive to cracking [28–32] and criteria suggested to avoid it [33–36].

A common theme running through all of these studies is that they are material specific. The complications which arise while taking all the material parameters and their concentration dependence into account can sometimes obscure the result. Moreover, no property maps are developed which are generic, i.e. that can be used across a variety of materials. A map for the stress as a function of the discharge rate and particle radius has been provided for lithium manganate and graphite in [23], while fracture maps have been developed for lithium manganate [33], lithium iron phosphate [36] and lithium cobalt oxide [30].

In this paper we aim to develop such property maps in order to identify the parameters which determine the stress response within storage particles for a variety of materials. We first develop a model for diffusion based on the work of Bohn [23]. The equations are then non-dimensionalized and three dimensionless parameters of influence are identified. Stress maps for insertion of lithium into the particle are then plotted, and the results are analyzed and explained. Finally, a comparison of results is made with those from extraction studies.

## 2. Methodology

In this section the model for the coupled diffusion-stress model is modified and non-dimensionalized. We consider the particle to be spherical in shape. Although in an actual electrode the particles do not have a regular shape, it is prudent to consider a regular shape initially for ease of calculations. The resulting analysis will also be clearer and help in our understanding of the coupling between the stress and concentration profiles.

### 2.1. Theory and equations

Bohn [23] developed an equation for chemical potential of lithium per mole when it is intercalating a storage particle. The following assumptions are used to arrive at Eq. (1).

(i). The intercalation solution is assumed to be ideal.