Modeling mechanical degradation in lithium ion batteries during cycling: Solid electrolyte interphase fracture

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HIGHLIGHTS

- A degradation model based on the fracture and reparation of the SEI is presented.
- Active material and SEI fracture are treated as different aging mechanisms.
- The model is validated against cycle life tests from commercial 18650 cells.
- The model reproduces the influence of the DOD and SOC_{mean} on the capacity fade.

ARTICLE INFO

ABSTRACT

During cycling, mechanical stresses can occur in the composite electrode, inside the active material, but also in the solid electrolyte interphase layer. A mechanical model is proposed based on a system made of a spherical graphite particle surrounded by the solid electrolyte interphase layer. During lithium intercalation or de-intercalation, stresses in the graphite are produced, governed by the diffusion induced stress phenomena and in the solid electrolyte interphase, driven by the graphite expansion. The stresses in both materials were simulated and a sensitivity analysis was performed to clarify the influence of principal parameters on both processes. Finally, assuming that the solid electrolyte interphase is the weakest material and therefore more prone to fracture than graphite, the experimental capacity fade during cycling was modeled based on its break and repair effect rather than on the fracture of the active material. The mechanical model of the solid electrolyte interphase was implemented in a single particle lithium ion battery model in order to reproduce capacity fade during battery lifetime. The model results were compared against cycle life aging experimental data, reproducing accurately the influence of the depth of discharge as well as the average state of charge on the capacity fade.

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1. Introduction

The increase of research and development of new materials and manufacturing processes in Li-ion batteries, due to the rapid increase of the electric vehicle market, have improved significantly their performance in terms of energy and lifetime. Many works dealing with the aging of lithium ion batteries have been published

constantly, nevertheless many questions are still open nowadays. When it comes to aging due to calendaric conditions, the scientific community has agreed that side reactions occurring between the electrolyte and the electrodes [1–3] are responsible for the degradation of the battery, which is accelerated at high temperature and high state of charges (SOC) [4].

However, addressing cycle aging is significantly more challenging since the side reactions interact with volume changes and temperature gradients in the cell. The interaction of such phenomena is not completely understood nowadays. In addition, the influence of stress factors such as C-rate, depth of discharge (DOD) and average state of charge (SOC_{mean}) is not fully determined.

It is generally accepted that the mechanical degradation is a key

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factor to understand the cyclic aging of lithium ion batteries. To date, cycle aging has been addressed based on the Diffusion Induced Stress (DIS) principle. In 2006 Christensen [5,6] presented the DIS formalism as driving force for particle fracture in carbon and LiMn$_2$O$_4$ particles. He reported that the maximum stress increases with the C-rate and particle size. Later on, the same author [7] and Renganathan et al. [8], investigated stress generation in porous electrodes. Many of the published literature deal with the improvement of the accuracy of the stresses investigating the influence of the particle shape [9], phase changes [10] or variable Young modulus [11] on the observed stresses, among others.

But recently, several investigations [12,13] have been carried out where the capacity fade during cycling was reproduced using a phenomenological model based on the DIS phenomena and a fatigue approach. The model re-creates the fracture of the graphite particles and subsequent reduction of the electrolyte in the newly exposed surfaces neglecting the solid electrolyte interphase (SEI) fracture. However, a recently published paper [14] reveals that the fracture of the particles does not occur unless very severe conditions are applied, such as very low temperatures (down to −10 °C). Hence, the possibility that exclusively SEI fracture occurs must be investigated. The fracture of the SEI can lead to the reduction of the electrolyte (that penetrates through the cracks) regenerating the SEI and henceforth increasing its thickness. This approach seems to be reasonable since the SEI is a non-homogeneous porous material [15–17] easier to fracture than the graphite. The mechanical behavior of the SEI has not been studied numerically so far to the author's knowledge although the scientific community is aware of its importance in the cycle life stability. Purewal et al. [13] mentioned that the effect of the SEI was implicitly explored in their model resulting in a small alteration of the mechanical parameters of the graphite material. However, despite active material stress and SEI stress apparently being equivalent phenomena, their investigation must be carried out separately because they lead to very diverse effects.

This paper presents a novel approach to explain and model the capacity fade behavior during battery cycling and which is able to clarify the influence of the stress factors in the capacity fade (C-rate, DOD and SOC$_{mean}$). Based on the reasons given previously, in our approach the active material damage due to DIS (Fig. 1a)) is believed to have a minor effect on degradation of the cell, leaving the SEI damage (Fig. 1b)) as the main aging mechanism contributing to the capacity fade.

The presented model was validated with experimental data obtained from extensive accelerated aging tests performed on Li-ion Sanyo high energy 18650 cells of 2.05 Ah and presented in Ref. [4]. The model was able to reproduce the DOD influence and the SOC$_{mean}$ influence on the capacity fade and thus presents an explanation for such behavior.

2. Experimental

In our previous work [4], a large collection of cycle aging data was presented for a graphite/NMC HE 18650 Sanyo cell. The cycle aging was thoroughly analyzed stressing the SOC$_{mean}$ and DOD influence on the capacity fade. All the tests were carried out at 1 C symmetric charge discharge cycles and 35 °C (cell temperature). The cycling was always performed at constant current conditions and the DOD was defined by the Ah throughput in respect to the nominal capacity. On the one hand, the cycle depth influence on the capacity was studied performing cycle tests at 50% SOC$_{mean}$. On the other hand, the SOC$_{mean}$ influence was investigated performing the cycle tests at 10% DOD and 20% DOD. The capacity of the cell was controlled performing standard charging (constant current followed by a constant voltage) followed by a 1 C discharge every 3

weeks. A summary of the investigated tests is shown in Table 1.

3. Modeling

3.1. Mechanical model: SEI and active material system

The SEI layer is a porous multicomponent material produced as the result of the irreversible decomposition of the electrolyte with carbon materials. Its exact composition is not completely elucidated. However, the non-homogeneous nature of the layer is accepted [18]. SEI is presented as a several Å to tens or hundreds of Å [15] thick layer surrounding the active material particle that is subjected to the volume change during the de-intercalation and intercalation of the lithium ions. Due to continuous expansion and compression of the material, the SEI layer could be damaged affecting the cycle life considerably.

A similar mathematical concept was presented by Hao et al. [19] where core−shell nanostructures stresses were investigated with the aim of enhancing the electronic conductivity of the electrode materials. Fig. 1c) shows the proposed model geometry composed of a spherical active material particle surrounded by the SEI shell.

When the dimension of the system under study goes below tens of nanometers, surface stresses and energies acquire a great importance on the mechanical properties of the materials. The influence of the surface stresses on the DIS has been mathematically investigated by Hao et al. [19] and by Cheng et al. [20]. Strictly speaking, for the micrometer size active material particle, this phenomena can be neglected but not for the nanometer size SEI layer. However, since the aim of our investigation is not the accurate calculation of the stresses, but their qualitative comparison at different working conditions of the battery, for simplicity, the surface effect has been neglected. Additionally, for mathematical simplicity a homogenous SEI layer was assumed.

The stress due to intercalation/de-intercalation of lithium ions in the active material is derived equivalently to the temperature induced stress and it is widely known as diffusion induced stress that is explained in Refs. [5–9], among others. The expression relating the strain and the stress for an elastic body and for the particular case of a spherical symmetry reads as follows:

$$\varepsilon_r = \frac{1}{E}[(1+\nu)\sigma_r - \nu\sigma_t] + \frac{c\Omega}{3} \tag{1}$$

$$\varepsilon_t = \frac{1}{E}[(1-\nu)\sigma_t - \nu\sigma_r] + \frac{c\Omega}{3} \tag{2}$$

where ε_r and ε_t are the radial and tangential strain respectively, σ_r and σ_t the radial and tangential stresses, E the Young modulus, ν the Poisson's ratio, c the concentration inside the active material particle and Ω the partial molar volume of the solute in the solid material (which describes the volume of a mol of lithium when it intercalates into the graphite).

It is assumed that the material is isotropic and any variation in the elastic properties with Li concentration has been neglected. Additionally, no external forces acting on the surface of the particle is assumed, resulting on the following equilibrium equation for the stress tensor:

$$\frac{d\sigma_r}{dr} + \frac{2(\sigma_r - \sigma_t)}{r} = 0 \tag{3}$$

The strain tensor is related to the displacement tensor u by the following expressions:

$$\varepsilon_r = \frac{du}{dr}, \ \varepsilon_t = \frac{u}{r} \tag{4}$$