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Design and fracture mechanics of lithium-ion batteries

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Abstract

Fracture mechanics plays a crucial role among the mechanisms causing damage, meant as capacity fade, in lithium-ion batteries. Mechanical stresses arise in the electrode active material particles because of the interaction of lithium ions with electrode microstructure during battery operation. The stresses lead to fractures growth in the electrode, which accelerates detrimental chemical reactions. In this work, a modelling approach is presented to assess the fracture level in the electrode microstructure, evaluating the influence of the current delivered by the battery, and electrode design characteristics, such as the electrode thickness, the electrode active material fraction and the size of the electrode micro-particles. The results show that stress intensity factor linearly increase with the current delivered by the battery. Furthermore, thicker electrodes, greater active material fraction and greater electrode micro-particles represent a more detrimental condition from the fracture mechanics point of view. The results provide a practical electrode design guideline for electrode manufacturing, especially for choosing the right particle size in the electrode powder, the electrode thickness and its composition to limit fracture according to the current expected to be delivered by the battery.

Keywords: Lithium-ion battery; mechanical degradation; fracture mechanics; stress intensity factor; electrode design

1. Introduction

Lithium-ion batteries (LIBs) are the leading technology in term of energy storage systems, and the current challenge of decarbonization is accelerating their demand in a wide field of applications. The main drawback of

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LIBs is their limited life. Indeed, their expected life is about 1000 cycles, after which they must be disposed or recycled. The high economic and environmental costs of the battery manufacturing and the exponential increasing of their production is mobilizing both the research and industrial community to find strategies to limit the battery damage and increase their lifespan.

Among different mechanisms causing battery damage, mechanical damage is one of the most detrimental, especially at high current rates. Comprehensive reviews of the damaging mechanisms occurring in LIB and their modelling can be found in literature Birkl et al. (2017), Mocera et al. (2020); O'Kane et al. 2021; Reniers et al. (2019), Li et al. (2019).

During charge and discharge, lithium-ions get into the microstructure of the electrode of one polarity, and are extracted from the electrode of opposite polarity, according to the electrochemical reactions regulating the battery working. During these processes, known as (de)lithiation, lithium ions cause the deformation of the active material particles of the electrodes were they are inserted Clerici et al. (2021), Clerici et al. (2020), Clerici et al. (2022). The amount of deformation is linearly proportional to the lithium-ion concentration. As lithium ions are much smaller than active material particles (~10μm in diameter), they diffuse within the particle, giving rise to an inhomogeneous lithium concentration, which causes differential strain and thus the so called diffusion induced stress (DIS) Clerici et al. (2021), Clerici et al. (2020), Clerici et al. (2020). Finally, such stress is the driving force for crack propagation, which causes isolation of some areas of the active material as well as triggers undesired side reactions, causing capacity loss and resistance increase ultimately Clerici et al. (2022), Pistorio et al. (2023); Pistorio et al. (2023), Pistorio et al. (2022).

In this work, an electrochemical-mechanical battery model is developed to assess the stress intensity factor (SIF), and then the fracture likeliness, as a function of different electrode design solutions, at different current rates. The electrode design parameters considered are the electrode thickness, the fraction of active material and the active material particle size. The goal of this analysis is to give electrode design guidelines to limit fracture and mechanical degradation in LIBs.

2. Method

The electrochemistry of the battery is modeled with a partial two dimensional (P2D) model implemented in Matlab Pistorio et al. (2023). The model has several parameters representing the battery geometry, kinetics, and material properties. In the electrode design study, the thickness of the electrodes layers, the active material fraction in the electrode and the size of the active material particles are adjusted to get the desired battery properties in terms of energy and power densities, rate capability and internal resistance. For this reason, the influence of these three parameters on SIF is evaluated, to give electrode design guidelines to limit fracture in electrodes.

Electrochemical models like P2D take in input the current profile delivered or injected into the battery, and gives as output its voltage response. Together with the voltage at electrode level, the P2D model resolves the lithium-ion concentration distribution at particle level. The concentration of lithium ions causes the deformation of the host material, according to Equation 1.

$$\varepsilon_{Li} = \frac{\Omega}{3}(c - c_{ref}) \tag{1}$$

Where Ω is the partial molar volume, telling the volume of the host material per mole of lithium ions, c is the concentration of lithium ions and c_{ref} is the reference concentration at zero strain.

The stress generated by the inhomogeneous concentration distribution at particle level is computed with a DIS analytical model already developed by the research group, and all the model details can be found there Clerici et al. 2020a. In such model the particle is assumed to be spherical, then just the radial coordinate is involved, and the principal directions are the radial and the two hoop (identical) directions. Considering Mode I as dominant, hoop stress is the driving force for crack propagation, as illustrated in Fig. 1. The expression of hoop stress as a function of the lithium concentration inside the active material particles is reported in Equation 2.

$$\sigma_c(r) = \frac{\Omega E}{3(1-\nu)}\left[\frac{1}{r^3}\int_0^r cr^2\,dr + \frac{2}{R^3}\int_0^R cr^2\,dr - c\ \right] \tag{2}$$

Where σ_c is the hoop stress, E and ν are the Young's modulus and Poisson's ratio of the host material, Ω the partial molar volume, R the radius of the particle and c the concentration distribution of lithium ions as a function of the particle radial coordinate (r).

At this stage, SIF is computed with an analytical method based on geometric factors, illustrated in a authors' previous work Pistorio et al. (2023). The difficulty in computing geometric factors in this case is that the stress distribution over the crack surfaces reported in Equation 2 is not constant, because the DIS changes along particle radius, and then along the crack surfaces, as graphically reported by Fig. 2b. To overcome this issue, the non-constant stress is expressed by a n-th grade polynomial function, as expressed by Equation 3.

$$\sigma(r) = \sum_{i=1}^{n} \sigma_i r^i \tag{3}$$

Where σ_i are the polynomial coefficients. The grade n is chosen high enough to get a proper representation of the stress distribution. Then, a general stress intensity factor is defined according to the principle of superimposition, as expressed in Equation 4. Other methods exist to compute SIF due to an arbitrary stress distribution over the crack surface, like Green functions and weight function, but the methods proposed in Pistorio et al. (2023) is definitely easier to handle.

$$K_I = \sum_{i=1}^{n} Y_i \sigma_i r^i \sqrt{a} \tag{4}$$

Where K_I is the stress intensity factor due to mode I, Y_i are the geometric factors computed in Pistorio et al. (2023) and a is the crack length. The geometric factors computed in Pistorio et al. (2023) are functions of the normalized crack length (a/R), and are in number equal to the grade n chosen to fit the stress distribution. Each geometric factor function multiplies a single polynomial grade, as expressed in Equation 4. This methodology is validated with the numerical computation of SIF with a finite element model, confirming the correctness of the results Pistorio et al. (2023).

The modelling framework explained here is schematically resumed in Fig. 1.

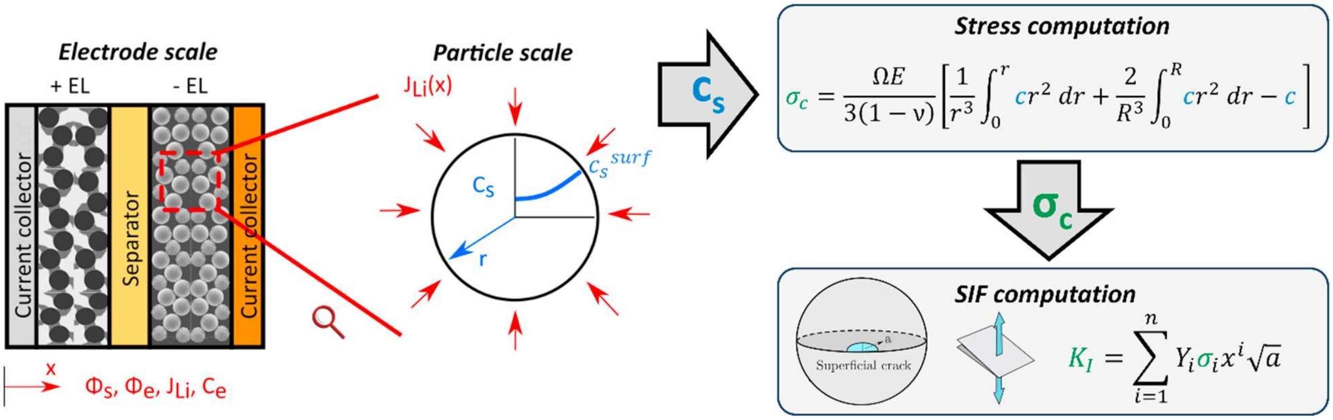

Fig. 1. Model framework. Left hand side is the electrochemical model, giving the concentration distribution as output. Then, concentration is the input of the mechanical model, computing stress intensity factor.

3. Results

The influence of the thickness of the electrodes layers, the fraction of active material in the electrode and the size of the active material particles on the SIF value is studied with a sensitivity analysis. In this way, the influence of each of these design parameters on fracture is quantified, so that it can be considered in the electrode design process.

Starting from the designed value of the three parameters, obtained from batteries tested in laboratory (Pistorio et al. 2023), two steps of positive (+ and ++) and one of negative (-) changes are considered to understand their sensitivity on the resulting SIF. Different percentage changes are considered for different parameters to get meaningful values. The summary of the parameters values are reported in Table 1.

Table 1. Sensitivity of electrode design parameters: thickness of the electrodes layers, fraction of active material in the electrode and the size of the active material particles.

Parameter	- change	Design	+ change	++ change
Electrode thickness [μm]	44	88	132	176
Active material fraction [%]	55%	69%	75%	79%
Particle size [μm]	5	10	12,5	15

The design parameters reported in Table 1 have an influence on the electrochemistry of the battery, in particular on the lithium ions concentration distribution within the particle, which affects the stress and SIF ultimately.

Graphite is chosen as case study, which is the most common material used as anode. The Young's modulus is 10 GPa, Poisson's ratio is 0,3 and partial molar volume is 4,25 10^{-6} m^3/mol.

During discharge lithium ions are extracted from the anode and inserted into the cathode, then graphite is delithiated, resulting in the concentration distribution and the hoop stress reported in Figs. 2a and b. In this condition, hoop stress is tensile at the particle boundary, then superficial cracks are considered, and the respective geometric factors are used to compute SIF. During charge, the flux of lithium ions is reverted, and the ions are inserted into the graphite, causing tensile hoop stress at the particle core, and propagating internal cracks.

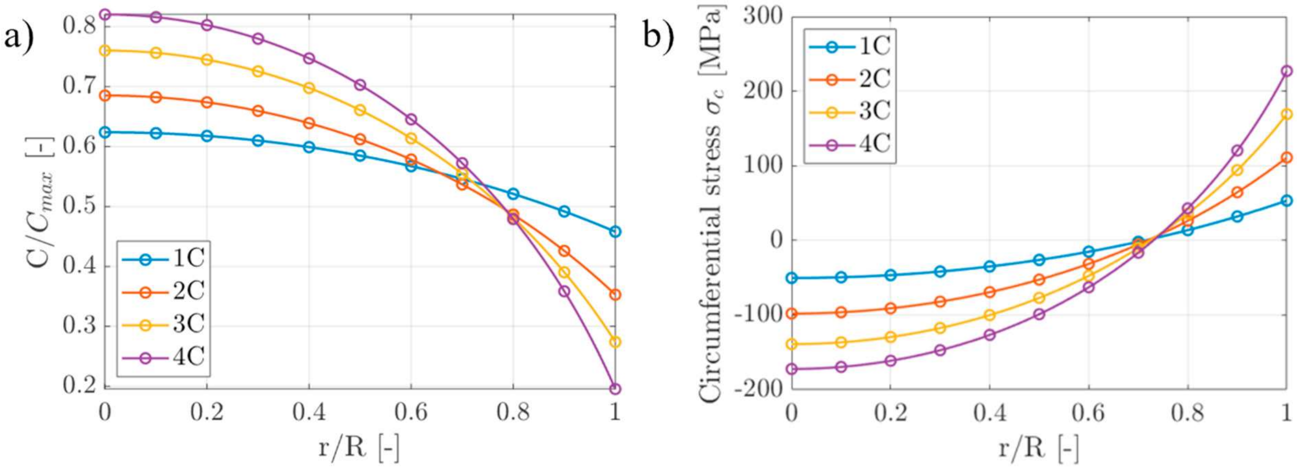

Fig. 2. (a) Concentration distribution; (b) Hoop stress within the active material (graphite) particle at different current rates during discharge (delithiation). C-rate is used to refer to current rate, 1C is equal to the Ampere current which completely discharge the battery in 1 hour.

The results reported in Fig. 2 highlight that higher the current delivered by the battery, higher the lithium flux at the particle boundary, and then steeper the lithium-ions concentration gradient in the particle. Steeper concentration gradients mean greater lithium ions inhomogeneity, and thus higher stress and SIF ultimately. Then, higher current rates always lead to higher stress and SIF, regardless of the electrode design parameters choice.

Fig. 3 reports the influence of the electrode thickness on the SIF. Generally, thicker electrodes are used for high energy density applications because thicker the electrode, lower the number of elementary cells (sequence of current collectors, cathode, separator, anode) connected in parallel in the battery, and the greater the energy that can be stored per unit of volume (or mass), basically because there are fewer inactive components like separators and current collectors. In this condition, assuming that the capacity of the battery is the same, fewer elementary cells are in the battery and then higher current is applied to them, considering that elementary cells are connected in parallel and the current delivered by the battery is the same. The higher current applied to the single elementary cell causes steeper concentration gradient, thus higher stress and SIF in thick electrodes, as graphically reported in Fig. 3. The differences become greater when increasing the current rate. Thinner electrodes are used for high power applications, because of the lower internal resistance and greater current capabilities. From the fracture point of view, thinner electrodes have also a better mechanical behavior at higher current rate.

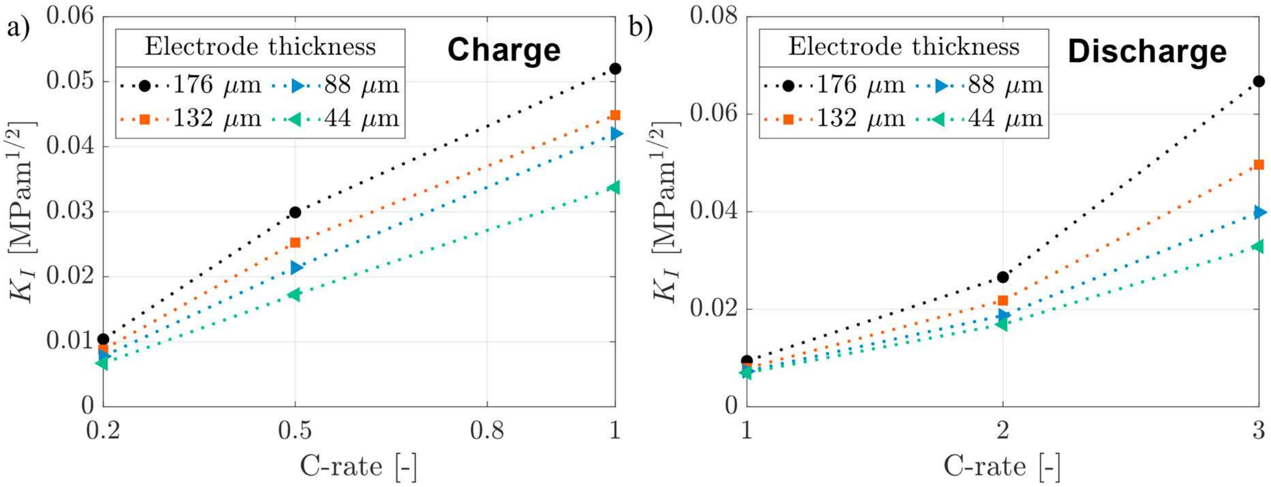

Fig. 3. Influence of the electrode thickness on the SIF during (a) charge and (b) discharge.

Fig. 4 reports the influence of the active fraction in electrode on the fracture behavior.

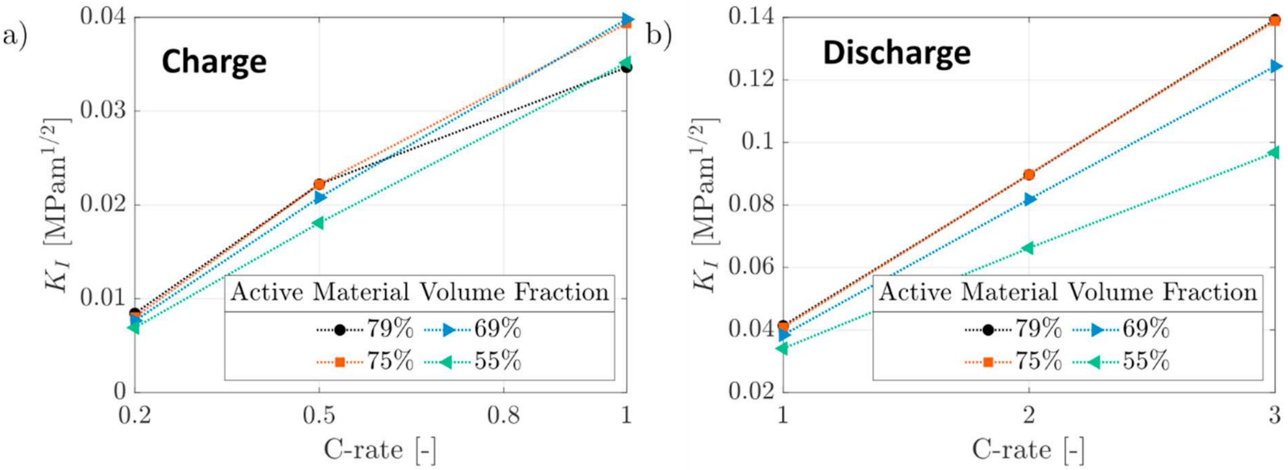

Fig. 4. Influence of the active material volume fraction on the SIF during (a) charge and (b) discharge.

Similarly to electrode thickness, higher active material fraction leads to fewer elementary cell, and thus higher flux, stress and SIF. The dependency is much more nonlinear, indeed at higher fraction of active material the SIF does not increase anymore, suggesting that high active material fraction is a convenient design solution. On the other hand, too high active material fraction is not acceptable from the electrochemical point of view because it would diminish the fraction of porosities and conductive agent, decreasing the electronic and ionic conductivities.

Fig. 5 reports the influence of the active material particle size on the fracture behavior. Smaller particles are preferred from the fracture mechanics point of view, because of the lower concentration gradient within the particle and the resulting lower stress and SIF. On the other hand, smaller particles result in electrodes with lower tap and energy densities. Furthermore, the manufacturing process to obtain active material particles with smaller size is more expensive.

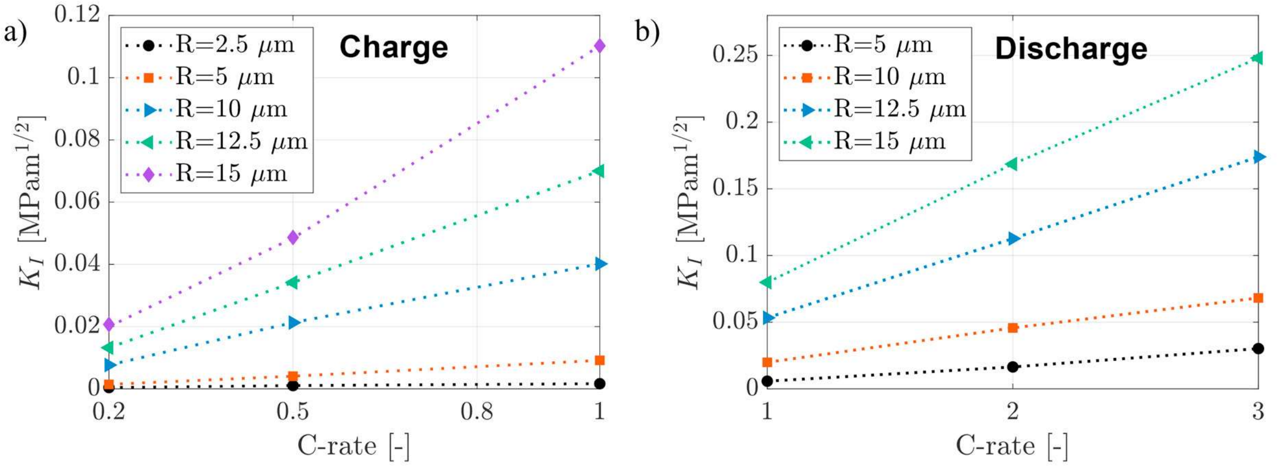

Fig. 5. Influence of the active material particle size on the SIF during (a) charge and (b) discharge.

4. Conclusions

In this work an electrochemical-mechanical model is proposed to evaluate the stress intensity factor in the microstructure of electrodes designed with different design solutions. The goal is to find electrode design solutions limiting fracture, and then the mechanical degradation of the battery, extending its life ultimately.

The P2D model is used to compute the concentration distribution at particle level due to a certain current profile and electrode design solutions. The inhomogeneous concentration in the active material particles causes differential strain and thus the so called diffusion induced stress. Then, the concentration distribution in the active material particles is the input of the mechanical model which computes hoop stress, driving force of Mode I crack opening, and stress intensity factor (K_I) ultimately.

In the electrode design, the adjusting parameters are usually the electrode thickness, the active material fraction and the active material particle size. Then, the influence of these parameters on the resulting SIF is evaluated, to get electrode design guidelines limiting fracture and then battery degradation.

It is observed that thicker electrodes lead to higher SIF values, due to the higher current applied to the single elementary cell, and the differences between thin and thick electrodes increases with current rate. This result is encouraging because high power batteries (delivering high current) are designed with thinner electrode to reduce the internal resistance. The influence of active material fraction in the electrode on the SIF is similar to the electrode thickness, but it becomes much more nonlinear at high active material fraction values, exponentially reducing the SIF increase. Finally, smaller active material particles are preferred to limit fracture, because a lower concentration gradient, and thus lower stress and SIF.

It is highlighted that these results must not be taken alone, these parameters have an influence on the electrochemical behavior of the battery as well. Then, a tradeoff between the mechanical degradation and electrochemical performance is needed when designing electrodes for lithium ion batteries.

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