Simulation of Lithium Plating Due to Spatial Inhomogeneous Separator Strain in Lithium-Ion-Cells

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ABSTRACT:
The electrodes and especially the separator of a lithium-ion-cell are exposed to mechanical stress due to expansion of electrode materials during operation if the electrodes are integrated in a stiff cell casing e.g. in a 18650 cell. As a result, the porosity and therefore the lithium-diffusion characteristics are altered. In this paper a simulative study of spatially resolved effects from inhomogeneous separator porosity reduction induced by mechanical strain is presented. The findings show significantly changed spatial current densities and local anode voltage potentials that match findings of post-mortem investigations.

KEY WORDS: EV and HV systems, lithium ion battery, battery technology, charge/discharge / Simulation, Mechanical stress, Lithium plating [A3]

1. Introduction
Lithium-ion-cells are the key components for next generation electric transportation. When designing a new type of battery cell, one can choose from a variety of electrode materials that differ in energy/power density and cycle stability.

The parameters in focus when cell aging is investigated are commonly temperature and the external electrical load profile. Aging mechanisms caused by these parameters are very well understood.

Nowadays, an additional factor for cell aging and performance gains more and more attention – mechanical stresses (1, 2). Electrode materials, especially anode materials like graphite and silicon, show measurable and considerable amounts of dilation due to lithium intercalation during the charging step and vice versa (3). A common lithium-ion cell consists of repeating anode/separator/cathode layers that are encased by a comparably rigid casing (round and prismatic hardcase cell types). Additionally, e.g. in a cylindrical cell, there are spatial inhomogeneities in the jellyroll due to the protruding current collector tabs.

During charging, electrode materials expand but are hindered by the cell casing and/or a constraining module construction. The predominant consequence is a compression of the separator and, to some extent, the electrode layers that have a comparably low Young’s modulus (separator - 25 MPa and anode coating - 300 MPa) (4, 5). These values are in high contrast with the Young’s moduli of the pure active materials (e.g. NMC - 199 GPa) (6) and are attributed to the binder content in the electrode (4). Strained separators and electrodes show diverging electrochemical properties that cause higher internal resistance, faster aging and in the worst case, lithium plating if the compression is locally inhomogeneous (1, 7) as is the case next to current collector tabs (figure 1) (8).

Fig. 1 Plating areas next to the current collector tab (yellow rectangles) and near the edge of the cell casing (areas of high local mechanical stress) in an opened 18650 cell (charged at 0 °C at C/10 for 50 cycles).

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The simulative parameter-dependent investigation for plating conditions of these local separator and electrode strain inhomogeneities is the main aspect of this paper.

Here, two different scenarios will be investigated. First, the simulation of a locally abrupt change in the separator diffusivity e.g. because of (electrolyte) gas bubbles or delamination areas in a cell. Second, a more spatially extended and smoother disturbance of local diffusion in a larger separator area due to a mechanically-generated effect (e.g. because of an protruding current collector tab) will be examined.

2. Simulation of a locally reduced separator porosity

2.1. Simulative approach

The simulations were carried out using COMSOL 5.3a Battery and Fuel Cells Module. The electrochemical model of the simulated Graphite/NMC cell is based on the Newman model (9) making the electrochemical simulation pseudo 3D. The full set of model parameters can be found in appendix. A galvanostatic charging (CC) process up to a cell voltage of 4.2 V was simulated.

To model a local strain-induced porosity reduction of a separator section in a cell, the separator of a mono-layer cell was segmented (figure 2). Beside a pristine separator area, a separator segment with different values of relative porosity reduction was implemented. Due to the high difference of the Young’s moduli of separator and electrodes, porosity reduction of the electrodes due to mechanical stress was neglected for this study. Additionally, the influence of temperature as an important operating parameter on the cell behavior is simulated.

Fig. 2 Schematic model geometry of the monolayer cell.

2.2. Influence of a reduced separator porosity on local current density and potential drop

The effect of a spatially-reduced separator porosity, especially for high degrees of separator porosity reduction (up to relative porosity of 1 % where 100 % corresponds to a pristine separator), on the local current density is significant (figure 3). When a global C-rate of 0.8 C is applied to the cell, the local C-rate at the defect boundary rises to values of almost 6 C for a temperature of 283 K and up to over 6 C for higher temperatures.

![Fig. 3 Local amplification of C-rate depending on temperature and relative defect porosity (100 % corresponds to a pristine separator).](image)

The global charging C-rate is 0.8 C. Black dashed values are at the end of the CC-step when the cell reaches 4.2 V. For better comparability the ordinates are scaled identically.
Additionally, the average C-rate in the section with a normal separator porosity is elevated. This can be attributed to balancing currents (figure 7) and will be discussed later.

For less severe porosity reductions, the simulated C-rates become more and more uniform but for a porosity of 25% the local C-rate is still almost twice as high as the global C-rate.

The simulated values for the potential drop (anode voltage vs. lithium) also have a large impact on the plating behavior because of a reduced separator porosity (figure 4). For a high reduction of separator porosity and a temperature of 283 K, the simulated cell locally reaches a very low anode voltage of almost -200 mV at the end of the CC-charging step and remains almost undischarged in the defect area. For similarly reduced defect porosities but higher temperatures, the simulated potential drop is not as high as expected according to the Newman model. One can observe that for low degrees of separator porosity but not completely clogged separator pores, the electrode area with a negative anode potential vs. lithium moves over the defect area whereas the plating area is at the defect border at very low separator defect porosity. This can also be attributed to balancing currents (figure 7) and will be discussed later. For mild degrees of separator porosity reduction, the local electrode potential becomes more and more spatially uniform. This is in agreement with the simulated local current densities (figure 3).

The chosen separator defect porosity values may seem high at first glance, but one has to consider that during operation of the cell, there is not only a reversible dilation of the electrodes but also nonreversible dilation due to SEI thickening and/or graphite exfoliation. This means that the separator is stressed not only periodically but also continually with every cycle. Investigation on aged cells showed a relative reduction of anode porosity at the end-of-life of 50% and more (10). The values were measured in a homogeneously aged part of the electrode; therefore, one can assume that the porosity reduction in mechanically high stressed areas like next to the current collector tab or near the cell casing edge will show an even higher degree of porosity reduction. As lithium plating occurs at the anode/electrode boundary, a simulation of a reduced separator porosity is equivalent to pore reduction in the anode.

3. Simulation of a smoother defect boundary

3.1. Simulative approach

In the simulations shown in the previous section, the transition between normal porosity in the separator and an area with reduced porosity was extended over a range equal to two separator
thicknesses. This assumption of a rather sudden defect is valid e.g. for an electrolyte gas bubble on the electrode due to gassing or local electrode delamination effects.

To investigate the effects of a smoother transition from defect to non-defect area that mechanically occurs due to electrode dilation while charging e.g. near a current collector tab (figure 1), the step function was modified (figure 5).

3.2. Influence of a reduced separator porosity with smooth transition on local potential drop

When the defect transition is not as steep as defined in section 2, the potential drop curves alter (figure 6).

Fig. 6 Potential drop (anode voltage vs. li-reference) at end of CC-charge at 0.8 C and 298 K for a smoother defect transition.

For high and mild degrees of separator porosity reduction, the voltage curves are comparable to the simulation results with the steep defect transition (figure 4). For intermediate degrees of porosity reduction, the voltage drop curves diverge from the results of the sudden porosity change simulation. One can observe a decline in the voltage drop within the defect region (arc-lengths < 1 mm). The reason for this behavior is the relatively smaller area of the defined defect porosity compared with the scenario before, whereby more out-of-plane ion current flows within the defect as discussed in the next section.

3.3. Balancing currents due to local inhomogeneous separator porosity

To understand the spatially inhomogeneous voltage drop and local current density curves, one has to investigate the spatial current vector field (figure 7). For high degrees of separator porosity reduction, high in-plane (within the electrodes) current is observable. This is due to the high diffusion resistance at low separator porosities. With increasing defect area porosities, more and more current flows out-of-plane (through the separator) as in homogeneous battery cells. Nevertheless, the in-plane current from the defect area and the electrode section that faces a separator with normal porosity are superimposed at the defect boundary. If one compares the voltage drop curves (figure 6) and the current density vector field (figure 7), one can observe some kind of tipping point in the spatial anode potential of the cell. This must be due to the fact that depending on cell temperature and the area of the defect eventually, even though the separator porosity still is low, the diffusion resistance for in-plane current is too high. As a result, out-of-plane lithium diffusion is favored despite high out-of-plane diffusion resistance, especially for areas far from the defect boundary.

Fig. 7 Current density vector field (balancing currents) and local SOC for a smooth defect transition at 0.8 C and 298 K at end of CC-charge (anode = top, cathode = bottom). Magenta areas fulfill the plating condition. For defect porosities of 40 % and higher no plating was observed.

4. Discussion

As demonstrated, local porosity inhomogeneities can have not only high local but also global impact on the electrochemical cell behavior. This means that the anode potential can drop locally below zero volts vs. the lithium reference (plating condition)
whereas the majority of the anode area has a potential vs. lithium over zero volts.

The maximum operating parameters for a new cell or electrode material are often determined with a homogeneous force on the electrodes and separator layers, e.g. in a spring-loaded lab-scale cell. If these parameters are later transferred to, e.g., a 18650 cell where mechanical inhomogeneities occur (figure 1), the cell could experience local plating due to local current densities that are too high (figure 3) at temperatures and global C-rates where the homogeneous lab-scale cell did not show lithium plating.

Another effect that was not yet modeled but will have a large impact over time is the locally higher current density at the edge of a diffusion discontinuity. It is well known that high C-rates result in faster cell aging, which is in this case highly locally confined. Aging of graphite anodes always also comes with a reduction of the electrode porosity and irreversible dilation itself due to SEI buildup. As plating occurs on the anode-separator interface, a reduced (local) anode porosity in addition to a reduced (local) separator porosity due to irreversible anode dilation will aggravate the effects shown in the simulation over time.

As with all electrochemical simulations, the results depend heavily on the chosen parameters and are therefore only to be considered as relative findings. By choosing a reasonable cell configuration in addition to state-of-the-art measured parameters, from recent publications and also with real-life operating parameters, the results presented here should be of assistance for further investigations.

In a real cell during operation, additional effects e.g. like viscoelastic creeping (11, 12) of the separator and a porosity reduction of the electrodes themselves occur to some extent due to electrode dilation. These effects were not implemented yet but are subject of ongoing work.

5. Conclusion
In this paper, the effect of two locally reduced separator porosity case scenarios was simulated. By varying operating parameters like the cell temperature in addition to different separator porosity reductions, the effect of highly local diffusion inhomogeneities on the spatial current density and the local anode potential was investigated. A configuration with a more smooth transition from a disturbed porosity section to a section with normal separator porosity was also modeled. The first case was to model e.g. electrolyte gas bubbles or local electrode delamination whereas the second case should simulate a locally strained separator e.g. due to a protruding current collector tab in a 18650 cell jellyroll.

The results illustrate a significant deviation of the local current density and the local anode potential as compared to the global cell C-rate and anode voltage depending on the amount of separator porosity reduction and temperature. The findings clearly show that electrochemical-mechanical effects must not be underestimated especially when defining maximum operation parameters that were ascertained in view of temperature and global C-rate.

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Appendix: Parameters for the electrochemical model

Tab. 1 Cell parameters

| Name       | Value   | Unit   | Description                                           |
|------------|---------|--------|------------------------------------------------------|
| Lsep       | 1.910^{-5} | m      | Thickness of the separator (4)                       |
| εs,neg     | 0.63    |        | Solid volume fraction in the anode (4)               |
| εs,pos     | 0.562   |        | Solid volume fraction in the cathode (4)             |
| εs,sep     | 0.51    |        | Solid volume fraction in separator (4)               |
| ε1,neg     | 0.31    |        | Liquid volume fraction in the anode (4)              |
| ε1,pos     | 0.33    |        | Liquid volume fraction in the cathode (4)           |
| ε1,sep     | 0.49    |        | Liquid volume fraction in separator (4)             |
| bru_g,neg  | 2.06    |        | Bruggemann exponent factor in the anode**           |
| bru_g,pos  | 2.0     |        | Bruggemann exponent factor in the cathode**         |
| bru_g,sep  | 2.5     |        | Bruggemann exponent in the separator **              |
| ρneg       | 2270 kg/m |        | Anode Density (Graphite) (COMSOL)                     |
| ρpos       | 4678 kg/m |        | Cathode Density (NMC) (13)                           |
| ρsep       | 900 kg/m |        | Separator Density (14)                               |
| M.neg      | 0.072 kg/mol |    | Anode Material Molar Mass (Graphite)           |
| M.pos      | 0.0964 kg/mol |    | Cathode Material Molar Mass (NMC)                        |
| c.max,neg  | 30897 mol/m |    | Maximum Li concentration in the anode, charge window (4) |
| c.max,pos  | 47314 mol/m |    | Maximum Li concentration in the cathode               |
| soc.min,neg|         |        | Minimum state of charge in the anode material (assumed) |
| soc.min,pos| 0.405   |        | Minimum state of charge in the cathode material **   |
| soc.max,neg| 0.98    |        | Maximum state of charge in the anode material *      |
| soc.max,pos| 0.975   |        | Maximum state of charge in the cathode material *    |
| R.neg      | 1.1^{-5} |        | Anode particle radius (4)                            |
| R.pos      | 5.510^{-6} |       | Cathode particle radius (4)                          |
| Ks,bulk,neg| 2200 S/m |        | Bulk ionic/electronic conductivity of solid phase in negative electrode (4) |
| Ks,bulk,pos| 57 S/m  |        | Bulk ionic/electronic conductivity of solid phase in the cathode (4) |
| D.neg      | 5 m²/s  |        | Bulk diffusivity in the anode (4)                    |
| D.pos      | 3 m²/s  |        | Bulk diffusivity in the cathode (4)                  |
| E.A.D.neg  | 40 J/mol |        | Activation energy for diffusion in the anode (15)   |
| E.A.D.pos  | 25000 J/mol |    | Activation energy for diffusion in the cathode (15)  |
| k.I.neg    | 2.2 10^{11} m/s | | Reaction rate in the anode (4)                     |
| k.I.pos    | 9.2 10^{11} m/s | | Reaction rate in the cathode (4)                    |
The anode equilibrium potential was implemented with the following function (15):

\[
E_{eq,neg} = 0.628 + 0.542 \exp \left( -0.351 + 0.531 \text{soc}_n \right) + 0.044 \tanh((0.016 - 0.0.196)/0.109) J - 0.198 \tanh((0.012 - 0.053) + 0.18 \tanh((0.056)/0.086)) J
\]

The cathode equilibrium potential was implemented with the following function (19):

\[
E_{eq,pos} = 3.72 + 0.026 \log \left( \frac{1 - \text{soc}_p}{1 - \text{soc}_p} \right) - 0.012 (1 - \text{soc}_p) - 3.85 (1 - \text{soc}_p)^2 + 102.933 (1 - \text{soc}_p)^3 - 845.20 (1 - \text{soc}_p)^4 + 3290.033 (1 - \text{soc}_p)^5 - 6567.953 (1 - \text{soc}_p)^6 + 6567.291 (1 - \text{soc}_p)^7 - 2605.076 (1 - \text{soc}_p)^8 - 5 \times 10^{-6} \exp \left( \frac{1}{1.08 - \text{soc}_p} \right)
\]

The local state of charge \( \text{soc}_{p/n} \) is defined as follows:

\[
\text{soc}_{p/n} = \frac{c_{\text{s,n}}}{c_{\text{max, pos/neg}}}
\]

The electrolyte conductivity was implemented by a function fitted to the data provided in (17):

\[
\kappa_i = \frac{m_s}{cm} \exp(-A c_i) \cos(B c_i + C) \sum_{i=0}^{2} \sum_{j=0}^{2} \beta_{ij} c_i^j
\]

with the following coefficients: