

# Batteries' end of life: Modelling the ageing phenomena

Clément Bernard Guy Lucien LESAGE  
clement.lesage@tecnico.ulisboa.pt

Instituto Superior Técnico, Universidade de Lisboa, Portugal  
December 2023

## Abstract

In the context of a growing deployment of renewable energy capacities, the electric grid faces challenges related to the intermittency of such energy sources. To ensure flexibility, energy storage is necessary. It may involve installing electrochemical batteries linked to the grid, designed to store the electricity overload, and deliver it back when needed. The service life of these batteries is expected to reach 10 years minimum and 20 years, if possible, with on average 1 cycle per day (amounting to 3000 to 8000 cycles). From that perspective, it is necessary to understand the ageing phenomena leading to battery end-of-life. Modeling those allows for accurate forecasts of the battery's behavior throughout its lifetime. For many lithium-ion systems, recent studies have shown that ageing happens in three phases, with first, the formation of the SEI layer at the anode which provokes a first drop in capacity. The second phase consists in a linear decrease of the battery capacity due to the growing of the SEI phase at the anode side. The third phase often referred to as knee-point consists in the sudden and drastic drop in capacity primarily due to the deposition of metallic lithium onto the anode material. The aim of this work is to present an overview of the different ageing mechanisms taking place in a lithium-ion battery and the attempts to model them, with a focus on the SEI/lithium-plating combination.

**Keywords:** Lithium-ion battery, Ageing, Simulation, Lithium-plating, Knee-point

## 1. Introduction

The most used battery technology today is referred to as lithium-ion. In this family, one can cite several battery configurations, with a negative electrode usually made of graphite and a positive electrode usually being made of either Lithium-Nickel-Manganese-Cobalt Oxide (NMC), Lithium-Nickel-Cobalt-Aluminum Oxide (NCA) or Lithium-Iron-Phosphate (LFP). Though the first two chemistries have proven their robustness over the years, the third has attracted a lot of attention as it avoids the use of nickel and cobalt, which extraction and processing have raised environmental and social issues (but also cost ones). As a result, the LFP chemistry is viewed as promising for stationary energy storage. Given the popularity of the LFP chemistry, this research work has been designed to

look for and present an electrochemical ageing model related to this chemistry, but more largely to lithium-ion batteries relying on the "rocking-chair" principle. A particularity of this model has been the incorporation of the lithium-plating phenomena, responsible for the knee-point observed on the capacity evolution curve with respect to cycle number. To my knowledge, few established electrochemical models present in the literature take into account the lithium-plating phenomena.

Throughout the study, research was done to identify already existing simulation models for lithium-ion batteries and what software could be used to perform these simulations. Existing battery models are exhibited and a full model description inspired by literature is given.

## 2. Lithium-ion battery fundamentals

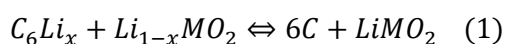
### 2.1 Important definitions and working principles

The first appearance of rechargeable Li-ion secondary batteries took place in 1990, and from then on, the capacity always increased in response to the more demanding energy market.[1] The corresponding cells can contain either liquid electrolytes or polymer electrolytes, with a wide range of anode and cathode materials, allowing for a fine tuning of the batteries' performance. Ideally, these devices are the best fit for having the greatest energy content than their counterparts.

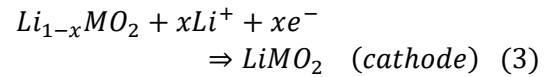
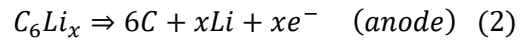
In classical Li-ion batteries, anodes are generally made out of carbon material such as graphite, which shows a potential close to 0V vs  $Li/Li^+$  (0.02V when fully lithiated). It follows that the energy properties of the cell, such as energy density and specific power are conditioned by the choice of the cathode material [2]. Furthermore, most batteries showcase a liquid electrolyte. To obtain a larger power output, researchers have tried to widen the cell's working window, but this favors instability of the electrolyte.

Still, to foster a good functioning of a Li-ion cell, liquids made up of a solvent with lithium salt are chosen as electrolytes. The solvents used are responsible for the formation of the "Solid Electrolyte Interface" (SEI), a solid layer made of components derived from the reaction taking place between the electrolyte molecules and the active electrode material particles. This layer is fundamental to prevent carbon delamination phenomena. The SEI layer is also essential for the stability of graphite [3].

Considering a classic Li-ion accumulator with a graphite anode, the total reaction taking place is given by Eq. 1:



where the  $M$  represents a metal. There is a Li ions exchange between the two active materials Eq.1. This equation is defined for the discharge process. The complete reaction comes from the two half-equations coming from the oxidation (Eq. 2) and reduction (Eq. 3) taking place, which have the following form during the discharging phase:



Electrodes usually showcase a porous structure in order to favor the intercalation process, which presents three major steps:

- 1) Diffusion of Li ions in the electrolytic solution
- 2) Fading of the electrolyte-ions bonds and start for the ions to go to the electrode material vacant sites
- 3) Diffusion of Li ions inside the active material structure

As with all diffusivity-linked phenomena, intercalation is a dynamic process, which means that different graphite layers are reached at different times. This induces a substantial raise in the ions' path length inside the active material, thus impacting the polarization and the overpotentials. Intercalation is considered to be reversible and non-destructive. The continuous intercalation/de-intercalation cycles can provoke volume variations, deformations, and tension inside the electrode, leading to a decrease in battery life.

Considering what could be macroscopically perceived, one must know what state of health is. The State-of-Health (SoH) is a metric measuring the ageing level of a battery. It often includes capacity or power fade [4]. The SoH can be defined by Eq. 4:

$$SoH = \frac{Q_t^{max}}{Q_0^{max}} \quad (4)$$

where,  $Q_0^{max}$  designates the battery maximum capacity at the beginning of its

life, and  $Q_t^{max}$  represents the battery maximum capacity at time  $t$ . Given the fact that battery ages, the SoH is bound to decrease throughout the battery's lifetime.

In electrodes, lithium can only be present in a certain amount within a host material structure. Therefore, one of the electrode materials characteristics is the maximum quantity of lithium that they can host in their structure. This is described by the reference equilibrium concentration, which shows the maximum number in moles of host sites for lithium atoms per cubic meters of electrode active material.

For an electrode, the State-of-Charge (SoC) (Eq. 5) designates the amount of cyclable lithium contained in the electrode at a given moment in time.

$$SoC = \frac{c_s}{c_{s,max}} \quad (5)$$

where  $c_s$  is the electrode current lithium concentration, while  $c_{s,max}$  is the maximum achievable lithium concentration for the studied electrode, both expressed in  $mol.m^{-3}$ .

On the other hand, for the whole battery, the SoC (Eq. 6) will be referred to as the ratio between the currently held capacity and the maximum capacity:

$$SoC = \frac{Q_t}{Q_{max}} \quad (6)$$

where,  $Q_t$  is the battery's charge at instant  $t$  and  $Q_{max}$  is the maximum capacity.

## 2.2 Materials involved in batteries

Below figures a small description of the materials involved in the studied Graphite/LFP cell.

For the positive electrode,  $LiFePO_4$ , is quite popular, cheaper than other technologies and widely used, for example, in electromobility [5]. It presents an olivine structure, showcases a good thermal stability and allows to reach a high delivery power. However, this material works at low

potentials, with low ionic and electric conductivity.

For the negative electrode, graphite is the currently most used materials for lithium-ion batteries. The theoretical specific capacity of graphite is  $372 mAh.g^{-1}$ [6]. It consists of a pile of carbon planes which are bonded between them through medium to low energy Van der Waals interactions. The intercalation of lithium ions happens between these planes.

To complete a battery, an electrolyte must be used. Its role is to separate the reactions taking place at the electrodes to guarantee the energy output and close the cell's circuit. [4] The electrolyte presents itself under the form of a solution constituted of a solvent (organic or inorganic) and a salt (generally a lithium salt).

As a battery is an assembly of different materials presenting different properties, several mechanisms are taking place, some of which lead to a drop in performance.

## 3. Ageing and modelling interest

### 3.1 Ageing

It is referred to as "ageing", the witnessed drop in battery performances after a certain number of use cycles. This ageing is due to "parasitic" reactions that can worsen the performance of the batteries and that are observed throughout the whole lifetime of a battery, such the formation and growth of the previously mentioned SEI layer.

One can distinguish two types of ageing for a battery. The first one is referred to as "calendar" ageing and takes place when the battery is not being used. One must beware not to confuse this ageing type, which induces an irreversible capacity loss, with the self-discharge phenomenon, which only provokes a reversible loss of capacity. The second ageing type for batteries is called ageing in use or in cycling, which takes

place when the battery is used either in charge or discharge mode.

In the case of cycling, ageing causes are more complex and with more contributions than for calendar ageing. It has been acknowledged that the battery's working temperature, the SOC variation range, the maximum current value for charge and discharge, the average current applied on a time interval and the current profile, count among the parameters influencing the ageing in cycling. Overall, degradation in lithium-ion batteries is caused by a variety of reactions involving one or more battery components, among which the electrolyte, the electrodes, the current collectors and the separator. Many degradation phenomena affect those different components, and these phenomena are sometimes interdependent. Simulating all of these phenomena becomes quite challenging when considering commonly available computing resources, and this is why a majority of physics-based models only take into account the dominant mechanisms, like the formation and growth of the Solid Electrolyte Interface (SEI) [7] or the loss of electronic contact through cracking [8].

At the negative electrode, mainly made of graphite for lithium-ion batteries, the main ageing mechanism is the formation and growth of the SEI layer. The volume change of graphite during lithium ions insertion can provoke cracks in the SEI layer, leading to new contact between the active material and the electrolyte and therefore leading the way for the creation of more SEI. This SEI layer is in part responsible for the increase of the battery internal resistance. Other degradation mechanisms can take place. For example, the lithium metal deposition taking place either at low temperature charging, high C-rate charging or overcharging can also contribute to the loss of cyclable lithium and ultimately to global capacity loss [9].

At the positive electrode, parasitic reactions are much less documented. The

degradation reactions product can be solid, so as to form a passivation layer similar to the SEI, called the cathode electrolyte interface (CEI), but can also be gaseous or soluble in the electrolyte.

Still regarding the negative electrode, another degradation mechanism that has been under scrutiny is lithium plating. Lithium plating consists in the deposition, under certain conditions, of lithium metal on the surface of an electrode. More precisely, when the local electrode potential becomes negative with respect to the  $Li^+/Li(s)$  couple, lithium-plating occurs. High charging C-rate, low temperature and high SoC are favouring factors for lithium-plating [10].

### 3.2 Ageing profiles

One of the main manifestations of the ageing phenomena for lithium-ion batteries is the capacity loss. From tests, such as calendar ageing or charge/discharge cycles, the battery capacity can be extracted and represented function of time or function of the number of cycles.

The evolution of the capacity through time will showcase several ageing profiles (Fig. 1). Each of the ageing phases, corresponding to different profiles, have been under scrutiny, to try to associate physio-chemical mechanisms with the different evolutions.

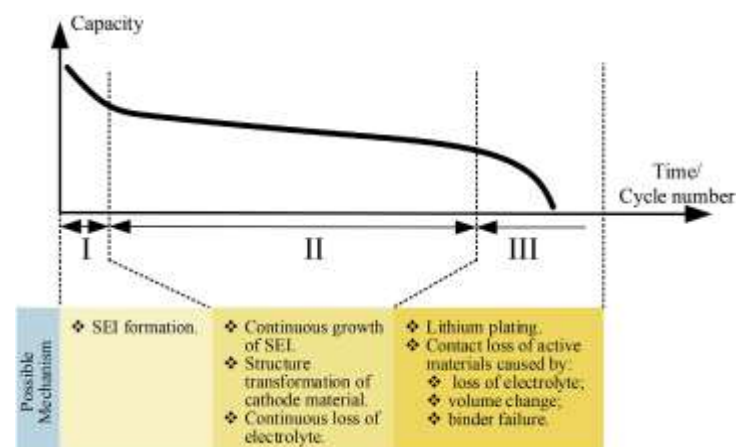


Figure 1: Battery capacity fade with possible mechanisms in different stages [11]

This profile has been observed experimentally (Fig. 2), following experiments conducted at the lab.

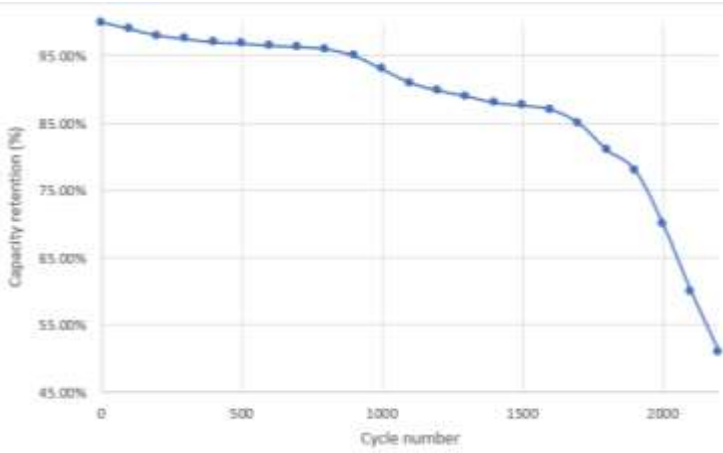


Figure 2: Gr/LFP cell ageing profile upon cycling

With the attribution of equations to degradation mechanisms taking place in a battery and the need to forecast the battery's lifetime comes the necessity of simulation. A popular model has been developed by Newman and Tiedemann in 1975 [12]. Referred to as the Pseudo 2D Model (P2D), it takes into account migration phenomena in the electrolyte (mass transport) and the electrodes (diffusion), as well as kinetics phenomena in the electrodes, represented by partial differential equations (PDE). The resolution of these equations is usually carried out by using Finite Element Analysis (FEA).

## 4. Mathematical model

### 4.1 P2D model

As mentioned prior, taken into account are the two degradation phenomena, SEI layer formation and growth and lithium-plating. Along with cell thickness, the proposed model considers three subdomains representing, respectively, the graphite anode, the separator, and the LFP cathode.

In the electrolyte-separator domain, the model solves for current conservation (Eq. 7) and mass conservation (Eq. 8), in which  $i_l$  is the ionic current density flowing in the liquid phase (electrolyte),  $\sigma_l$  denotes the electrolyte conductivity,  $f$  is the activity

coefficient for the salt,  $t_+$  is the transport number for  $Li^+$ , also called transference number,  $\Phi_l$  is the electrolyte potential,  $c_l$  is the electrolyte salt concentration,  $\varepsilon_l$  is the electrolyte volume fraction, and  $D_l$  is the salt diffusivity in the electrolyte.  $T$ ,  $F$  and  $R$  are, respectively, the temperature, Faraday's constant, and the universal gas constant.

$$i_l = -\sigma_l \cdot \nabla \Phi_l + \frac{2 \cdot \sigma_l \cdot R \cdot T}{F} \left( 1 + \frac{\partial \ln f}{\partial \ln c_l} \right) \cdot (1 - t_+) \cdot \nabla \ln c_l \quad (7)$$

$$\varepsilon_l \frac{\partial c_l}{\partial t} = \nabla(\varepsilon_l D_l \nabla c_l) - \nabla \left( \frac{i_l \cdot t_+}{F} \right) + \frac{\nabla i_l}{F} \quad (8)$$

As the electrode is considered porous, pores and channels are present within. The paths leading to active material surface are not all equal and to be more representative of reality, path tortuosity as to be considered. Therefore, corrected values of diffusivity and conductivity are adopted, known as "effective" [13]. In this model, the Bruggeman relationship is considered, in which tortuosity is assumed to be a function of the material porosity. The effective diffusion coefficient  $D_{l,eff}$ , the effective liquid phase conductivity  $\sigma_{l,eff}$  and the effective conductivity of the solid phase  $\sigma_{s,eff}$  are expressed in Eq.9

$$\begin{cases} D_{l,eff} = \frac{\varepsilon}{\tau_{l,Brug}} D_l \\ \sigma_{l,eff} = \frac{\varepsilon}{\tau_{l,Brug}} \sigma_l \\ \sigma_{s,eff} = \frac{\varepsilon}{\tau_{l,Brug}} \sigma_s \end{cases} \quad (9)$$

The Bruggeman relation expresses the tortuosity factor in Eq. 10,

$$\tau_{l,Brug} = \varepsilon^{-0,5} \quad (10)$$

where  $\tau_{l,Brug}$  and  $\varepsilon$  represent, respectively, the tortuosity and the porosity of the given material.

Therefore Equation 11 is obtained,

$$\begin{cases} D_{l,eff} = \varepsilon^{1.5} D_l \\ \sigma_{l,eff} = \varepsilon^{1.5} \sigma_l \\ \sigma_{s,eff} = \varepsilon^{1.5} \sigma_s \end{cases} \quad (11)$$

Regarding the intercalation/deintercalation process of lithium ions within the active material, chemical kinetics are described by the Butler-Volmer equation (Eq. 12). In this particular case, the equation linked to the intercalation phenomenon

$$i_{int} = i_0 \left[ \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(\frac{-\alpha_c F \eta}{RT}\right) \right] \quad (12)$$

where  $i_0$  is the reference exchange current density of lithium intercalation,  $\alpha_a$  and  $\alpha_c$  are the anodic and cathodic charge transfer coefficients usually set to 0.5, assuming  $\alpha_a + \alpha_c = 1$  [14].

The overpotential  $\eta$  due to the electrochemical reaction can be expressed in Eq. 13, where  $E_{eq}$  represents the open circuit potential (related to the SoC), here the equilibrium potential for the lithium intercalation reaction:

$$\eta = \Phi_s - \Phi_l - E_{eq} \quad (13)$$

Following the work of Safari et al. [15] and Yang et al. [16], the model considers that the rate of SEI formation reaction presents two contributions. One from the diffusion rate of EC (electrolyte solvent molecules) across the already formed SEI layer, and the second one from the surface kinetics.

To take into account these two phenomena, one must consider both the following Tafel equation (Eq. 14), about the surface kinetics,

$$i_{SEI} = -F \cdot k_{0,SEI} \cdot c_{EC,s} \exp\left(-\frac{\alpha_{c,SEI} \cdot F \cdot \eta_{SEI}}{RT}\right) \quad (14)$$

And the mass conservation of EC (Eq. 15), given by,

$$-D_{EC} a_v \frac{c_{EC,s} - c_{EC,0}}{\delta_{SEI}} = \frac{i_{SEI}}{F} \quad (15)$$

where  $D_{EC}$  is the diffusivity of EC,  $c_{EC,0}$  is the concentration of EC in the bulk electrolyte, and  $\delta_{SEI}$  is the thickness of the SEI layer. If the left part of the equation represents the diffusive flux of EC across the SEI layer, the right part represents the consumption rate of EC through the SEI formation reaction.

The combination of those two contributions gives the following current density (Eq. 16) for the formation and growth of the SEI layer,

$$i_{SEI} = -\frac{F \cdot k_{0,SEI} \cdot c_{0,EC}}{\exp\left(\frac{\alpha_{c,SEI} \cdot F \cdot \eta_{SEI}}{RT}\right) - \frac{k_{0,SEI} \cdot \delta_{SEI}}{D_{EC}}} \quad (16)$$

Based on the work of Yang et al. [17], the following current density (Eq. 17) for the formation of growth of lithium plating can be adopted,

$$i_{lip} = -i_{0,lip} \exp\left(\frac{-\alpha_{lip} \cdot F \cdot \eta_{lip}}{RT}\right) \quad (17)$$

where  $i_{0,lip}$  represents the exchange current density of lithium metal deposition,  $\alpha_{lip}$  is the cathodic reaction coefficient for lithium plating, arbitrarily set to 0.5, and  $\eta_{lip}$  corresponds to the lithium plating associated overpotential.

## 4.2 Model input

For the simulation to give an appropriate representation of reality, battery structural data must be obtained and entered into the model. This is particularly true for a model done, for example, on the Comsol Multiphysics software.

Geometrical attributes like the electrodes' and separator's thickness or the electrode material particle size should be obtained by lab measurements. The mass of the electrode is also important to know as it gives information on the gravimetric capacity of the cell and its components. As priorly said, the porosity of the electrodes should be considered. It can be calculated,

and a method provided by Chen et al. [18], gives the following formula for the solid volume fraction (Eq. 17) and the liquid volume fraction (Eq. 18):

$$\varepsilon_s = \frac{M_{coat.}}{L_{electrode} \times \rho_{electrode}} \quad (17)$$

$$\varepsilon_l = 1 - \varepsilon_s \quad (18)$$

where  $M_{coat.}$  designates the mass of the electrode (only one graphite or LFP layer),  $L_{electrode}$  is the thickness of the electrode, and  $\rho_{electrode}$  is the density of the electrode. In a simple model, though electrodes, can be subjected to volume change during battery operation, these solid volume fractions are assumed to be constant.

Based on those first input, a first result of the model is given in Fig.3,

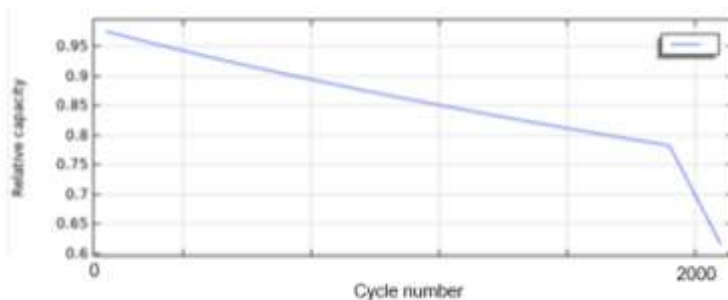


Figure 3: Knee-point phenomenon observed for the simulated Gr/LFP cell

Though comforting, this first result observable for capacity, is not fully conclusive as it is suspected that the observed *knee-point* could be a side effect. For that reason, and to render the model more reliable, one must also be aware of the impact of the formation cycles on the characteristics of the electrodes and the impact of the initial SEI layer formation on the initial capacity. Furthermore, the effects of C-rate, initial SoC and temperature need to be accounted for in the initial conditions as ageing trajectories are influenced by the cell's initial state.

## 5. Conclusion

The adequate choice of an electrochemical device for energy storage needs to undergo scrutiny. The knowledge of materials and physico-chemical phenomena at play is key to understanding a system's behavior and, as seen in this study, a system's behavior through time. Once known, different equations need to be attributed to different phenomena in order to be able to build a computer model that would allow one to perform simulations. Provided a model's robustness, these simulations aim at forecasting the behavior of a battery and, therefore, choose the appropriate one for the adequate application and use. During this project, an attempt was made to describe the ageing of a Gr/LFP cell, taking into account two degradation phenomena, respectively SEI layer formation, growth and lithium-plating. Though many teams have succeeded in implementing those phenomena, work still needs to be done to build more robust models.

## Acknowledgements

I would like to thank the EIT InnoEnergy team, both at Instituto Superior Técnico and Politecnico di Torino for their support and guidance.

## References

- [1]: M. Winter, R. J. Brodd (2004) What are batteries, fuel cells, and supercapacitors? *Chemical Reviews*. 104(10) p. 4245-4270
- [2]: Ma et al. (2016). Surface and interface issues in spinel  $LiNi_{0.5}Mn_{1.5}O_4$ : insights into a potential cathode material for high energy density lithium-ion batteries. *Chemistry of Materials* 28(11)
- [3]: S. Megahed, B. Scrosati (1994). Lithium-ion rechargeable batteries. *Journal of Power Sources*. 51(1-2) p.79-104

- [4]: Zou et al. (2015). Combined State of Charge and State of Health estimation over lithium-ion battery cell cycle lifespan for electric vehicles. *Journal of Power Sources*. 273. p. 793-803
- [5]: (2021) The pricing power at LFP producers increased with its cost-effectiveness on rising costs; SMM
- [6]: Jeffrey W. Fergus (2010). Recent developments in cathode materials for lithium ion batteries. *Journal of Power Sources*. 195(4). P. 939-954
- [7]: P.U. Nzereogu et al. (2022). Anode materials for lithium-ion batteries: A review; *Applied Surface Science Advances*. 9, 100233
- [8]: Rutooj Deshpande et al. (2012) Battery cycle life prediction with coupled chemical degradation and fatigue mechanics. *J. Electrochem. Soc.* 159(10)
- [9]: Zhe Li et al. (2014) A review of lithium deposition in lithium-ion and lithium metal secondary batteries. *Journal of Power Sources*. 254, p.168-182
- [10]: Languang Lu et al. (2013) A review on the key issues for lithium-ion battery management in electric vehicles. *Journal of Power Sources*. 226(3), p.272-288
- [11]: Xianke Lin et al. (2021) Lithium plating mechanism, detection and mitigation in lithium-ion batteries. *Progress in Energy and Combustion Science*. 87,100953
- [12]: James Le Houx et al. (2020) Physics based modelling of porous lithium ion battery electrodes-A review. *Energy Reports*. 6(5) p.1-9
- [13]: Bernhard Tjaden et al. (2016) on the origin and application of the Bruggeman correlation for analysing transport phenomena in electrochemical systems. *Current Opinion in Chemical Engineering*. 12, p.44-51
- [14]: C. Heubner et al. (2015) Investigation of charge transfer kinetics of Li-intercalation in LiFePO<sub>4</sub>. *Journal of Power Sources*. 288, p. 115-120
- [15]: M. Safari, M. Morcrette, A. Teysot, C. Delacourt (2008) Multimodal physics-based aging model for life prediction of Li-ion batteries. *J. Electrochem. Soc.* 156
- [16]: Xiao-Guang Yang et al. (2017) Model of lithium plating induced aging of lithium-ion batteries: transition from linear to nonlinear aging. *Journal of Power Sources*. 360, p.28-40
- [17]: Chang-Hui Chen et al. (2020) Development of experimental techniques for parameterization of multi-scale lithium-ion battery models. *J. Electrochem. Soc.* 167(8)
- [18]: Ruoyu Xiong et al. (2023) Overpotential decomposition enabled decoupling of complex kinetic processes in battery electrodes. *Journal of Power Sources*. 232296