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A process model for the electrolyte filling of lithium-ion batteries

Thomas Knoche[a,*], Florian Surek[a], Gunter Reinhart[a]

[a]*Technische Universität München, Institut for machine tools and industrial management, Boltzmannstraße 15, 85748 Garching, Germany*

* Corresponding author. Tel.: +49-89-289-15493; fax: +49-89-289-15555. *E-mail address:* Thomas.Knoche@iwb.tum.de;

Abstract

Filling a lithium-ion battery with electrolyte liquid is a core process in battery manufacturing. Better understanding of this process will reduce costs while enabling high product quality. Nonetheless, the process has not been sufficiently examined by science yet. This work aims at a process model systematically depicting empirical knowledge about electrolyte filling. The model is supposed to analyze the inner structure and behavior of the process. It focuses on a graphical and qualitative description of knowledge. A concept for the process model is developed by combining and complementing different modeling approaches and applied to the electrolyte filling. The resulting hierarchical model organizes existing knowledge by illustrating the correlations between the battery structure, cell materials, filling apparatus, filling procedure, process phenomena as well as the product and process quality. It is demonstrated how the process model can be refined and guide the design of filling process and machinery

Keywords: Process; Fluid; Model

1. Introduction

1.1. Motivation

Lithium-ion batteries (li-ion batteries) are the dominant energy storage technology in mobile consumer electronics. Recently, li-ion batteries have advanced into the market of electric cars and are seen as one key technology buffering the fluctuating power generation of renewable energies in stationary applications. Yet, especially large-scale batteries show room for improvement and to achieve broad acceptance among customers, the costs for batteries have to be reduced. Besides the development of new cell structures and materials, the production process of li-ion batteries decisively influences product quality and costs [1, 2]. One critical manufacturing step is the filling of the cell with liquid electrolyte [3, 4]. Despite its crucial importance for battery quality and costs, this process has not been sufficiently studied by science yet. The electrolyte liquid enables ion exchange between the electrodes. As insufficiently wetted parts of the porous media (electrodes, separator) do therefore not contribute to the electrochemical reactions within the cell, the wetting degree considerably influences the battery performance. Moreover, insufficient wetting is associated with the formation of needle-like structures (dendrites) on the electrodes that penetrate the separator and short-circuit neighboring electrodes, causing severe safety issues [3, 4].

1.2. Background and challenges for production technology

However, spreading the electrolyte homogenously is a time-consuming process. The electrolyte filling process aims to dose the necessary amount of electrolyte into the battery within the shortest possible time. In general, the voids of the cell stack are not completely filled after electrolyte dosing. To allow the liquid to penetrate the porous media completely, the cells are warehoused. This process is usually referred to as wetting process and represents a decisive bottleneck in cell production with a high potential of reducing production costs due to process times of several days at elevated temperature [2]. To shorten the wetting process time, the electrolyte filling has to be conducted in such a way that the pores of electrodes and separator are soaked as completely as possible by the liquid right after the filling process. A common approach is

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the evacuation of the cell [5] to reduce the amount of gas within the porous media and several patents employ further (alternating) pressure gradients, believed to be the driving force behind electrolyte spreading [6-8]. But there is no common agreement on the optimal electrolyte filling process due to its dependency on the product's and machine's specifications.

1.3. Aim of this work

It is expected that an optimized filling process significantly reduces wetting time and production costs while enabling a high product performance. These improvements require a comprehensive understanding of the electrolyte filling, but the process has not been sufficiently examined by science yet and reliable literature is scarce. Several patents on the topic were filed, but the diversity of processes, systems and effects described shows that the process is not understood. There is an urgent need for a model describing the process and the filling apparatus in a neutral way, incorporating electrochemical effects and depicting the interdependencies between product design, manufacturing system and process. This model allows for the systematic depiction and investigation of process phenomena and provides a base for deriving a process design method.

2. Modeling Approach

As aforementioned, there is a considerable need for the advancement of scientific knowledge in order to improve the electrolyte filling process of lithium ion batteries. Due to the complexity and the lack of knowledge about of the electrolyte filling, it is assumed that a graphical and qualitative approach is appropriate in a first step. The model is supposed to provide the basis for quantitative methods and deriving process and machine design guidelines in subsequent steps.

The model is intended to depict cause-and-effect relations between different parameters of the electrolyte filling process. Merging the cause-and-effect relations quickly leads to a network of interdependencies between different process elements. In order to structure and simplify the model, the process elements and the interactions between them have to be classified and hierarchized by suitable means. Moreover, it is essential that the model is easily expandable by new process elements and interactions. On the other hand, it is crucial that the user of the model can quickly focus on specific relations by reducing the model's complexity.

The illustration of cause-and-effect relations hints at the proposed explanatory character of the model. Considering the electrolyte filling process, the model is supposed to elucidate the effect of the cell design, cell materials as well as the filling machine and its configuration on the product and process quality. However, the model is not only intended to explain coherences in the electrolyte filling process, but shall finally guide the optimization of the electrolyte filling. Therefore, the model also has to show how a set of requirements regarding the product and process quality leads to a certain process implementation and filling machine. There are several existing elaborate approaches analyzing and optimizing manufacturing processes [10-12]. In [13], a method for identifying quality parameters in battery cell production is presented. However, the objective of these methods is rather the optimization of whole process chains comprising plenty of interdependent process steps. That is why, all of these approaches regard single process steps as black boxes with a set of input and output parameters. The cause-and-effect interactions between the input and output parameters of a single process step are not regarded. Due to the lacking depiction of cause-and-effect relations within one process step, these approaches are not suitable for the intended model. As there are no applicable models in the field of manufacturing systems, various models which are well-known in product development and software engineering have been investigated. The most promising models are the interdependency network, the relation-based functional model [14], the morphological box and the class diagram from the Unified Modeling Language (UML) [15]. Each of these models has specific advantages, but does not fulfill all requirements of the intended model. Therefore, the listed modeling approaches have been combined and complemented for a new modeling approach which will be described in the next chapter.

3. Structure of the Model

3.1. 1st level: Domains

The process model is divided into three levels. The first level (see fig. 1) specifies domains representing the product design, the machine, the process implementation, the process phenomena as well as the quality of the product and the process. The domain *product design* describes attributes of the processed product and can be divided into subdomains. This is particularly recommended, if the interaction of the proposed subdomains with the other domains is significantly different. Taking the example of the electrolyte filling, the lithium ion cell is described by its cell geometry and by its materials: Whereas the first subdomain describes the macroscopic structure of the cell, the latter subdomain refers to the physical and chemical properties of the cell's materials. The domains *machine* and *process implementation* depict the influence of the manufacturing system on the process. It is crucial that the manufacturing system is divided into two domains: Whereas the domain *process implementation* describes the possible process steps and their parametrization in a neutral and abstract perspective, the domain *machine* illustrates the necessary technical equipment for the execution of the process steps. The separation of the domains is supposed to foster a solution-neutral engineering of the process.

The domain *process phenomena* is the core of the modeling approach, as it depicts the cause-and-effect relations between the other domains and therefore represents the "interior" of the black box. In case of the electrolyte filling process, the domain predominantly delineates the impact of different product attributes and process parameters on the penetration of the cell's porous media. Finally, the result of the process is depicted by the domain *quality,* which is divided into the two subdomains *product quality* and *process quality*. The

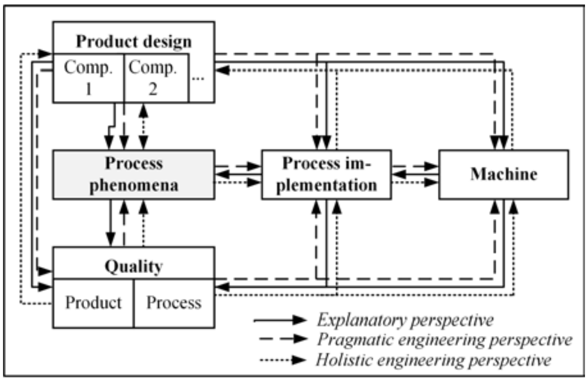

Fig. 1: 1st level of the model (domains)

subdomain *product quality* describes the resulting attributes of the product. Any other performance features are incorporated in the subdomain *process quality*, as for example the processing time, the processing cost or the safety of the process. Fig. 1 does not only define the domains of the modeling approach, but also defines directions for the interaction between the different domains. The *explanatory perspective* follows the general understanding of a process with the input domains product design, machine and process implementation leading to a certain quality of the product and process. However, the user of the model might also focus on the engineering of an optimal process. The *pragmatic engineering perspective* inverts the perspective of the explanatory approach and regards the quality domain as an input leading to a certain process implementation and machine, but still regards the product design as an input domain. The *holistic engineering perspective* also incorporates product design changes due to requirements of the manufacturing process. The concepts of “Design for Manufacturing” (DFM) and “Simultaneous Engineering” verify this approach, which is also present in battery technology as some literature links an optimized electrolyte filling process to specific adaptions in the battery design [9, 16, 17].

3.2. 2nd level: Cause-and-effect-relations

The second level of the model depicts the cause-and-effect relations in the different domains and is illustrated by fig. 2. As clarified in the following, different elements of the interdependency network, the relation-based functional model and the UML class diagram have been incorporated in the second level. To put it simple, all domains are described with process elements, their attributes and relations between the process elements similar to an interdependency network. The relations between the process elements are defined according to the UML class diagram: directional associations, aggregations and compositions. If only certain attributes of one process elements have an impact on another process element, this can be noted as shown in the diagram. On top of that, a sequence between certain process elements can be defined. The process elements can be marked as external factors and interfaces. An external factor describes the impact of previous manufacturing steps. Again using the electrolyte

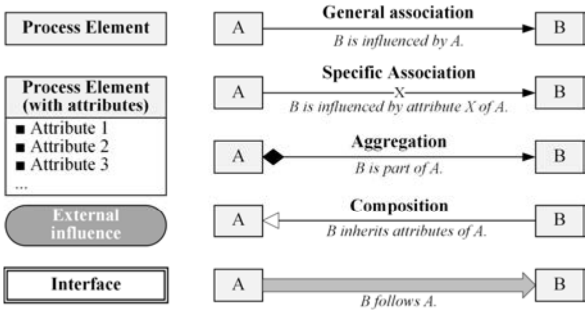

Fig. 2: 2nd level of the model (detailing)

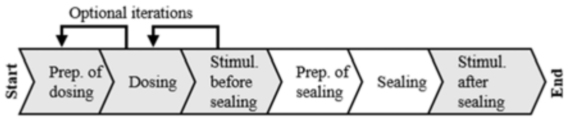

Fig. 3: Subprocesses

filling as an example, the geometric and material properties are determined by the manufacturing of the electrodes and the assembly of the cell body to a great extent. An interface links two or more different domains and allows the independent analysis of single domains. The definition of the interfaces demands great diligence, as the complexity of the model can quickly rise if too many interfaces are defined. In order to define condensed interfaces, it helps to regard them as functions as proposed by the relation-based functional model, although it is not recommended to use the specific notation of the latter.

3.3. 3rd level: Detailing

Finally, the third level of the model allows detailing different process elements and relations between. As the requirements for a detailed description vary, no modeling approach is generally recommended. A morphological box can be used to describe a specific process element in detail and derive its attributes, which will be demonstrated later on. Logical expressions, either empirical or analytical, describe the relation between two process elements. In conclusion, a systematic and flexible approach to facilitate a deeper understanding of a manufacturing process is provided in contrast to common “black box” approaches. The model is classified and hierarchized by suitable means and can be easily extended or reduced to focus on certain process relations. The approach is applicable to any manufacturing step. In order to illustrate the developed approach, its application to the electrolyte filling of lithium ion batteries is shown in the next chapter. If applied and updated continuously, the model will pave the way for quantitative investigations as well as process and machine design guidelines.

4. Application to the electrolyte filling process

4.1. Overview and scope of the developed model

Modeling a process as described above is based on a precise definition of boundaries and sub-processes. Electrolyte filling can be divided into several sub-processes, which are conducted subsequently with optional iterations as shown in figure 3. These sub-processes are dosing of electrolyte liquid, sealing of the cell, stimulation of electrolyte spreading before and after sealing as well as preparation steps for dosing and sealing. Stimulation describes all technical means to enhance the spreading of electrolyte within the cell. Integrating the sealing into the filling process is optional as it is common to seal pouch-cells within the filling apparatus in low pressure conditions, whereas rigid-body-cells are usually sealed in ambient pressure after wetting. The procedure of sealing will not be discussed in detail. It is just assumed that all filling openings are hermetically closed if this sub-process is conducted or all openings are left unsealed if this process is skipped. In the following, the domains machine, process implementation, process phenomena, cell material and cell design are outlined to elucidate the function of every domain in the model. It should be noted that the scope of this paper only allows a brief simplified description of the different domains. Knowledge and data represented in the following were collected from literature and experiments conducted by the authors. As there are hardly any reliable scientific publications, mostly patents were taken into account. To enable a broad range of solutions, no methods of knowledge management to evaluate the quality of references were applied yet.

4.2. Domain *"process implementation"*

The domain *process implementation*, shown in fig. 4, links the process phenomena to the machine and is supposed to describe all decisive process characteristics. Due to the high number of different configurations of the different sub-processes, a morphological box has been developed for every sub-process and integrated into the third level of the model. As an example, the morphological box of the dosing step is depicted in fig. 5 and briefly explained in the following:

- There may be one to multiple dosing steps.
- The electrolyte is injected into the cell without or without the intention of an electrolyte surplus, or the cell body is immersed in an electrolyte bath [18].
- One or multiple injection apertures are possible. Their position can be described by their vertical position.
- The port between filling system and cell may be sealed.
- Apart from the injection of a fixed volume, the filling volume may be controlled per cell respectively batch [19] or regulated [20].
- The penetration of the porous media can be stimulated during the dosing by establishing a pressure difference between the filling reservoir and the void cell volume by either evacuation (e.g. [21, 6]) or increased pressure [7].
- An overflow reservoir may inhibit an electrolyte leakage.

As shown, the morphological box allows a systematic development of the attributes of every sub-process on the third level of the model.

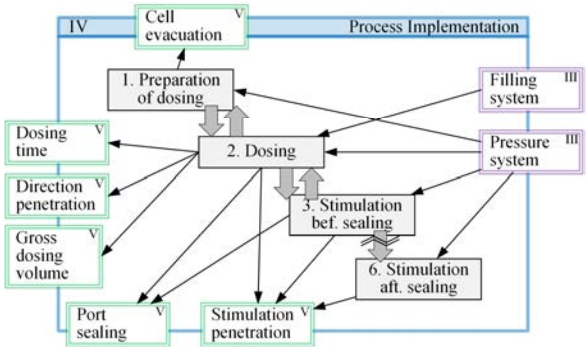

Fig. 4: Domain "process implementation"

2. Dosing						
Dosing steps	one			multiple		
Dosing method	Body in envelope			Body not in envelope		
	Simple injection	Surplus injection		Immersion		
Filling ports	one			multiple		
	botton		side		top	
Port connection	Sealed			Open		
Dosing volume	fix		Control		Regulation	
			Cell	Batch	Active	Pass.
Stimulation via pressure difference	Yes				No	
	Suction		Overpressure			
Overflow reservoir	Yes			No		

Fig. 5: Morphological box

4.3. Domain *"machine"*

The filling apparatus comprises a pressure system, a dosing system and a mounting device. Figure 6 illustrates the use of the UML class diagram in this domain. The pressure system may integrate means to establish a negative pressure (vacuum pump) and a positive pressure (booster pump) which are described by similar parameters. There is a decisive correlation between the cell apertures and the pressure system as well as filling system, as their size and number determines the feasible ports, the flow rate of the electrolyte, the course of the pressure and many other attributes not depicted. Otherwise, the cell has to be mounted in the apparatus which is impacted by the outer cell dimensions for geometric reasons. It should be reaffirmed that the machine is predominantly seen as the necessary equipment to enable a specific process implementation, which defines the decisive characteristics of the electrolyte filling process.

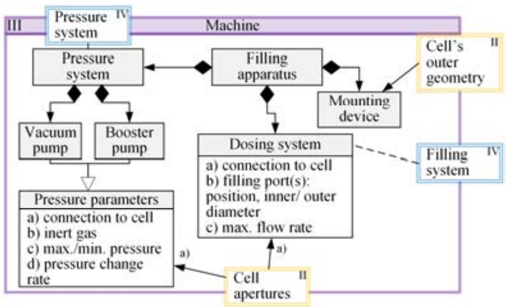

Fig. 6: Domain "machine"

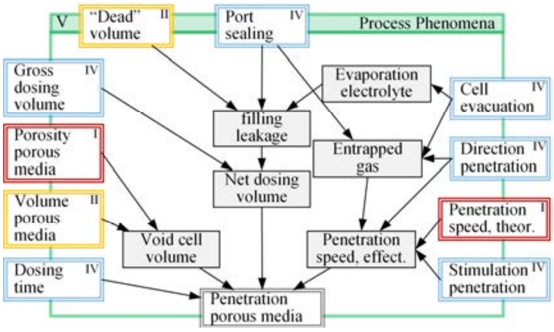

Fig. 7: Domain "process phenomena"

4.4. Domain *"process phenomena"*

The domain *process phenomena* is delineated in fig. 7. It serves as the link between cell design, cell materials and the process implementation on the one hand and the quality domains on the other hand. As aforementioned, the penetration of the cell's porous media is the dominant parameter that determines the performance of the electrolyte filling process. It is directly influenced by the dosing time, the void cell volume, the net dosing volume and the effective penetration speed. Whereas the void cell volume is directly determined by the cell design (volume of porous media) and the cell materials (porosity), all the other influence factors are mostly dependent on the process implementation. The effective penetration speed is of particular interest. Its limits are set by the material properties, but several patents suggest that it can be considerably stimulated by suitable process steps, e.g. cycles of alternating pressure [6, 8, 21]. Gas entrapments may significantly decrease the penetration speed

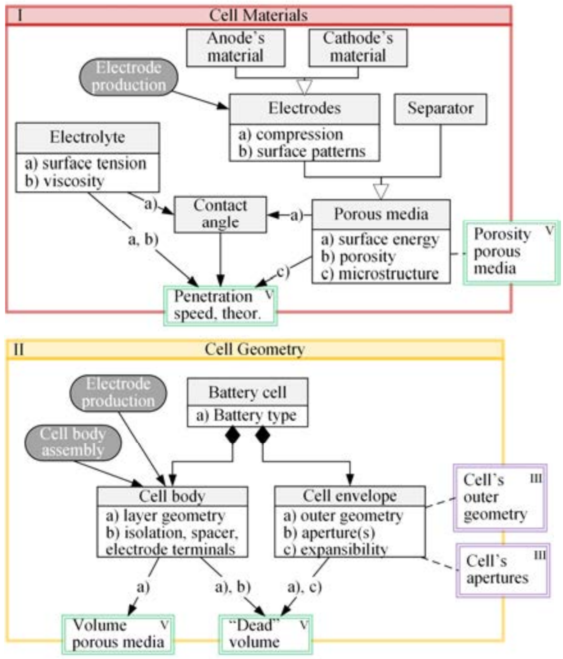

Fig. 8: Subdomains "cell materials" and "cell geometry"

and various process parameters (cell evacuation, penetration direction, port sealing) have to be carefully analyzed to avoid them. The net dosing volume is formally determined by the gross dosing volume and the filling leakage. The latter can be avoided by sealing the port between the electrolyte filling apparatus and the cell. However, it is also common to inject the electrolyte into the cell without sealing the connection. In this case, the dead volume of the cell (void volume in the cell apart from the porous media) must not be exceeded by the electrolyte volume that has already been injected into the cell, but not penetrated the porous media yet, in order to avoid a filling leakage.

4.5. Domain *"product design"*

This domain is divided into the two subdomains *cell materials* and *cell geometry*, both shown in fig. 8. The subdomain *cell materials* focuses on the impact of the chemical and physical properties of the electrolyte and the porous media on the process phenomena. Most importantly, the cell materials determine the theoretical penetration speed of the electrolyte in the porous media. The penetration speed can be described by the Washburn equation for horizontal capillaries which exposes that the penetration speed is dependent on the electrolyte (viscosity, surface tension), the microstructure of the porous media and the contact angle between the electrolyte and the porous media [22]. Although the penetration speed is also highly process dependent, its limits are set by the material properties. Otherwise, the figure depicts that the porous media can be divided into the separator and the electrode materials which can be further split up into the materials at the anode and the cathode. The microstructure of the electrodes is highly dependent on the compression during the electrode manufacturing [23, 24]. Moreover, microscopic surface patterns are not only seen as a mean to improve the electrolyte wetting, but also the battery performance [16]. Batteries can be divided into different types according to their shape (cylindrical, prismatic), the flexibility of their envelope (pouch, hard case) and their size. The cell body is the result of the previous manufacturing steps in the battery production and is usually integrated into the cell envelope before the electrolyte filling process. The geometric dimensions of the cell's layers directly determine the volume of the porous media. The cell envelope is described by its geometry and its apertures which directly impact the necessary technical equipment for geometrical reasons as mentioned above. Obviously, the dead volume of the cell is influenced by the geometric dimensions of the cell body and the cell envelope. However, the expansibility of the cell's envelope and therefore the battery type needs to be taken into account, as a flexible pouch envelope significantly increases the dead volume of the cell.

5. Prospects and future benefit of the model

5.1. Refining the process phenomenology

The modeling approach and its application to the electrolyte filling provide a base for further investigations aiming to improve empirical process knowledge. Enhancing the understanding of process phenomena and the correlations between elements paves the way for an optimized manufacturing process and a methodology for process and machinery design. While the domains of product, machinery and process implementation are highly elaborated, especially the process phenomena are still to be refined in further investigations. First numerical models have been developed for some effects, see e.g. the simulation of electrolyte intake into single electrode layers with various porosities [24]. Moreover, there are analytical models to describe simple configurations of wetting materials like the Washburn-equation [16, 24]. Other effects, like the formation of foam, have been reported as process obstacles [4, 7, 9], but never been scientifically evaluated. The same applies for evaporation and its influence on ionic conductivity and the fluid properties during the filling process. The interdisciplinary challenges require cooperation between production technology and electrochemistry.

5.2. Deriving requirements for filling process and machinery

Up to now, the filling process has to be newly designed for every type of electrochemical system and cell type [4]. The process model therefore aims to assist in the conception of a filling process. Though the total number of elements will rise by refining the model, the interfaces between the domain *phenomenology* and the other domains will hardly change. Therefore the procedure for the elaboration of methods for designing a filling process and suitable machinery is outlined though the detailed methods are still to be developed. Taking the pragmatic engineering perspective allows extracting data necessary to design the filling process and apparatus. Process phenomenology, desired quality as well as product specifications determine which sub-steps of the filling process should be implemented. Basic parameters for each step will be proposed. This way, the process model assists the user in designing an electrolyte filling process for a random battery. The proposed implementation of the filling process serves as a base for the design of the filling apparatus. Yet, the model does not provide any guidelines for the construction of the filling machinery, but assists by systematically creating requirements for its design, presented by the interfaces between the machine and other domains. This way, a comprehensive set of requirements can be deducted. It assists the user in the construction of suitable machinery and eases ramp-up.

6. Conclusion and Outlook

An approach for the systematic depiction of process knowledge is proposed and applied to electrolyte filling. The model combines several methodologies to enable an intuitive understanding of the investigated process. Interdependencies and cause-and-effect relations are mainly described graphically. While most domains are highly elaborated, refining the process phenomenology needs interdisciplinary research. Based on the model, design guidelines for the filling process and machinery will be proposed.

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References

[1] BCG. Batteries for electric cars, 2010, http://www.bcg.com/documents/file36615.pdf

[2] Wood DL III, Li J, Daniel C. Prospects for reducing the processing cost of lithium ion batteries. J Power Sources 2015; 275: 234-242.

[3] Reddy TB, Linden D. Linden’s handbook of batteries. New York: McGraw-Hill; 2011.

[4] Pettinger K.-H. Fertigungsprozesse von Lithium-Ionen-Zellen. In: Korthauer R. Handbuch Lithium-Ionen Batterien. Berlin, Heidelberg: Springer Vieweg; 2013. p. 221-235

[5] Wu MS, Liao TL, Wang YY, Wan CC. Assessment of the wettability of porous electrodes for lithium-ion batteries. J Appl Electrochemistry 2004; 34:797-805.

[6] Reschke B. Method for filling electrolyte into battery cell and apparatus for carrying out the method. US 8047241 B2, 2011.

[7] Morizane Y. Method for electrolyte injection. US 6497976 B1, 2002.

[8] Takimoto K, Maekawa Y. Appartus and Method for Injecting Liquid into Container. US 6706440 B1. 2000.

[9] Nemoto H, Kitho K, Enomoto A. Electrolyte-solution filling method and battery structure of lithium secondary battery. US 6387561 B1, 2002.

[10]Hielscher T. Qualitätsmanagement in fertigungstechnischen Prozessketten. Vorgehensweise zur fehlerbasierten Optimierung der gefertigten Bauteilqualität. Diss. Techn. Univ. Kaiserslautern. 2008.

[11]Eichgrün K. Prozessicherheit in fertigungstechnischen Prozessketten - Systemanalyse, ganzheitliche Gestaltung und Führung. Diss. Techn. Univ. Kaiserslautern. 2003.

[12]Jung D. Praxis- und prozessnahes Optimierungsmodell (PPO-Modell) zur systematischen, kontinuierlichen Verbesserung komplexer industrieller Prozesse. Diss. Univ. des Saarlandes, Saarbrücken. 2000.

[13]Westermeier M, Reinhart G, Zeilinger T. Method for quality identification and classification in battery cell production. 3rd international electric drive production conference, 2013.

[14]Lindemann U. Methodische Entwicklung technischer Produkte. Methoden flexibel und situationsgerecht anwenden. Berlin: Springer 2009.

[15]Fowler M. UML Distilled. A Brief Guide to the Standard Object Modeling Language. Boston: Addison-Wesley; 2004.

[16]Pfleging W, Kohler R, Pröll J. Laser generated microstructures in tape cast electrodes for rapid electrolyte wetting: new technical approach for cost efficient battery manufacturing. Proc. SPIE 8968, laser-based micro- and nanoprocessing VIII, 89680B, 2014.

[17]Sebastian G, Ogihara H, Zielke C, Metzdorf K, Fischer P. Method for filling a battery conditioned according to the method. EP2688124(A1), 2014.

[18]Hecht T. Self-limitating electrolyte-filling process. WO2014001212 (A1), 2014.

[19] Hecht T. Model-based electrolyte filling method. WO2013171057 (A1), 2013

[20]Meissner E. Method for producing a battery filled with a liquid electrolyte, filling vessel therefor, machine, and battery. WO2013024020 (A1)

[21]Hohenthanner CR. Klien, A. Method and device for filling an electromchimcal cell. WO 2012069100 (A1), 2012.

[22]Washburn EW. The Dynamics of Capillary Flow. Physical Review (1921) 17 (3), S. 273-283.

[23]Sheng Y, Fell CR, Son YK, Metz BM, Jiang J, Church BC. Effect of calendering on electrode wettability in lithium-ion batteries. Front. Energy Res. 2:56. 2014.

[24]Lee SG, Jeon DH. Effect of electrode compression on the wettability of lithium-ion batteries. J Power Sources 2014; 265: 363-369.