Lithium ion batteries have emerged as the power source of choice for portable devices\(^1\) and also the electric vehicle market.\(^2,3\) To increase the batteries energy density, the automotive industry tends to produce thicker and larger cells. According to this upscaling tendency, process times; manufacturing costs and also quality failures increase. Particularly electrolyte filling is a time consuming and also quality critical process step.\(^4,5\)

Poor wetted areas influence the battery performance by increasing the internal ion resistance and decreasing the discharge capacity. To compensate these limitations, longer than necessary formation cycles are applied. In addition, insufficiently saturated areas may result in an inhomogeneous current distribution. This inhomogeneity may increase the probability of dendrite growth, which can lead to a puncture of the separator and thus to the death of the cell by a thermal runaway.\(^6,7\)

The filling and soaking processes of the battery stack are driven by capillary forces. Unfortunately, capillary forces are not strong enough to saturate the complete stack with liquid electrolyte. But to avoid performance and safety limitations, all gaps and voids of the stack needs to be filled with liquid electrolyte. Therefore, especially large sized cells are stored for hours.\(^8\) Reasons for high wetting times are according to:10,2 the poor wettability of the components, structural limitations against liquid penetration on different scales and gas inclusions inside the electrodes pore structure.

To overcome these drawbacks research activities aim to improve the surface wetting of the non-polar polyolefin separator.\(^9,17\) The first approach is to enrich electrolytes with a wetting agent. The second is to modify the surface of the polyolefin separator by grafting hydrophilic functional groups.\(^18\) Further strategies to accelerate flow velocity of the electrolyte are to fill cells under low pressure conditions in a vacuum chamber.\(^10,19\) Also, cycles of alternating pressure are applied to foster these infiltration processes.\(^20\) Approaches to accelerate the electrolyte infiltration by means of a mechanical device like press rolling and vibration are also known.\(^21\)

In summary a few approaches are known, which demonstrate a positive effect on reducing filling and wetting time. Despite this potential, there are only few research activities in this field and even fewer capable methods for analyzing the filling process in situ. Reason therefore are challenges given by the cell structure and the conditions of the filling process.

**Challenges for in situ characterization of the electrolyte filling process.—**The in situ characterization of the electrolyte distribution processes are impeded by different aspects of the cell structure and the filling process. The structure of a large-scaled lithium ion battery is characterized by its multi-layer system consisting of porous anode-, cathode- and separator sheets or coils.\(^14\) In addition, the separator and electrodes differ in composition and structure. Commercial separators are usually a composite of one or more polymers.\(^17,22,23\) The electrodes, on the other hand, consist of a particulate ceramic coating on a metal substrate e.g. aluminum or copper.\(^24,25\) In situ characterization methods have to differentiate between the several layers and should be able to detect the electrolyte between the complex materials. The process conditions also complicate the in situ characterization of the filling process. In order to accelerate the electrolyte distribution, the filling process takes place in a vacuum chamber under low pressure conditions. The vacuum chamber hampers the integration of a measuring technology and the non-destructive recording of the measured signal.

**Overview in situ characterization methods.—**The wetting time of a large-scaled lithium ion batteries is usually determined empirically. To define the wetting time, the cell is opened to qualify the wetting state after the filling proceeding has finished. Based on the quantified degree of wetting the process time is determined taking account a high safety factor.\(^7\) This post-mortem analysis can thus provide a first indication for process times. Unfortunately, the determined wetting time is often intentionally oversized due to the high safety factor. Moreover, the evaluation of the influence of different material and process parameters is associated with a high preparative effort. The understanding of the filling process was highly increased by introducing neutron radiography as an analytical method. By applying neutron radiography, the flow front of the electrolyte could be visualized non-destructively and in situ during the filling process.\(^13\) Investigations show an isotropic course of the flow front from the outer sides of the cell to the center. In addition, it has been proven by reducing the differential pressure during filling, the wetting process can be accelerated by a factor of two.\(^7\) The use of neutron radiography is limited by the limited availability of suitable neutron sources and the...
unavoidable contamination of the analyzed materials. Within the production line, the value of the AC impedance is used to characterize the wetting state of the cell. A constant low value over time is seen as rough indicator for a stack saturated with liquid electrolyte. Whether less wetted areas exist between the sheets and to what extent the voids of the porous electrode and separator layers are filled with electrolyte cannot be assessed.

To overcome these drawbacks this paper intends to introduce X-ray as an innovative method for in situ visualization of the electrolyte filling process in large scaled lithium ion batteries. In comparison to given in situ characterization methods, X-ray shows a lower preparative effort, higher availability and resolution. To enable in situ X-ray measurements on filling process of large scaled cells an experimental setup is developed. Furthermore, an evaluation process for the optical data is proposed. Based on these images the suitability of X-ray as visualization method is discussed considering three exemplary filling parameters, which are gas inclusions, the filling level of the cell and the possible fluids flow front.

Experimental

For qualifying the general capabilities of the X-ray method for in situ visualization of the filling process, Lithium ion pouch cells have been prepared at the BatteryLab Braunschweig. In cooperation with Viscom AG an X-ray based inspection system was utilized to visualize the cells internals while filling it with liquid electrolyte. The acquired images were inspected, image processing algorithms suitable for evaluating the images determined and applied.

Preparation of large scaled lithium-ion batteries.—For the X-ray measurements large scaled cells with 15 compartments have been built. Therefore, cathodes with LiNi0.33Co0.33Mn0.33O2 as active material coated on 20 µm aluminum current collector and a SMG-A5 graphite anode on a 10 µm copper foil was used. Electrodes are separated by a Al2O3 based membrane (SEPARION S240P20, Litariion GmbH). This electrically insulating porous ceramic is characterized with a thickness of 21 µm, a porosity of 48% and a gurley number of 20 s. Cathodes are tailored to BLB2 standard with a shape of 105 mm×145 mm, anodes to 110 mm×150 mm and separator to 370 mm×156 mm. The electrode-separator compound (ESC) was then z-folded using 15 anode and 15 cathode sheets. After assembling, the ESC was enhouse in a pouchfoil bag. Therefore, commercial available pouch foil (Targray) was used and sealed on three sides. As a consequence, the bag was still open so that the ESV and also the electrolyte could be filled inside. The open cell was filled with V = 60 ml of the electrolyte solvent (EC/EMC with mass ratio 3:7) mixed with 50 Ma.% of a commercial iodine based contrast agent. Since the filling experiments could not be carried out in a dry atmosphere, the conductive salt was omitted. The contrast agent allows the visualization of the liquid electrolyte. Without contrast medium, neither the filling nor the wetting process would be resolvable.

Experimental setup: visualization and filling procedure.—The experimental setup depicted in Fig. 1 is integrated in an X-ray machine originally intended for quality inspection of electronic assemblies.

As the filling procedure typically is carried out with the cell standing to allow gravity to assist the transport of the fluid through the cell, a simple frame was utilized to stabilize the standing cell. This frame holds the cell and was placed between X-ray source and detector. To dose the electrolyte solvent a syringe and a hose were used and the cells manually filled. To visualize the filling process, the Viscom X-ray inspection system X8060 2DV3D for destruction free applications was used. This system is characterized by its horizontal beam direction to investigate objects up to a size of 660 x 510mm which enables investigations of cells in BLB2 scale. Parameters of the X-ray observation are the tube voltage of 120kV the tube current 339 µA and the exposure time of 160 ms.

Image interpretation.—The recorded video was split into single frames (depicted in Fig. 2) and visually analyzed. Contours of electrodes and separator are clearly distinguishable.

Once the contrast agent enters the cell (Figs. 2b and 2c), a stable but narrow flow front starts to develop. Further the fluids flow through the cell stack in thin, less stable paths becomes apparent. With more and more fluid entering the cell, the void volume within the electrode stack fills up, starting from the fluids point of entrance (Figs. 2c and 2d). Fig. 2d also clearly shows entrapped gas bubbles. As the cell was filled in a standard atmosphere, these bubbles mainly contain atmospheric gases induced by the filling process. Gasses entrapped in the separator and released by the wetting process are less visible.

Based on these observations the three effects of interest the entrapped gasses, the cells fill level and the fluids flow front are potentially quantifiable. First, the combined number of pixels representing a bubble can be utilized to quantify the amount of entraped gas. Second, the gray scale distribution which indicates the amount of fluid within the void spaces and the active material’s pores. Third, the width and locations of the fluids flow front can clearly be distinguished from the cells components by its contouring pixels.

Image processing.—For the first parameter, the number and size of entrapped gas bubbles, the contours of the bubbles need to be detected. To maximize the visibility of the bubbles contours, the processing pipeline starts with increasing the contrast of each image (Fig. 2b). Using the resulting image, the canny edge detection algorithm was applied. The canny edge detection algorithm combines various kernel operations to extract edges from input images and present them as a binary image, shown in Fig. 2c. The algorithms parameters were chosen for a single image, ensuring that as many contours of bubbles as possible were detected. Fig. 2c also shows other contours, such as the fluids flow path through the cells stack and the fluid level. To remove these contours, each connected contour was measured and contours vastly larger than any visible bubble discarded. Further thin contours resulting from a noisy input image are visible after applying the canny algorithm. To remove those, erosion and dilation filters were used. The remaining contours were filled using convex hulls and result in the image shown in Fig. 3d. Particularly tricky to detect are bubbles next to sparsely wetted areas, due to their low contrast. The detected contours of these bubbles tend not to be closed, which makes them prone to be removed by the erosion and dilation filtering. This effect can be see for some bubbles, when comparing Fig. 3a to Fig. 3d. Accordingly, the measured amount and area of bubbles is slightly lower than the actual amount of gas entrapped in the cell.
Figure 2. Filling procedure of a lithium-ion-pouch cell using X-ray imaging.

Figure 3. Image processing pipeline used for bubble detection – a: source Image, b: contrast optimized image, c: binary image acquired using canny, d: filtered and filled binary image, e: flow front, f: flow front filtered.

The second parameter, the filling level can be determined by averaging the gray scale values of the image. The darker the image, the more fluid is contained within the cell. The third parameter, the width and location of the fluids flow front can also be determined by applying edge detection algorithms, similar to the bubble detection. As primarily the width of the flow front at the point of entrance determines how much of the cells active material initially contacts the fluid, a narrow region of interest (ROI) was chosen to evaluate the flow front. Within this ROI, the contrast optimization, canny-algorithm, dilation, convex hulls and erosion were used to create the image shown in Fig. 3e. To extract the flow front, the tallest object with this image was retained, as seen in Fig. 3f. For determining the absolute width and location of the extracted flow front, a bounding box was fitted around it and measured in its dimensions and location.

Results and Discussion

The described image processing chain was applied to every frame of the recorded X-ray video. The filter parameters were determined based on one frame (Fig. 3a). Due to the length of the video sequence (88s at 16Hz = ~1400 frames), tuning the filter parameters for each frame was not feasible. As a result, the measured process parameters are most precise around the frame the filter parameters were tuned for (frame 600, see Fig. 3a). The progression of the overall area of bubbles shown in Fig. 4, was filtered using outlier detection and smoothing algorithms to remove some of the noise induced irregularities in the measurements.

Starting at around 100, the brightness drops down to ~63 around frame 1000 while fluid is dosed into the cell. After this point, the fluid flow stops and the images brightness starts to increase slowly, as fluid runs down the cell sheets into the lower part of the pouch which is not within the analyzed ROI. The small irregularities of the curve reflect the slight irregularities of the manual dosing procedure. Steeper declines (e.g. around frame 580) represent a higher fluid flow, while small jumps (e.g. around frame 910) represent bubbles entering or leaving the analyzed ROI. By measuring the amount of fluid used beforehand and enlarging the ROI to capture the entire cell, the system could be calibrated to indirectly measure the absolute amount of fluid within the cell. Using multiple calibration variations, even nonlinear correlations could be mapped. This approach is, compared to the canny based detection of bubbles, remarkably simple, yet effective. Both, the width and the location of the fluids flow front over the number of frames, displayed in Figs. 6 and 7, are almost constant.
Figure 5. Progression of the fill level of the cell during the filling procedure.

The width of the fluids flow front continually measures 76 pixels, whilst its location lies around pixel 300 and slightly varies as the cell is filled. Towards the process start and end, where no flow front is present, the algorithm tends to fail. As it uses the tallest detected contour to measure the flow front, it fails once the largest object no longer is the flow front. The width and location of the flow front for frames above 900 (the end of the fluid dosing) exemplify this. By manually setting the start and end of the measurement this behavior may be avoided. Based on the results and the visual inspection, the X-ray method is assessed as promising for the visualization and quantification of the filling processing of lithium ion batteries. The next stage should build on these results and focus on improving the X-ray process’ parameters and designing a test rig capable of realizing actual process constraints while fitting into the X-ray chamber.

Conclusions

This paper contributes a first analysis of the X-ray based visualization of the filling process of lithium ion batteries. The visibility and quantifiability of effects characteristic for the filling process were assessed. Therefore, a frame was constructed and applied to hold an open pouch based lithium ion battery cell in the X-ray chamber of an inspection system X8060 (Viscom) 2D/3D. While manually filling a contrast agent into the cell, an X-ray video sequence with high resolution, contrast and framerate was recorded. Visually analyzing the recording, the parameters of the amount of entrapped gasses, the filling level and the characteristics of the fluids flow front were derived. To quantify each of these parameter approaches based on image processing were proposed and implemented. Using these implementations, the progressions of the afore mentioned parameters were quantified. Filling with electrolyte including the conducting salt like LiPF₆ can be done by adjusting the experimental setup. Therefore, in the next step, a complete filling system will be integrated in an X-ray chamber, which enables filling in a dry atmosphere.

As the overall conclusion, based on the experiments carried out, X-ray as a method for understanding and quantifying the effects occurring when filling lithium ion battery cells seems promising. There is no other method known which can resolve the electrolyte distribution in cells with the shown amount of compartments. The extent to which the method can be integrated into a production line still needs further investigations e.g. how the contrast agent influences the battery performance.

These understandings can be utilized to further optimize filling process parameters. Thus an X-ray based method can potentially contribute to a significant rationalization of lithium-ion batteries production by minimizing the cost driving process time of electrolyte filling. Further the method could possibly be used for in situ and inline process monitoring and quality control of lithium ion battery production. Future research should focus on refining the X-ray procedure specifically for battery cells. Also the visualization of the filling procedure under actual process conditions should pursued to specifically allow the analysis of the wetting process. Once a procedure for reliably quantifying the filling and wetting processes is established, the optimization of the process parameters should be aspired.

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