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Visualization of electrolyte filling process and influence of vacuum during filling for hard case prismatic lithium ion cells by neutron imaging to optimize the production process

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HIGHLIGHTS

- First visualization of electrolyte filling process for hard case lithium ion cells.
- Application of vacuum can cut soaking time in half (experimentally shown).
- Vacuum also increases the amount of electrolyte soaked into the stack (+10%).
- Soaking of the electrode stack takes place mostly isotropic from all sides.
- Soaking speed is reduced over time, follows a logarithmical behavior.

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ABSTRACT

The process of filling electrolyte into lithium ion cells is time consuming and critical to the overall battery quality. However, this process is not well understood. This is partially due to the fact, that it is hard to observe it in situ. A powerful tool for visualization of the process is neutron imaging. The filling and wetting process of the electrode stack can be clearly visualized in situ without destruction of the actual cell. The wetting of certain areas inside the electrode stack can clearly be seen when using this technique.

Results showed that wetting of the electrode stack takes place in a mostly isotropic manner from the outside towards a center point of the cell at very similar speed. When the electrolyte reaches the center point, the wetting process can be considered complete. The electrode wetting is a slow but rather steady process for hard case prismatic cells. It starts with a certain speed, which is reduced over the progress of the wetting. Vacuum can assist the process and accelerate it by about a factor of two as was experimentally shown. This gives a considerable time and cost advantage for designing the production process for large-scale battery cell production.

1. Introduction

Lithium ion cells are becoming increasingly used in all kinds of applications from consumer electronics up to large cells for electric vehicles and stationary storage systems. Certain processes become more important in this context due to the substantially rising cell size.

The manufacturing process of lithium ion cells is generally known. There are three main parts to this process: electrode production, cell assembly and formation, i.e. start of electrical operation of the cell. The electrolyte filling and soaking is - combined with the pre-formation - the last process in the cell assembly step. However, the cells are not completely closed at that point. This is because early in the formation process a lot of gas is generated by parasitic electrolytic effects. This gas has to be removed from the cell before closing it.

For reducing the processing cost of lithium ion batteries the electrolyte filling process is a bottleneck in the cell production [1]. The filling process is critical as well, as it has to be conducted under a controlled, inert gas environment. This is necessary, as the electrolyte solution is highly hygroscopic. Thus, contact with humidity has to be avoided.

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The electrolyte filling process consists of two parts. First, the filling of the electrolyte into the cell, which is rather fast, only taking a few seconds to fill the void space in a cell with the liquid organic electrolyte solution. Secondly, the absorption of the electrolyte into the electrode stack, generally referred to as wetting or soaking process. This process is very time consuming – especially for prismatic hard case battery cells –, e.g. in the range of hours for large format cells used in electric vehicles or stationary applications. These two steps, filling and soaking, often have to be repeated several times. Between these single filling steps, the cells have to be stored under dry room conditions for several hours to obtain a homogeneous electrolyte distribution within the electrode stack.

There are several possible problems resulting from an incomplete wetting of the whole electrode stack. Incomplete wetting can result in an unnecessarily slow formation process. An equal distribution of electrolyte is further necessary as it has a crucial influence on the current distribution inside the cell and thus also the safety behavior, as it can cause lithium plating on the surface of the electrode. Even failures in cell operation or possible long-term performance decreases can result from inhomogeneous wetting [2,3].

The electrification of the powertrain demands for new lithium battery specifications, such as high gravimetric and volumetric energy densities [4]. To boost the energy density, besides increasing the cell size, inter alia the loading level of the electrodes has to be decreased. Furthermore the porosity of the electrodes is possibly decreased. Decreasing the porosity below a certain level could result in longer wetting times since the electrolyte intake into the porous medium is hampered [5–7]. Another approach to enhance the volumetric energy density is to decrease the void space in the battery cell. This, however, reduces the amount of electrolyte that can be injected into the cell in a single filling step and hence increases the number of necessary filling steps and wetting iterations.

To tackle the two main issues, the long process time and determination of percentage of wetted active material, several approaches were undertaken. Multilayer separators utilizing SiO_2-PMMA coating [8], cellulose nanofibers [9] or polymer nanofibers coated by a ceramic SiO_2 layer [10] showed an increased wettability compared to separators consisting only of PE/PP. Adding surfactants to the electrolyte or decreasing the lithium salt concentration have a positive influence on wettability and wetting speed, respectively [11,12]. A common method to decrease the electrolyte filling and wetting process time of hard case cells is to reduce the gas pressure in the cell prior to injecting the liquid (multiple patents [13–16]). Using impedance spectroscopy, Wu et al. suspected the wetting progress to be accelerated by applying vacuum to round cells prior to filling the electrolyte [12].

Process and design optimizations are mostly done empirically today. Nowadays, the wetting progress is monitored in laboratory experiments by waiting a certain time and opening the cell afterwards to determine its wetting state. From this determination, the production process parameters are derived with a rather large safety margin.

Despite its importance, the effective principles of the electrolyte filling and soaking are poorly known and understood. One reason for this lack of understanding is that it is impossible to follow the process optically due to the cell case and collector foils limiting the sight into the cell.

The only measurement for checking the process online in production is up to now an AC-impedance measurement [17]. A leveling off of the AC-impedance value at a low reading after a certain time only delivers a rough estimate about the wetting degree of the separator and electrode surface. It gives no clear indication about the wetting inside the electrode layer. The measured value for the AC-impedance is dominated by the ionic impedance of and between the surfaces as it is much higher than the dominant electrical impedance inside the electrodes. The effect of electrolyte soaked into the electrode cannot be reasonably measured by AC-impedance spectroscopy. Neither does it give a quantitative result for the completion of the wetting process. Today, quality control mostly relies on this value, however.

Thus, there is an urgent need for a technique, where the filling and wetting process can be visualized in detail and in situ, especially without destroying the cell and thus continually during the whole process. Such a probing technique is given by neutrons, which penetrate deep into materials because of their weak interaction with most elements. Due to their energy in the meV range they are completely non-destructive. Modern neutron sources as the FRM II [18] in Garching near Munich provide very high neutron flux (on the order of 10^8 neutrons/cm^2/s) at the sample position with a large beam cross section and hence enable the visualization of dynamic processes with good counting statistics. Thus, neutron radiography is ideally suited to study a whole cell (e.g. 100×150 mm^2) in situ and in operando. As lithium is a strong absorber for neutrons while many metals can be easily penetrated, the visualization of complete battery cells is possible. Furthermore, the high contrast that neutron imaging provides for hydrogen makes this technique ideally suited for the visualization of the distribution of the organic electrolyte in batteries, containing a lot of hydrogen atoms.

Using neutron radiography, Knoche et al. gained valuable knowledge about the electrolyte wetting behavior of pouch cells. By applying various courses of pressure to the cells, the electrolyte uptake of the stack could be increased. Additionally, flow paths of the liquid were identified [19]. To our knowledge, no in depth research on prismatic hard case cells with focus on vacuum filling was reported in the literature yet. As the electrolyte filling and wetting behavior of hard case cells is expected to significantly differ from round cells and pouch cells (stiff hard case, limited electrolyte reservoir), research is urgently necessary and first results are provided in this paper.

Goal of the work was to visualize the electrolyte filling and wetting process for hard case prismatic cells and to determine the influence of vacuum on the wetting process. From these findings, valuable guidance for improving the process was derived.

2. Experimental

For our experiments, cells in hybrid electric vehicle (HEV) format made of aluminum were used. According to DIN SPEC 91252 for

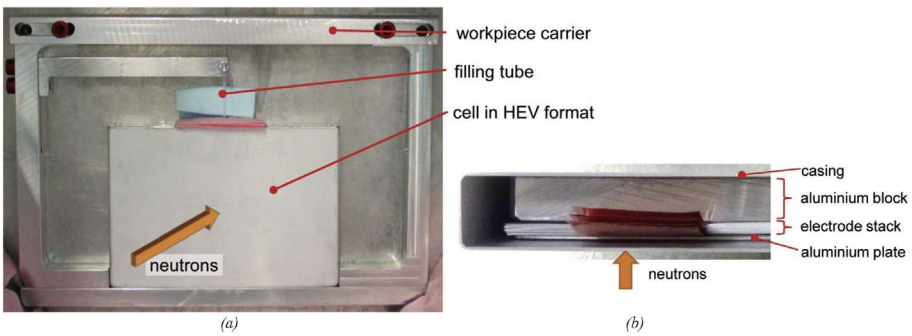

Fig. 1. (a) HEV cell in vacuum chamber; (b) cell can with electrode stack with reduced number of layers without lid in top view; neutron beam direction indicated by orange arrows. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)