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# In situ visualization of the electrolyte solvent filling process by neutron radiography

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## HIGHLIGHTS

- A method for observing the electrolyte filling process of Li-ion cells is proposed.
- The spreading of electrolyte liquid is observed in-situ with neutron imaging.
- A filling device with vacuum chamber is run in a neutron radiography instrument.
- The influence of process parameters on the wetting behaviour is derived.
- The results enable a better understanding of the electrolyte filling process.

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## ABSTRACT

In the manufacturing of Li-ion battery cells, filling with electrolyte liquid is a crucial step in terms of product quality and cost. To gain insight into the process phenomena, a non-destructive imaging method is presented. It is shown that the spreading of electrolyte liquid within the cell during filling and wetting can be visualized by neutron radiography. The experiment allows for the first time to visualize the soaking behaviour of electrolyte liquid in battery cells. The influence of the process parameters on the wetting behaviour is studied and flow paths of the liquid are identified. The electrolyte intake into the cell stack is discussed with two different analytical approaches. Based on the experimental data, the production process can be optimized, leading to stable cell performance and cost reduction due to faster processes and lower scrap rates.



## 1. Introduction

Lithium-ion batteries (LIB) have been established in consumer electronics for more than two decades. Meanwhile they have advanced to large-scale applications and are promising candidates for application in electromobility and stationary energy storage. The trend towards large-scale cells presents manifold challenges to production technology due to the limited scalability of the established production processes [1], resulting in high prices and large quality fluctuations [2,3] Besides the development of cheaper components and active materials, optimizing the production processes is one way to achieve lower cost and also stable product quality. One of the most difficult and critical steps in cell production is electrolyte filling. Applying low pressure on the cell before, during or after dosing the electrolyte liquid appears to be the commonly accepted method. For this purpose, the assembled electrode stack in the (unsealed) housing is placed in a vacuum chamber equipped with a dosing device. This paper will focus on pouch bag cells, which are sealed under low pressure at the end of the filling process before the vacuum chamber is flooded with air [4]. The injected electrolyte is drawn into the pores of the electrodes and separator by capillary forces.

After electrolyte filling, the LIB cells are warehoused to enable a homogeneous distribution of the liquid [4]. This so called wetting process is a distinctive bottleneck in cell production especially in large-size cells due to poor wettability, long diffusion distances and gases trapped within pores [5,6]. As shown in Ref. [7], the electrode

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manufacturing as well as the wetting process reveal a high potential to reduce costs in cell production. Besides its impact on cost, the electrolyte filling process and the resulting distribution of electrolyte liquid have a high influence on the product quality.

Despite the difficulty of the process, reliable scientific data on the subject is scarce. Several approaches for filling LIB cells with electrolyte liquid have been reported in patents, see e.g. Refs. [8–11]. As deducted in Ref. [12], the broad range of solutions shows that the process has not been sufficiently understood.

The visualization of a production process is an important means to foster the understanding of its behaviour. Visualizing the electrolyte filling process is challenging. Electrodes, separator sheets and the housing of the cell are obviously not transparent to visible light. Usually, a LIB cell is filled under low pressure conditions in a vacuum chamber, which complicates in-situ observation of the process. Due to these reasons, the spreading of electrolyte liquid in and between the cells layers during the filling process has not been visualized yet.

This paper describes the experimental setup, the procedure and the transmission neutron imaging approach to gain insight into the phenomena of the electrolyte filling. The purpose of the experiment was to visualize the spreading of electrolyte liquid within the cell. An automated filling device, comprising a vacuum chamber with dosing and sealing functionality, was set up in a neutron radiography instrument (ANTARES operated at Heinz Maier-Leibnitz Zentrum (MLZ) in Garching, Germany [13]). The pouch bag cells were imaged in-situ while being filled with electrolyte liquid. The radiographic images allow tracing the liquid within the cell. The influence of process parameters on the intake of electrolyte liquid is derived and the wetting behaviour is characterized using analytical approaches. The results allow drawing conclusions for the optimization of the filling process and the battery itself.

## 2. Neutron radiography

### 2.1. Fundamentals of neutron radiography

Radiography is an imaging technique that transmits a beam of radiation through an object to visualize its internal structure. If a beam of the intensity $I_0$ is applied to an object, the intensity $I$ of the passing radiation is diminished according to the particular attenuation coefficient $\mu$ of the screened object. This principle is described by the Lambert-Beer-law as follows:

$$I = I_0 \cdot e^{-\int \mu(x,y,z)\, ds} \quad (1)$$

The intensity of the transmitted radiation is detected by a position sensitive detector behind the object. The probably most popular transmission imaging method is X-ray imaging [14]. Neutron radiography (NR) is an alternative transmission imaging method using neutron radiation for the image acquisition [15].

While X-rays mainly interact with the electron shell of atoms, neutrons interact with the nuclei. Due to this elementary difference in the physical principle of interaction, neutrons are strongly attenuated by some light elements like hydrogen, lithium or boron whereas metallic elements like aluminium hardly alter the beam intensity [16]. NR therefore allows to visualize different materials than with X-rays and is often complementary [14].

### 2.2. Neutron imaging methods for LIB

Neutron imaging methods have been applied to visualize various phenomena in the context of energy storage [17,18], but never regarding the production of LIB. In Ref. [19], NR was used to visualize gas evolution on graphite electrodes during charging. It was shown that by NR, gas entrapments can be distinguished from the liquid electrolyte. A quantitative analysis of the gasing of electrolyte was shown and discussed in Ref. [20]. In Ref. [21], NR was used for non-destructive testing of macroscopic changes during charge/discharge of a prismatic lithium-ion cell. The consumption of excess electrolyte during the first cycles was shown. The authors therefore concluded that NR could be a useful tool for optimizing the soaking of the electrolyte liquid.

The electrolyte liquid can be detected because its hydrogen groups present a much higher mass attenuation coefficient to the neutrons than other cell materials and the aluminium of the experimental setup [16]. In the NR image, the electrolyte liquid therefore appears darker than other components. If parts of the cell are not wetted, the neutrons are less attenuated, and the dry spots appear bright on the NR images. Therefore, the electrolyte liquid within the battery can be localized. Here, this effect was utilized to visualize the spreading of electrolyte liquid in situ during the filling process.

## 3. Experimental

### 3.1. Experimental setup

This work is based upon experiments performed at the ANTARES instrument operated at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching, Germany. Further details on this instrument can be found in Refs. [22,13]. A vacuum chamber was placed in the neutron beam close to the detector. Fig. 1 (left) shows a schematic drawing of the experimental setup, whereas Fig. 1 (right) displays a photo of the vacuum chamber containing a sample. The ambient and electrolyte temperature was kept at a constant temperature of 25 °C at an ambient pressure of approx. 950 mbar.

#### 3.1.1. Pouch bag cells

The experiment was conducted with pouch bag cells manufactured on automated machinery at the Technical University of Munich. Each cell stack consisted of four cathode sheets, five anode sheets and a z-folded Polyethylene separator (Brueckner Evapore®). The electrode material was coated on both sides with average porosities of 30% and of commercial origin. The footprint of the cathode coating was 101 × 73 mm$^2$. The z-folded cell stack with lateral tabs was sealed into a standard pouch foil. The top end of the pouch bag remained open for introducing the liquid. As the thickness of the cell stack was approx. 1.2 mm, the pouch foil was not deep drawn. A mixture of ethyl carbonate (EC) and ethyl methyl carbonate (EMC; weight ratio EC:EMC of 3:7) was used as electrolyte liquid. $LiPF_6$ was not included for security reasons as neither

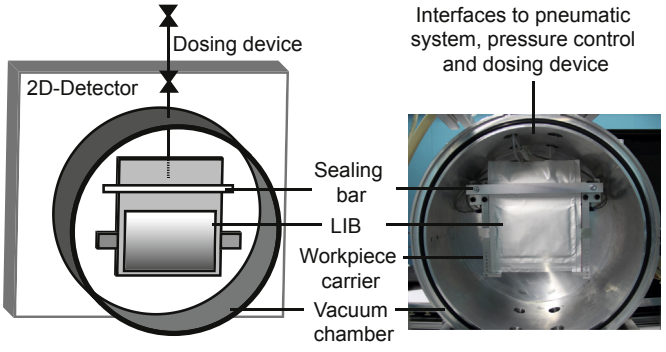


**Fig. 1.** Drawing (left) and photograph (right) of the experimental setup including the relevant components.