

EIS in Wetting of Lithium-ion Battery Materials

Introduction

Lithium-ion batteries (LIBs) as electrochemical energy storage systems are key substitutes for fossil fuels. They are valuable also because of their low weight, high energy-density and long service life. These batteries have established a dominant role in consumer electronic markets and triggered the success of mobile devices like cell phones and portable computers. But improvements, such as better prices and efficiency, are still required.

To make LIBs, packaged cells need to be filled with an electrolyte so that lithium ions can move freely between cathode and anode. After this filling step the nearly finished battery needs time to absorb the electrolyte into all its pores before it can be charged for the first time (called *formation*). This waiting period is crucial in order to achieve a high-quality product with long service life. In today's industrial production, this waiting period, also called *wetting*, is merely estimated based on experience, and validated with cell tests. This raises the question of how to reduce or even remove this bottleneck in production and therefore lower the costs significantly.

Florian Günter and colleagues at the Technical University of Munich in Germany posed precisely this question, and we give (with their permission) their results.

Theory

Every electrical system has key characteristics which describe how that system works and how it reacts to external excitation. One characteristic is the impedance, which combines different aspects of electrical resistance. If we drive an electrical system with a sinusoidal signal (with particular frequency), the resulting system response may have a different amplitude and phase-angle (shifted in comparison to the input signal). This behavior is quantified by the impedance, which, on the one hand demonstrates the ability of a system to resist the flow of electrical current (different amplitude), and, on the other hand, reflects the ability of a circuit to store electrical energy on a short term (different phase-angle). But how do we measure the impedance? A powerful

nondestructive way to do so is electrochemical impedance spectroscopy (EIS). (See our Application Note "[Basics of Electrochemical Impedance Spectroscopy](#)".) By applying a sinusoidal current (or voltage) over a range of frequencies, and measuring the sinusoidal voltage (or current) response, it is possible to determine the system's impedance at each frequency.



Figure 1. Schematic of EIS on a lithium-ion battery.

Previous experiments on LIBs have shown that, during wetting, the ohmic resistance (HFR) of a LIB changes until it is fully wetted and therefore reaches its final value. Considering this phenomenon, we can continuously measure the HFR of the cell through EIS and hence evaluate if the cell is completely wetted. In this way, we can resolve the problem of inaccurate waiting times.

Experiment

To prove there is a correlation between the impedance and wetting status we had to find a nondestructive way to see what happens in the cell while constantly measuring the impedance. One way to achieve this is neutron radiography (NR). By transmitting neutrons through an object and detecting the neutron density behind the object, it is possible to gather an image during the detection time. This imaging technology (similar to x ray imaging) is especially useful, because (other than x rays) neutrons interact with a few light elements like hydrogen, lithium or boron. Thus, the beam won't get absorbed heavily by the aluminum case or the electrodes of the battery, but instead will interact with the electrolyte itself. Thus this technology is suited to monitor the wetting status of the cell nondestructively.

We constructed a mobile filling station in order fill the cell at the instrument where we performed the neutron radiography (Fig. 2). Completing the experimental setup, we used a Gamry Instruments Interface™ 5000E potentiostat to perform EIS during the entire wetting period.

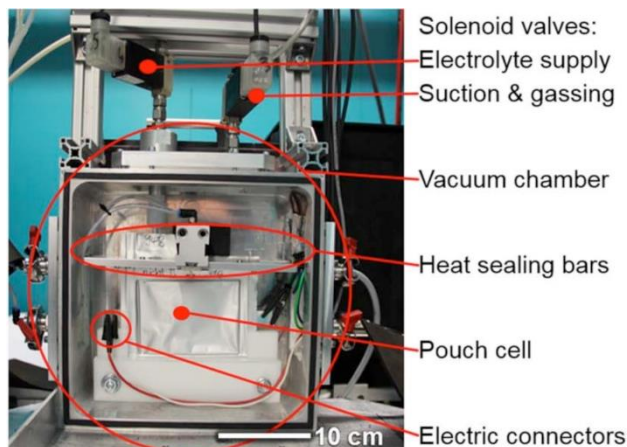


Figure 2. Internal view of the filling station.

The measurement sequence consisted of an open-current potential (OCP) and EIS measurements, and was programmed to repeat itself over 90 min. First the OCP was measured over 15 s with a sample period of 0.5 s. Subsequently the EIS ran from of 100 kHz to 1 Hz with 10 points per decade and an amplitude of 10 mV rms as an AC excitation signal applied to the cell. We performed the tests on two different LIBs with different electrode characteristics so that we could compare the different results and confirm the validity of these experiments.

Results

The images in Fig. 3 were taken at different times after filling of cell A through NR. The wetting degree was defined by comparing the amount of gray and white pixels of the pictures. The gray pixels represent a threshold neutron-density value by which the cell can be seen as wetted. Plots of the wetting degree over the time (the pictures were taken) are shown in Fig. 4. If we now look at the validated data of EIS measurements (Fig. 5), in which we extracted the HFR and plotted it over time (of each data point) we get the upper plot. On the bottom is a comparison of both wetting degree and HFR over time.

We can clearly see the correlation of both approaches to determine the wetting degree in this specific case.

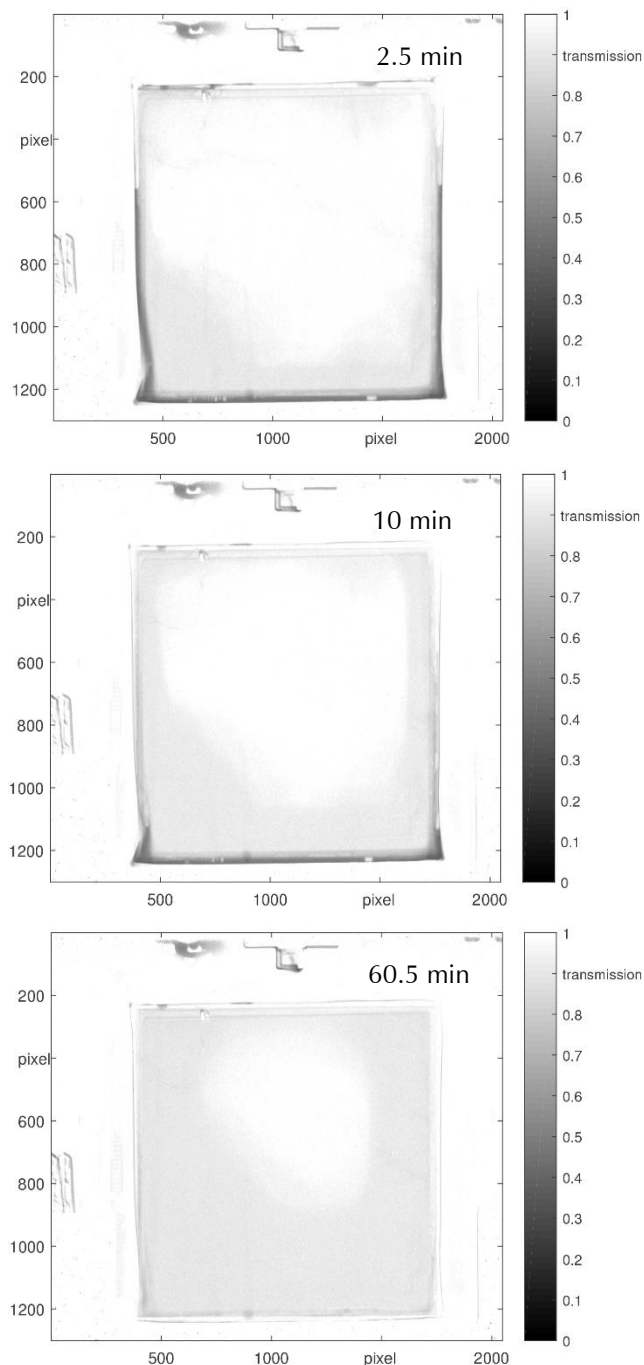


Figure 3. Neutron-radiography images of battery A taken 2.5, 10, and 60.5 min after filling.

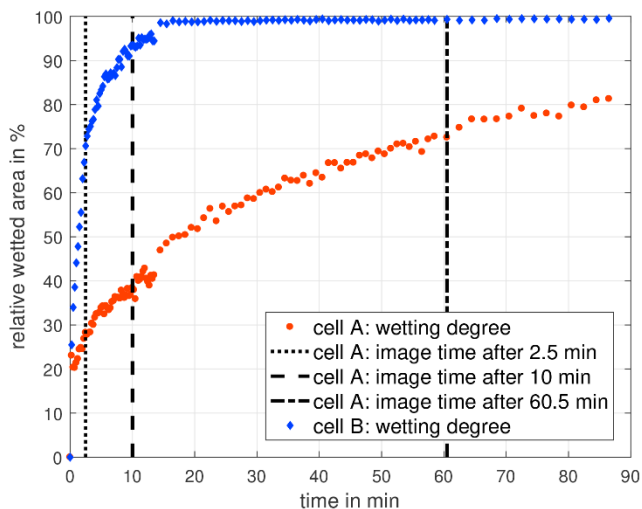


Figure 4. The wetting degree of battery A (red, unstructured, 30% porosity) and battery B (blue, structured, 30% porosity) with respect to time.

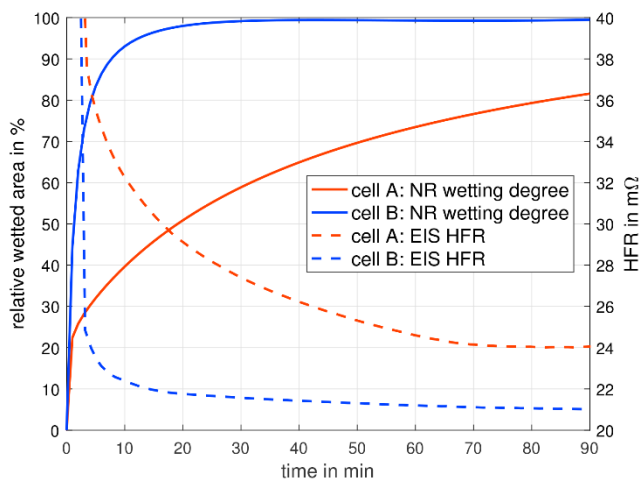
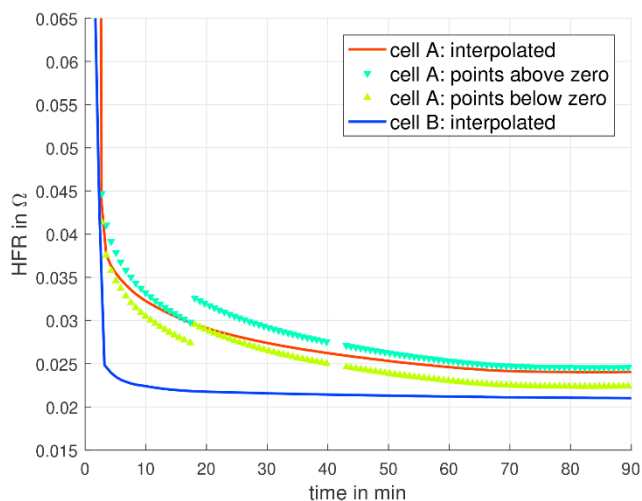


Figure 5. (Upper) HFR plotted over time. (Lower) Comparison of wetting degree and HFR with time.

We can also make statements about other characteristics of the cell. In Fig. 6, if we examine the HFR plot of battery A 87 minutes after filling, for instance, the plot suddenly doesn't change its value. Comparing this with the last-taken NR picture in which the wetting degree is just over 80% and grey areas are not as grey as the ones of cell B, we have an indication that cell A was insufficiently filled.

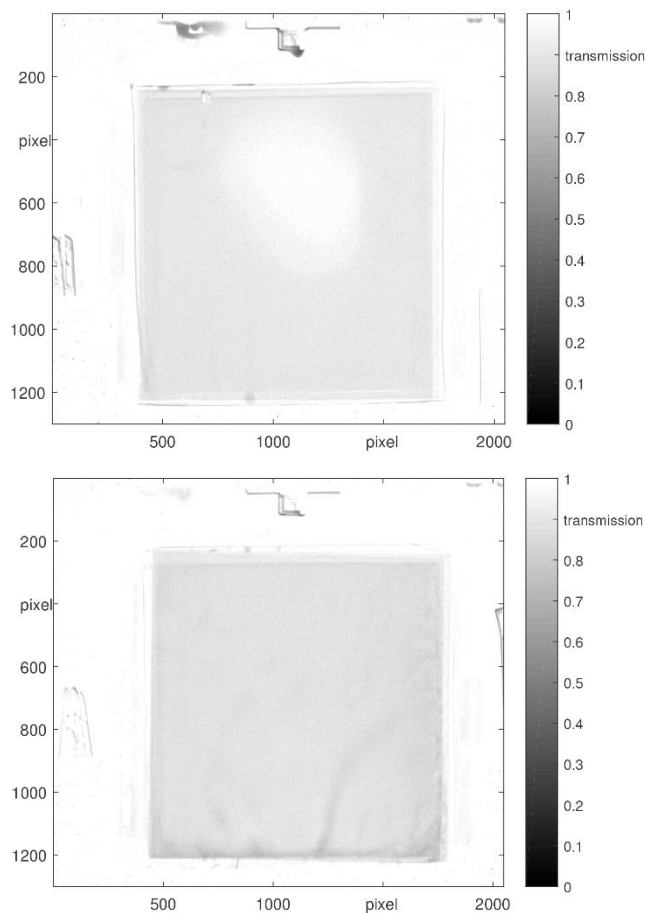


Figure 6. NR images of (upper) cell A and (lower) cell B. Note the large blank area in cell A, indicating insufficient wetting.

Conclusion

The authors conclude that the electrochemical impedance changes during the wetting process of LIBs. In particular, the HFR is directly linked to the wetting state of the cell. They can produce stable measurements without influencing the cells by charging or other means. As a result, the researchers propose the idea of using the observed correlation to directly determine the minimum time required per cell for wetting in production. Note that the experiments are not enough evidence to draw quantifiable conclusions. Therefore, future research of the authors will focus on

quantification of this effect and the reliability of the method to ensure a high accuracy and stability of the measurements

In future LIB production the researchers envision the use of EIS measurements in order to reduce time and cost of the overall process through precisely triggered formation without any dead waiting time. Additionally, it may be possible to directly cull bad cells and thus improve efficiency of the process. That is, the filled cell would directly be connected to a multichannel instrument like

our EIS Box™. A software script would constantly check, via EIS, the wetting state of a cell and automatically trigger the formation at the exact moment.

For more information on this use of EIS for assessing the quality of LIBs, see Florian J. Günter, et al., *J. Electrochem. Soc.*, **165** (14) A3249–A3256 (2018).

EIS in Wetting. Rev. 1.0 1/7/2019 © Copyright 2018 Gamry Instruments, Inc. Interface and EIS Box are trademarks of Gamry Instruments, Inc.



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