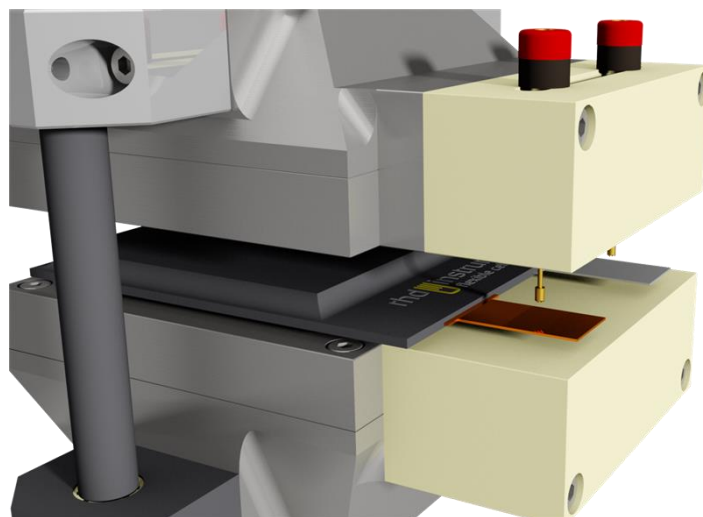




# Application note

## *In Operando* Pouch Cell Thickness Monitoring during Cycling under Controlled Temperature and Pressure



## Introduction

Pouch cells constitute an important step in the battery development process, as certain performance parameters cannot be determined with small coin cell tests. It is also a popular commercial cell format with high specific energy and power. Characterization of pouch cells requires precise control of the testing conditions, such as the temperature and pressure applied to the cell stack. The temperature should be measured – and ideally also controlled – for each individual cell, since heat will be produced internally during cycling [1]. Pressure has been shown to have a large impact on the cycle life of lithium-ion battery pouch cells [1, 2, 3, 4, 5]. For lithium-metal batteries, the effect of pressure is even greater [6]. The pressure needs to be applied uniformly to the cell stack, since inhomogeneities accelerate ageing [1, 4]. Active pressure control, rather than passive control *via* springs, has also been shown to be beneficial to cycle life [5]. Since the anode and cathode swell and contract during normal operation (and also as an effect of ageing), *in operando* monitoring of the pressure can be used as an indicator of state of charge (SOC) and state of health (SOH) [2]. Observing the pouch cell thickness during cycling can also be used to gain a deeper understanding of the electrochemical performance and the underlying electrode reactions [1]. Unfortunately there are very few technical solutions on the market that are suitable for this type of measurement.

## Experimental

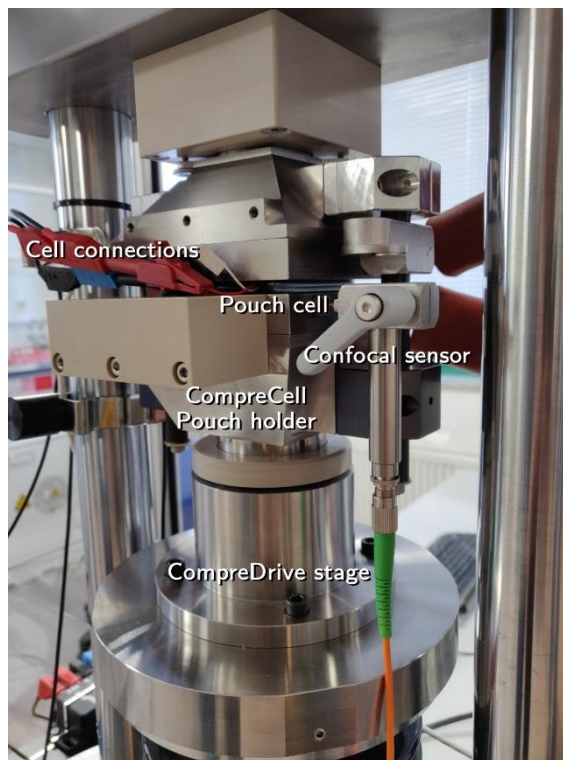
For this application note, a commercial pouch cell type rechargeable lithium ion battery (ICP606168PRT, Renata AG) with a nominal capacity of 2800 mAh and a nominal average voltage of 3.7 V (Figure 1) was used. It had a LiCoO<sub>2</sub> (LCO) cathode and a graphite anode, with LiPF<sub>6</sub> in ethylene carbonate / ethyl methyl carbonate / diethyl carbonate (1 : 1 : 1) electrolyte and a polyethylene / polypropylene separator.



Figure 1. Lithium ion battery pouch cell tested herein.

The battery terminals (B+/B-) were connected to a protection circuit that can disconnect B- under abnormal voltage or current conditions by a MOSFET (STG8209). Under normal working conditions, the protection circuit did not affect electrochemical impedance spectroscopy (EIS) (*i.e.* no significant difference was observed between EIS spectra when connected directly to B+/B- compared to the protected terminals P+/P-). The dimensions of the pouch cell itself (excluding protection circuitry) without any pressure applied was 63.1 mm

× 58.3 mm × 5.3 mm. According to the data sheet, the cell should withstand being pressed between two flat plates at a force of 13 kN (3.5 MPa) at 100% SOC without explosion or fire.



**Figure 2.** Experimental setup with the pouch cell mounted in the CompreCell Pouch cell holder within the CompreDrive.

The cell fixture used here was a CompreCell Pouch 10S HC cell holder mounted in a CompreDrive unit (rhd instruments GmbH & Co. KG) fitted with a confocal distance sensor add-on (Micro-Epsilon Messtechnik GmbH & Co. KG) and a 10 kN force sensor. A Huber Unistat 405 circulator (Peter Huber Kältemaschinenbau AG) with an external Pt100 sensor placed in the CompreCell Pouch cell holder was used for temperature control. The software

CompreDriveControl 1.13 (rhd instruments GmbH & Co. KG) with the rhd MicroEpsilon Confocal Server plugin (rhd instruments GmbH & Co. KG) was used for data logging and control of the CompreDrive and circulator. The pouch cell P+/P- terminals were contacted by alligator clips, rather than by the standard CompreCell Pouch pins, which are used for flat tabs (see figure on title page). The experimental setup with the pouch cell in place can be seen in Figure 2. After the CompreDrive stage was approached (8.2 kPa applied stack pressure for this size of pouch cell), the distance value of the confocal sensor was tared according to the *ex situ* measured cell thickness.

A Metrohm Autolab PGSTAT302N equipped with a FRA32 module and controlled through the NOVA 2.1.5 software was used for all electrochemical measurements. The tests were automated through the CompreDriveRemote 1.13 (rhd instruments GmbH & Co. KG) functionality, allowing automated control of the CompreDrive pressure and temperature from a NOVA procedure. The standard parameters of the charge/discharge protocol were as follows: The cell was charged by a C/2 (1.4 A) constant current (CC) to 4.2 V, followed by a 4.2 V constant voltage (CV) stage to C/20, and a 30 min rest period. The discharge was done by a C/2 CC to 3.0 V, followed by 30 min rest. The C-rate was calculated based on the nominal capacity of 2800 mAh. At each new temperature or

pressure setpoint, a 3 h equilibration time was employed after the temperature and pressure values had stabilized, to allow the pouch cell to settle before proceeding.

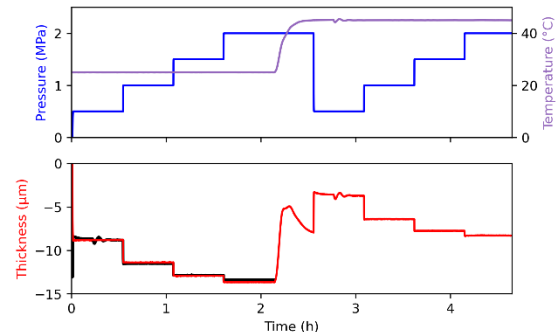
Initially, a temperature of 25 °C and a pressure of 0.5 MPa was applied to the cell, and three charge/discharge cycles were performed to verify the cell capacity. EIS was then measured at varying temperature, pressure and SOC, which is described in a separate application note [7]. Afterwards, the cell was cycled at 5, 25, and 45 °C and 0.5, 1.0, 1.5, and 2.0 MPa (3 cycles per condition). Finally, 6 cycles were performed at the initial conditions (25 °C, 0.5 MPa) to reveal any ageing effects. Throughout all testing, the thickness of the pouch cell was monitored *in operando*.

**WARNING!** Lithium-ion batteries are flammable! Thermal runaway can be caused by applying improper voltage, current, temperature or pressure to the cell!

## Results

In order to quantify the contribution to the variation in thickness originating from the CompreCell Pouch holder itself, a pressure and temperature ramp experiment was performed without a cell present (Figure 3). The thickness equilibrated within 10 seconds in response to pressure steps, and within one hour to temperature steps, after which it remained stable, without any

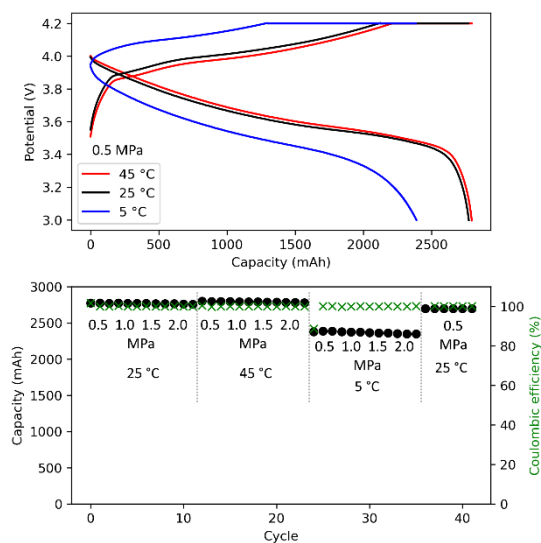
noticeable drift. The thickness offset between 0.5 and 2.0 MPa originating from the cell holder was less than 5 µm.



**Figure 3.** Pressure/temperature ramp measurement performed without any pouch cell in the CompreCell Pouch holder. The upper graph shows the pressure (blue, left y-axis) and temperature (purple, right y-axis), and the lower graph shows the distance sensor reading (red). The black curve in the lower graph represents an overlay of the data at 45 °C on top of the 25 °C data, using 0.5 MPa as a reference.

Under the standard cycling protocol described above, the initial discharge capacity of the pouch cell was 2780 mAh, in close agreement with the nominal capacity. Upon further cycling, the capacity decreased by about 2 mAh per cycle (99.9% cycle-on-cycle charge efficiency). The overpotential decreased with temperature, while the capacity increased accordingly (Figure 4). This is in accordance with the EIS behaviour observed for the cell [7]. The pressure only had a minor impact on the charge/discharge behaviour, with slightly higher discharge capacities at higher pressures. It is expected that the pressure would have significant impact on the cycle

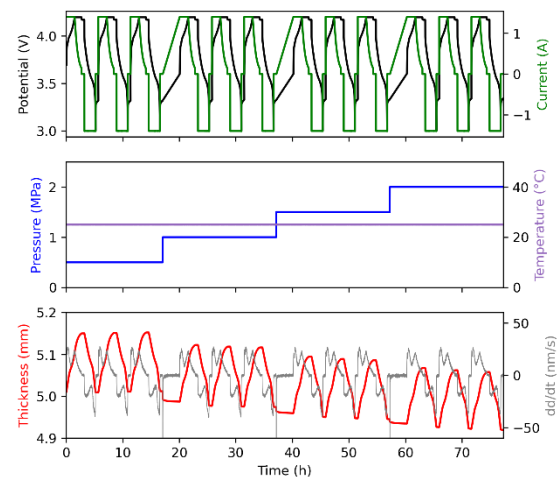
life [1, 3], but such long-term effects were not investigated here.



**Figure 4.** The upper graph shows charge/discharge curves at 45, 25, and 5 °C (3<sup>rd</sup> cycle for each temperature at 0.5 MPa shown). The lower graph shows the discharge capacity (black circles, left y-axis) and coulombic efficiency (green crosses, right y-axis) during the cycling procedure.

The cell potential and current, as well as the measured pressure and temperature of the cell, for the first cycles measured at 25 °C can be seen in **Figure 5**. Also the *in operando* cell thickness ( $d$ ) is shown, together with its time derivative ( $dd/dt$ ), showing that the pouch cell swelled by around 0.14 mm upon charging. This corresponds to 2.6% of the total thickness of this LCO based pouch cell, which is more than previously reported for other cell chemistries such as  $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$  (NMC, 1.5%) [8] and  $\text{LiFePO}_4$  (LFP, 0.8%) [9]. The cell was increasingly compressed at higher pressures, and the cell thickness

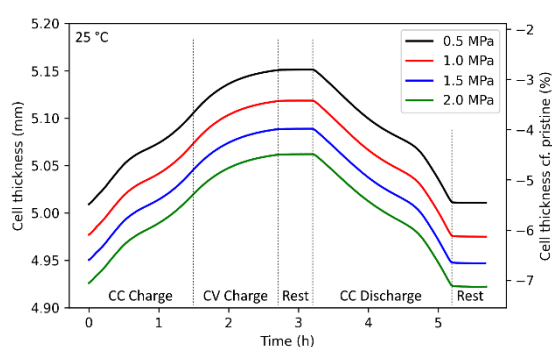
increased again upon returning to a lower pressure. It did however not return to the original thickness due to a degree of plastic deformation. It is also evident that even after the equilibration time of 3 h after each new pressure setpoint, the cell thickness was not completely stable, but still showed a small drift. Additionally, the three cycles at each pressure setpoint were not identical. Hence, a longer equilibration time, as well as additional cycles at each condition, would be necessary to ensure a completely stable cell thickness baseline.



**Figure 5.** Excerpt of the cycling data (first twelve cycles). The upper graph shows the cell potential (black, left y-axis) and current (green, right y-axis), the middle graph shows the pressure (blue, left y-axis) and temperature (purple, right y-axis), and the lower graph shows the measured cell thickness (red, left y-axis) and its time derivative (grey, right y-axis).

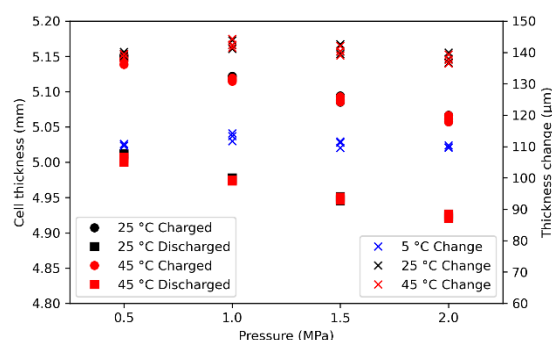
The cell thickness for one cycle at each pressure (25 °C) is shown in **Figure 6**. During the rest periods, the cell thickness was stable, showing only very minor signs

of relaxation. The cell thickness changed more slowly in the middle of the charge or discharge processes compared to the beginning or end. This is also evident as two separate peaks in  $dd/dt$  (Figure 5). The changes in cell thickness during cycling arises from the electrode layers, which expand as lithium is intercalated or inserted and contract upon losing the lithium ion. The relative extent to which this happens on the anode and cathode determines the overall thickness variation during cycling. Since the cell thickness increased during the charging process, when lithium is removed from the  $\text{LiCoO}_2$  cathode and intercalated into the graphite anode, the anode evidently undergoes larger thickness changes than the cathode in this cell. Graphite itself has been shown to exhibit a two-stage thickness change during lithium intercalation [10], and the cell thickness behaviour observed here can therefore be assumed to be dominated by the graphite anode.



**Figure 6.** *In operando* cell thickness during one cycle at each pressure (25 °C, 2<sup>nd</sup> cycle at each pressure setpoint shown). The right y-axis shows the thickness relative to the pristine pouch cell (without applied pressure).

The cell thickness in the charged and discharged states was very similar at 25 and 45 °C, and decreased more or less linearly with pressure (Figure 7). Moreover, the charged and discharged states were affected by pressure to the same extent, so that the thickness change was relatively constant with pressure. This indicates that the cell can exert very high forces on the cell holder if not allowed to expand, highlighting the need for pressure control. This can be achieved either through flexible spacers for passive pressure control, or by active pressure control as in the case of the CompreDrive.



**Figure 7.** Cell thickness (left y-axis) vs pressure in the charged (circles) and discharged (squares) state, respectively, at 25 °C (black) and 45 °C (red), (all three cycles shown for each condition). Crosses show the charge/discharge thickness change (right y-axis), also including data at 5 °C calculated from the motor position.

Unfortunately, condensation on the confocal sensor mirror at 5 °C lead to uncertainties in the data measured at that temperature. Further development is underway to allow for low-temperature

measurements using this sensor in the near future. Nonetheless, it is also possible to calculate the cell thickness changes from the motor position information of the CompreDrive servo motor that is used to apply the pressure to the cell. This allows for cross-checking of the obtained thickness values, and in this case for an auxiliary source of thickness variation data at low temperatures. The value of the charge/discharge thickness change calculated from the motor position and the confocal sensor matched closely for 25 and 45 °C (within 10 µm). Therefore, the charge/discharge thickness change at 5 °C was evaluated from the motor position rather than the confocal sensor data. The charge/discharge thickness change was much smaller at 5 °C than at the higher temperatures (Figure 7), most likely due to the incomplete discharge process as a consequence of the higher overpotential (Figure 4).

## Summary

The *in operando* thickness was monitored for a commercial lithium-ion battery pouch cell during cycling under active temperature and pressure control. The total pouch cell thickness increased by 2.6% during charging and decreased correspondingly during the discharge. The thickness variation occurred in a two-stage process, following the behaviour of the graphite anode as lithium was intercalated. The battery performance was comparable

at 25 and 45 °C, but at 5 °C the overpotential was larger, and the useable capacity decreased accordingly. The CompreDrive system with the CompreCell Pouch cell holder allows for active pressure control and applies uniaxial and homogeneous pressure to the cell stack, which is necessary for high reproducibility. The confocal distance sensor add-on increases the possibilities for precise measurements of the thickness during operation, aiding in the cell development process by providing deeper insights into the cell performance.

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