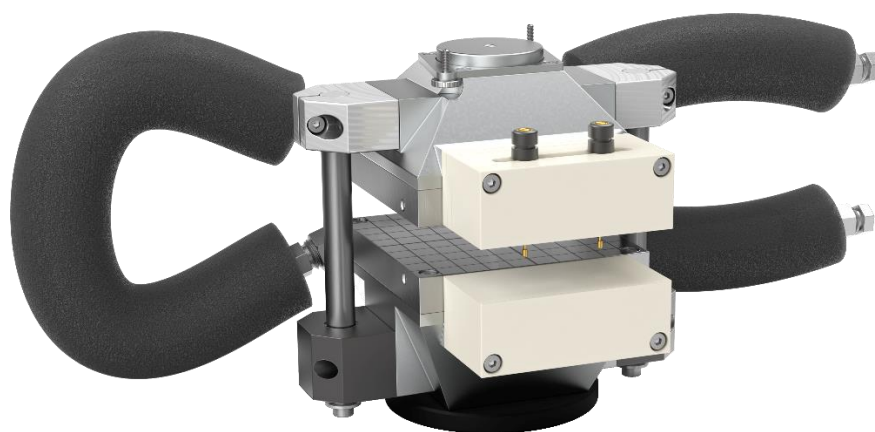




Application note

Lithium Metal Solid-State Pouch Cell: Pressure Dependence of Rate Performance



Introduction

The realization of lithium metal anodes in solid-state batteries is currently a high-priority research target, as it has the potential to drastically increase energy density [1, 2]. In order to achieve high safety, longevity, and power of lithium metal solid-state battery cells, several challenges still remain, many of which are related to the compatibility of the solid electrolyte with the lithium metal, and the interface between them [1, 2]. Often, a solid electrolyte interface (SEI) layer is formed *in situ*, and its properties are crucial for the cell performance [1, 2]. For example, the ionic conductivity of the SEI layer has a huge impact on the specific power and rate capability of the cell [1, 2].

Since lithium is repeatedly stripped and plated during cell cycling, the environment close to the interface is constantly changing, both chemically and mechanically [1]. Preferably, a homogenous and dense lithium metal layer should be generated each cycle, avoiding porous (“mossy”) lithium, disconnected (“dead”) lithium, or lithium dendrite formation [2]. One critical parameter influencing the lithium stripping and plating is the pressure acting on the cell stack [1, 3]. Pressure optimization has been successfully applied to improve the longevity and rate performance of lithium metal batteries. Furthermore, pressure monitoring during cycling can be used to gain insights into the reversible and irreversible volume changes occurring during cycling.

In this application note, we show the influence of pressure on the rate performance of a solid-state pouch battery cell comprising a lithium iron phosphate (LiFePO₄, LFP) cathode, a lithium metal anode, and a poly(ethylene oxide) (PEO) based electrolyte. The CompreFrame [4] with CompreCell Pouch [5] was used to subject the cell to a range of pressures. In this setup, the actual pressure is continuously monitored during cell cycling and a stiff spring acts to minimize pressure changes as a result of internal or external influences. The temperature is measured close to the pouch cell surface and can be automatically controlled via an external circulator.

Experimental

The pouch cell was produced as described elsewhere [6], with a 5.0 × 5.0 cm² lithium metal anode and a 5.5 × 5.5 cm² LFP cathode (47.7 mAh nominal capacity), separated by a 6.5 × 6.5 cm² PEO based solid electrolyte film. The cell was placed in a CompreFrame [4] equipped with a 2 kN force sensor and a CompreCell Pouch 10S cell holder (rhd instruments GmbH & Co. KG, see title page figure [5]) and was connected to a Presto A40 circulator (Julabo GmbH). CompreDriveControl 1.14 together with CompreFrameControl (rhd instruments GmbH & Co. KG) was used for temperature control and data logging.

A Biologic SP-200 potentiostat/galvanostat controlled by EC-Lab 11.52 (Biologic) was used to charge the cell at C/10 and discharge at different C-rates.

The cell potential limits were set at 2.0 V and 3.7 V. All measurements were carried out at 80 °C. At each new pressure level, the cell was allowed to equilibrate for 3 hours before the start of cycling. Edelweiss (rhd instruments GmbH & Co. KG) was used for data analysis and for creating the figures.

Results and Discussion

The LFP | Li pouch cell exhibited very flat charge and discharge plateaus at 3.50 V and 3.35 V, respectively (Figure 1), which is expected since the LFP delithiation is accompanied by a phase change [3]. The applied pressure had a large effect on the charge and discharge capacity available at C/10 (Figure 1). Applying too low pressure (see 100 kPa, solid line) resulted in poor contact between the layers, leading not only to a low capacity, but also to a large internal resistance of the cell, which was visible as a larger polarization during charge and discharge. At modest to high pressures, there was very little change in overpotential or polarization at C/10. The maximum capacity was reached at moderate pressures (300 – 500 kPa), as the capacity diminished at too high pressures (see 700 kPa, long dashed line).

Increasing the C-rate yielded lower discharge capacity and larger overpotential (Figure 2, see e.g. 100 kPa, solid lines). As a low cut-off potential was used, the decrease in capacity was not an effect of the larger overpotential pushing the discharge plateau out of the potential window. There was a strong pressure

dependence of the rate capability, visible especially as a decrease in capacity for the higher pressures (500 – 700 kPa), with the maximum capacity reached at 300 kPa.

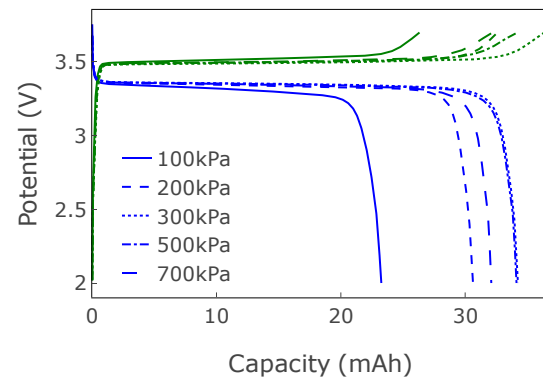


Figure 1. Charge (green) and discharge (blue) curves at C/10 and varying applied pressure.

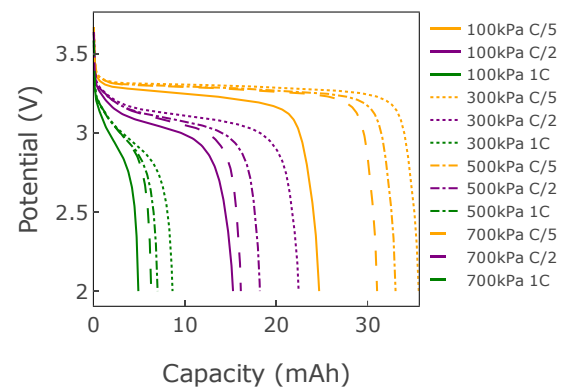


Figure 2. Discharge curves at varying pressure (line style, as in Figure 1) and C-rate (color, yellow: C/5, purple: C/2, green: 1C).

Plotting the discharge capacity versus the pressure (Figure 3), it is clear that applying the correct pressure is crucial for optimizing the performance of this type of LFP | Li cell. With insufficient pressures, the full capacity of the cell cannot be reached, even at low currents. Conversely, applying excessive pressure hurts the rate performance of the cell, and eventually limits the useable capacity also at low currents.

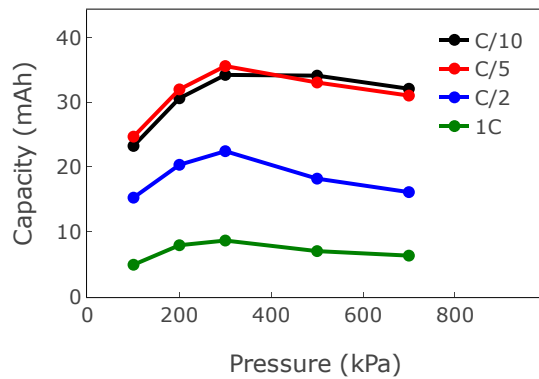


Figure 3. Discharge capacity as a function of the applied pressure at different C-rates.

While the pressure was adjusted to the various setpoints before the start of cycling, charging and discharging the cell lead to pressure changes since the expansion and contraction of the respective electrodes do not perfectly balance out, especially if the plated lithium layer is porous [7, 3]. The spring in the CompreFrame acts to partly level these pressure changes, but a full discharge step still induced a pressure release of around 20 kPa at all investigated pressure setpoints (Figure 4). Considering the spring constant of this pressure frame, this is consistent with a cell contraction of around 20 μm upon discharge. In addition to the pressure change during charge and discharge, an overall pressure decrease can be observed during the time shown in Figure 4, which is a result of the cell slowly being compacted by the applied pressure of 500 kPa. If a completely constant pressure would be desired, that could be achieved with the CompreDrive which actively controls the applied pressure based on a force sensor feedback loop [7, 8, 9].

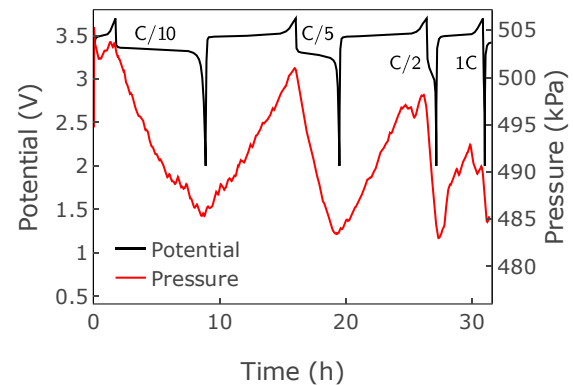


Figure 4. Cell potential (black, left y-axis) and stack pressure (red, right y-axis) during cycling after applying 500 kPa. Discharge currents indicated (charge current was always C/10).

Summary

An LFP/Li pouch cell was investigated under various pressures applied in a CompreFrame. The rate capability of the cell was found to be severely impacted by the pressure, with optimal rate performance at 300 kPa. At both lower and higher pressures, the capacity decreased and the overpotential increased, especially at higher C-rates. The swelling and contraction of the cell during cycling could be observed as changes in pressure of around 20 kPa. Controlling the pressure applied to such a solid-state battery cell is thus key to improving its performance, and pressure monitoring provides a means to gain deeper insights into its function.

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Literature

- [1] T. Krauskopf, F. H. Richter, W. G. Zeier and J. Janek, *Chemical Reviews*, vol. 120, no. 15, p. 7745, 2020.
- [2] K. B. Hatzell, X. C. Chen, C. L. Cobb, N. P. Dasgupta, M. B. Dixit, L. E. Marbella, M. T. McDowell, P. P. Mukherjee, A. Verma, V. Viswanathan, A. S. Westover and W. G. Zeier, *ACS Energy Letters*, vol. 5, no. 3, p. 922, 2020.
- [3] R. Koerver, W. Zhang, L. d. Biasi, S. Schweidler, A. O. Kondrakov, S. Kolling, T. Brezesinski, P. Hartmann, W. G. Zeier and J. Janek, *Energy & Environmental Science*, vol. 11, p. 2142, 2018.
- [4] rhd instruments GmbH & Co. KG, "CompreFrame," February 2024. <https://rhd-instruments.de/en/products/cell-stands/compreframe>.
- [5] rhd instruments GmbH & Co. KG, "CompreCell Pouch," February 2024. <https://rhd-instruments.de/en/products/cells/comprecell-pouch>.
- [6] L. Helmers, L. Froböse, K. Friedrich, M. Steffens, D. Kern, P. Michalowski and A. Kwade, *Energy Technology*, vol. 9, no. 3, p. 2000923, 2021.
- [7] C. Karlsson, S. Kranz and B. Huber, "Application Note: In Operando Pouch Cell Thickness Monitoring during Cycling under Controlled Temperature and Pressure," November 2022. https://rhd-instruments.de/download/appnotes/application-note_CompreDrive_Pouch_Cell_Thickness.pdf.
- [8] C. Karlsson, S. Kranz and B. Huber, "Application Note: Pouch Cell Impedance with Active Pressure and Temperature Control," November 2022. https://rhd-instruments.de/download/appnotes/application-note_CompreDrive_Pouch_Cell_EIS.pdf.
- [9] rhd instruments GmbH & Co. KG, "CompreDrive," February 2024. <https://rhd-instruments.de/en/products/cell-stands/compredrive>.