

Featured Product: PAT-Cell in PAT-Single-Stand with BioLogic VSP Potentiostat

Because of the outstanding reliability of the built-in lithium metal reference electrode, the PAT-Cell is the ideal test cell for long-term 3-electrode experiments on Li-ion battery systems. The BioLogic VSP potentiostat, on the other hand, is a perfect match for controlling this type of experiment, as it is capable of monitoring the half cell voltages while controlling the full cell voltage.

In this report, we describe a typical cycling experiment of a lithium-ion battery comprised of an NCM cathode and a graphite anode (both with a capacity of approx. 2 mAh/cm², purchased from CCI) in a conventional LiPF₆ based electrolyte (1M in EC/DMC 1:1 with 2% VC, BASF).

Experimental set-up

Fig. 1 depicts the PAT-Cell docked into the PAT-Single-Stand, and connected to the BioLogic VSP potentiostat. For comparison, the legacy ECC-PAT-Core test cell is shown on the left-hand side as well. Both test cells make use of the new PAT-Core single-use concept. However, the PAT-Cell is the most advanced and recommended design. For more information on the PAT system, on building the PAT-Core inside the glove box, and on the different BioLogic potentiostats, please refer to the pdf and video links given at the end of this text.

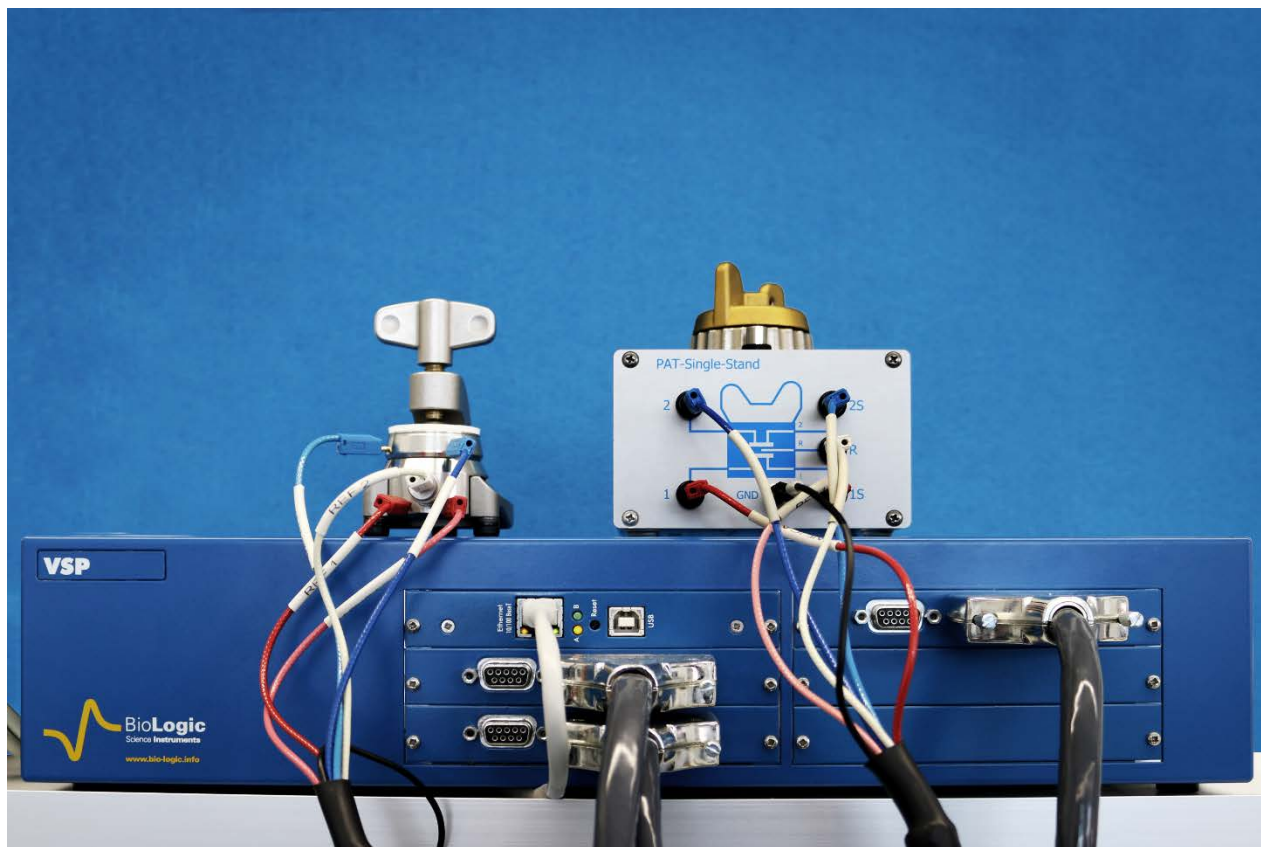


Fig. 1: Experimental set-up with the PAT-Cell docked into the PAT-Single-Stand (right) and the BioLogic VSP-240 potentiostat below. For comparison, the legacy ECC-PAT-Core test cell is shown at the left.

EC-Lab software set-up

The BioLogic EC-Lab software provides several powerful GCPL techniques which can be used for the cycling of batteries with constant current/ constant voltage (CC/CV) including sophisticated galvanostatic intermittent titration techniques (GITT). GCPL is the acronym for **G**alvanostatic **C**ycling with **P**otential **L**imitation. The GCPL techniques differ in several options such as the available step end conditions and the potential control modes used.

In the present experiment, we have applied the GCPL6 technique, which allows control of the full cell voltage between the NCM cathode (socket 1 at the PAT-Single-Stand) and the graphite anode (socket 2). At the same time, the GCPL6 technique is recording the two half cell voltages: the voltages between NCM and the lithium reference (sockets 1S and R), and between graphite and the reference (socket 2S and R). Fig. 2 shows a screenshot of the GCPL6 settings, the second of overall 4 sequences.

Turn to OCV between techniques ↶ ↷

+ 0 1 2 3 4

① Set I to $I_s = 1.000$ mA vs. $\langle \text{None} \rangle$
 for at most $t_1 = 100$ h 0 mn 0.000 0 s
 Limit $E_{\text{cell}} > E_M = 4.200$ V
 Record every $dE_1 = 2.0$ mV
 or $dt_1 = 0.000 0$ s

Hold E_M for $t_M = 0$ h 30 mn 0.000 0 s
 Limit $|I| < I_m = 0.000$ mA
 or $|dI/dt| < dI/dt_f = 0.000$ mA/s
 Record every $dQ = 0.001$ mA.h
 or $dt_q = 0.000 0$ s

Limit $|\Delta Q| > \Delta Q_M = 0.000$ mA.h
 $\Leftrightarrow \Delta x_M = 0.000$

E Range = -5 V; 5 V ...
Resolution = 200 μ V
 I Range = 10 mA
 Bandwidth = 5 - medium

② Rest for $t_R = 0$ h 10 mn 0.000 0 s
 Limit $|dE_{\text{cell}}/dt| < dE_R/dt = 0.0$ mV/h
 Record every $dE_R = 2.0$ mV
 or $dt_R = 30.000 0$ s
(if $t_R = 0$ or $|\Delta Q| > \Delta Q_M$ go to ④)

③ If $E_{\text{cell}} < E_L = \text{pass}$ V go to ①

④ Go back to seq. $N_s' = 0$ (9999 ends technique)
 for $n_c = 0$ time(s) (0 for next sequence)

Fig. 2: Sequence 1 of the GCPL6 setting.

Test results

Fig. 3 shows the voltage and current profiles of the overall experiment. The cut-off cell voltages were changed from 2.5/4.2 V during the initial cycle to 2.5/4.5 V in the 2nd cycle, 1.0/4.5 V in the 3rd cycle, 0.0/4.5 V in the 4th cycle, and 2.5/4.5 V in the last cycle. The magnitude of the current was set to 1 mA, corresponding to a rate of approximately 0.2C during the initial cycle.

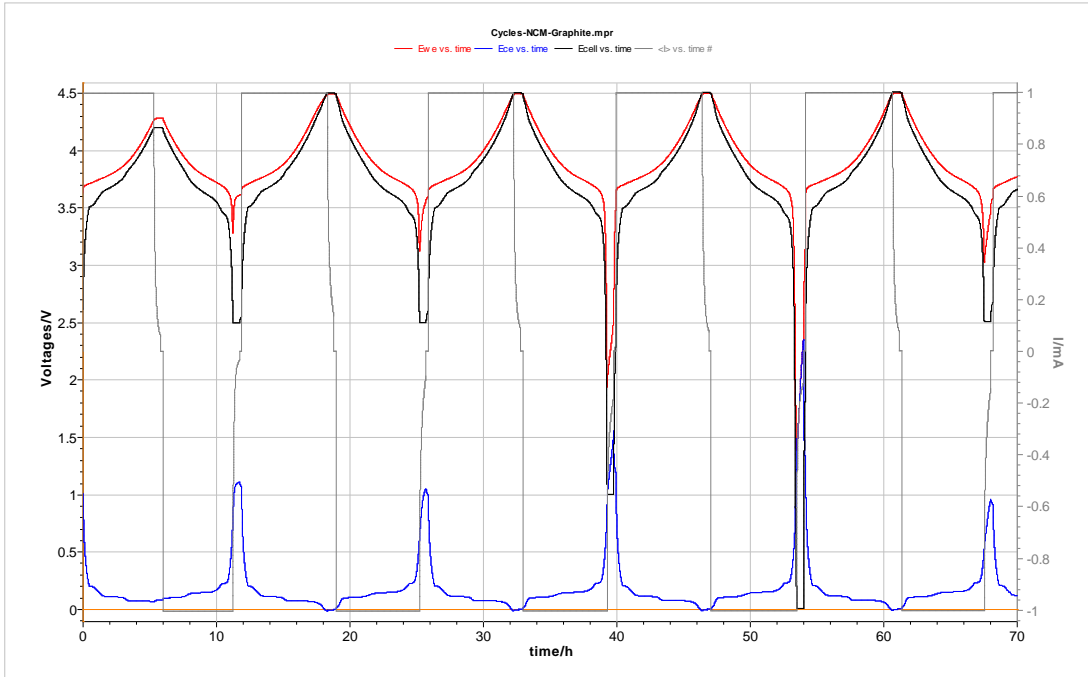


Fig. 3: Voltage and current profiles of the overall experiment. The red line corresponds to the positive half cell voltage, the blue line to the negative half cell voltage, and the black line to the full cell voltage.

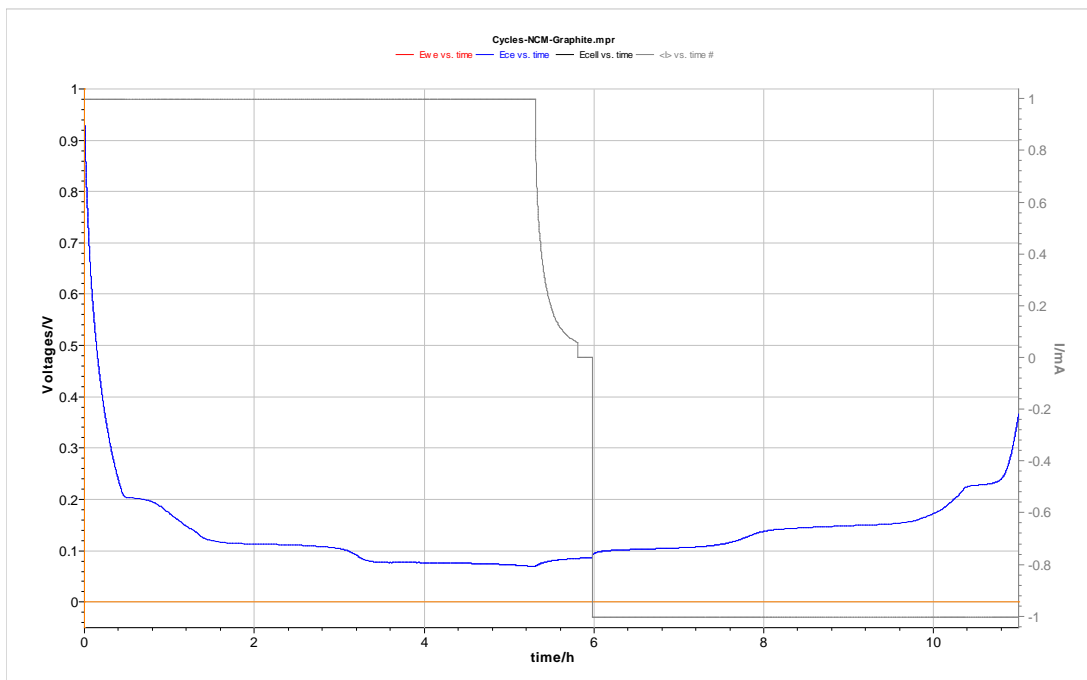


Fig. 4. Evolution of the graphite half cell voltage during first lithiation. The cut-off of the cell voltage was set to 4.2 V.

The following diagrams are just details of Fig. 3. Fig. 4 shows the evolution of the negative half cell voltage during the formation cycle. One can nicely observe the staging plateaus of graphite. At the end of discharge, the graphite was still not fully lithiated.

The situation was changing when increasing the upper cut-off voltage to 4.5 V, see Fig. 5. The graphite electrode is no longer able to accommodate the lithium released from the cathode. Accordingly, plating of Li metal takes place, as can be seen from the drop of the negative half cell voltage to 0V.

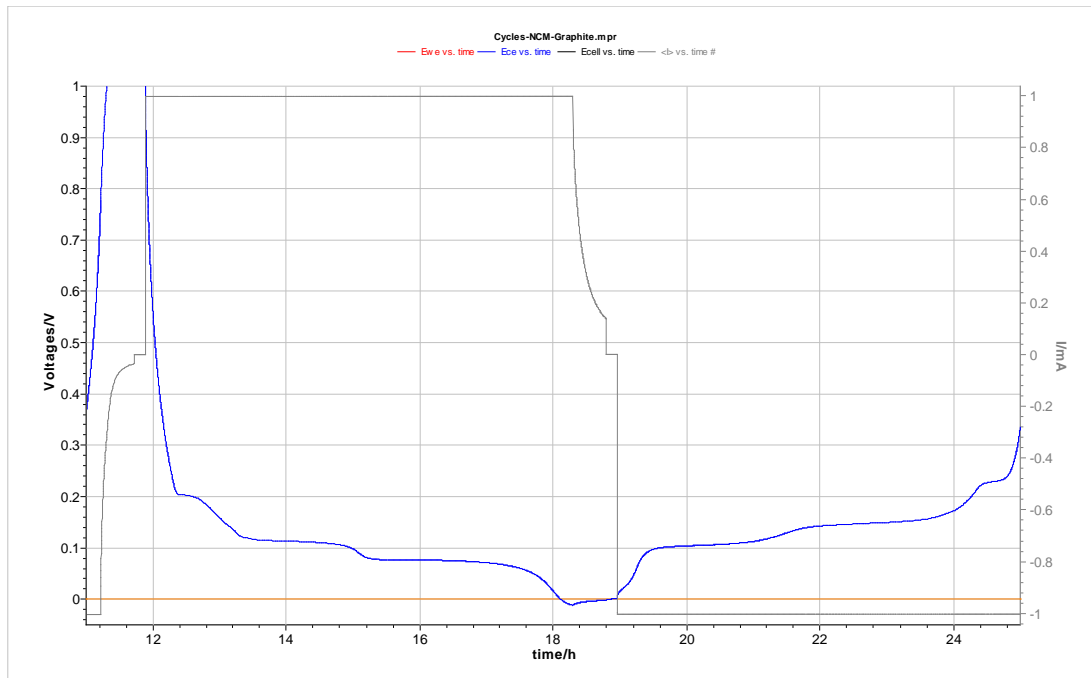


Fig. 5: When increasing the cut-off cell voltage from 4.2 to 4.5 V, the graphite electrode can no longer accommodate all the lithium released from the cathode. As a consequence the graphite potential drops to 0 V. Plating occurs.

During the 3rd cycle, the lower cut-off voltage was decreased to 1.0 V, so as to see the effects of deep discharge. Discharge to below 2.5 V cell voltage is generally considered to potentially damage the Li-ion battery because the copper current collector of the anode may start to corrode at potentials above 3 V vs. Li. In the present experiment, however, we have kind of good luck: At a cut-off voltage of 1.0V the graphite potential does not exceed 1.6 V vs. Li (Fig. 6). Even when lowering the cell voltage to 0 V in the subsequent cycle (Fig. 7), the graphite potential stays well below 3 V vs. Li.

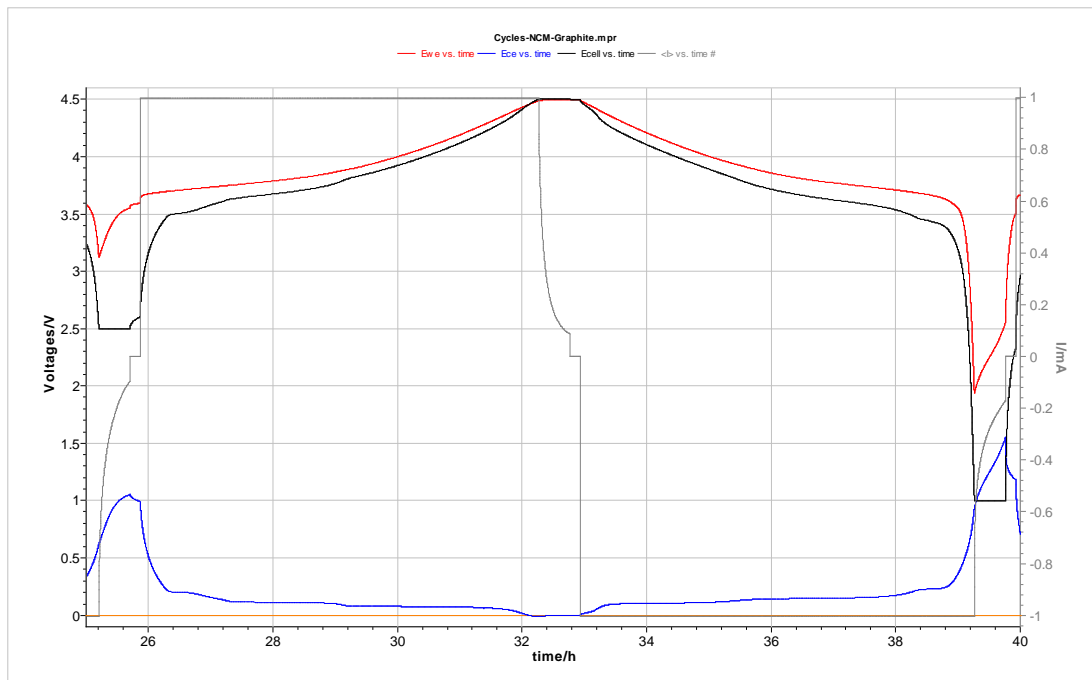


Fig. 6: When lowering the cut-off cell voltage below 2.5 V one may face corrosion of the copper current collector. We had good luck with the present battery, however. The graphite potential reached only 1.6 V vs. Li.

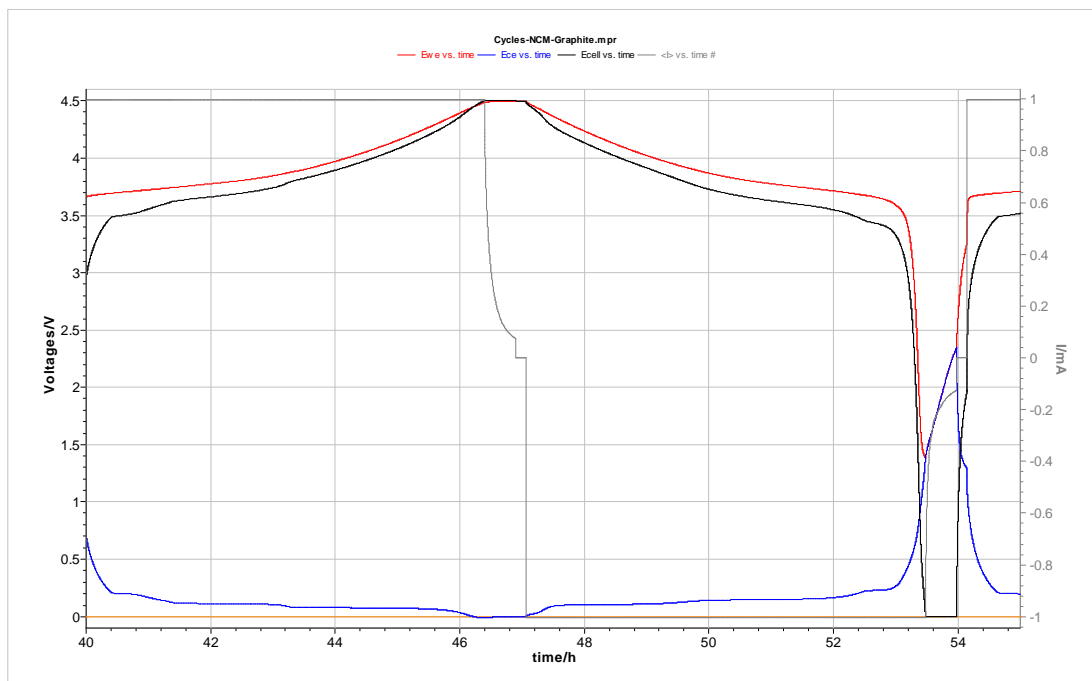


Fig. 7: The second but last cycle. Even at a cell voltage cut-off of 0V, the graphite potential stayed well below 3 V vs. Li.

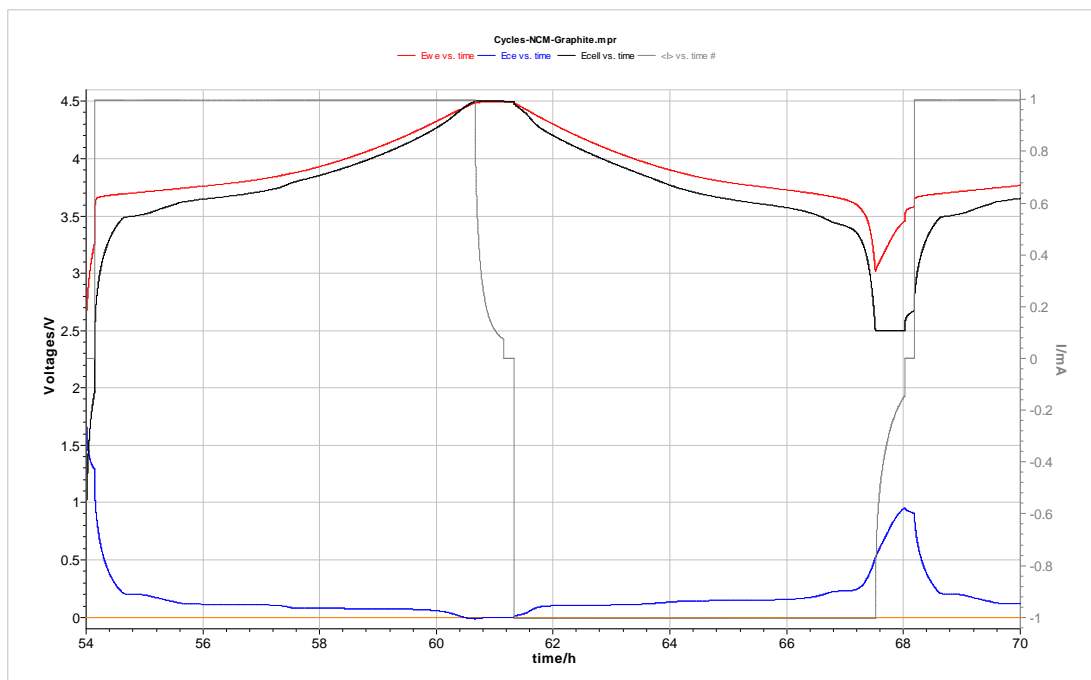


Fig. 8: The last cycle. The battery has fully recovered from the deep discharge before.

Fig. 8 depicts the last cycle of the experiment, again with the more regular cut-off cell voltages of 2.5 and 4.5 V. Surprisingly, the battery did survive the two deep discharge cycle. The situation may change, however, when continuously cycling the battery, as the evolution of the absolute electrode potentials depends on the ratio of the two half cell capacities. If the capacity loss of the graphite exceeds that of the NCM electrode, then the potential of the graphite electrode will continuously rise and eventually, well above 3 V vs. Li, the copper current collector will start to corrode.

Further links:

PAT test cell system

<http://el-cell.com/products/test-cells/pat-core/>

<https://youtu.be/1MIC6-hFzv8>

BioLogic potentiostats

<http://www.bio-logic.info/potentiostat-electrochemistry-ec-lab/instruments/>

<http://www.bio-logic.info/instruments/mpg-2/>