# Safety assessment of swollen consumer Li-ion pouch cell

Zhangqi Wang, Reiner Weyhe

**ACCUREC Recycling GmbH**
Bataverstrasse 21 | DE – 47809 Krefeld

**Keywords:**

Li-ion battery
swollen
pouch cell
abuse test
safety
thermal runaway

**Abstract:**

In this study, the safety risk of swollen consumer Li-ion pouch cells has been studied and evaluated. Scientific abuse tests were carried out to reproduce external extreme conditions which could happen to End-of-Life Li-ion batteries when they are being handled in waste and recycling stream. These comprehensive test series shows that swollen consumer Li-ion pouch cells are safe, against commonly understanding of specific high-risk fraction. Independently of the state-of-the-charge (SOC) of batteries, no thermal runaway (TR) was triggered in any test. Furthermore, the study investigates chemical background of swollen pouch cells (SPCs) as well as the swelling mechanism and explains their moderate behavior under external abuse conditions.

## 01. Introduction and background

### Specific technical characteristics of Li-ion Pouch Cells

Pouch cells have taken up consumer Li-ion battery market (Figure 1) since 2010 due to their flexibility in format and high energy density compared to cylindric cells.

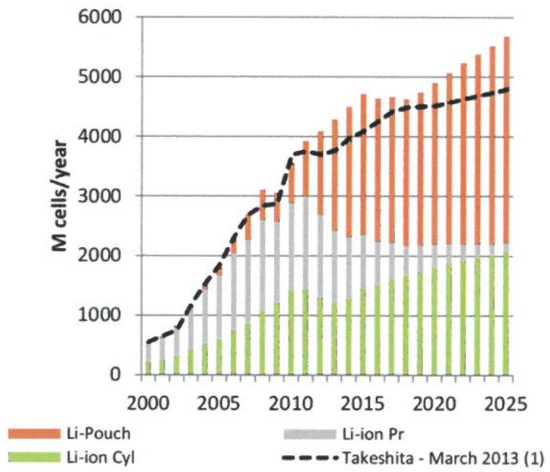



**Figure 1. 2000-2025 LIB market by for form factor (3C) [1]**

To protect Li-ion batteries from abuse, and prolong their lifetime, different safety devices are utilized internally for cylindrical cells. Due to limited space in pouch cells, only external safety devices can be attached to the cell. Detailed structures of both cylindrical and pouch cells are shown in Figure 2. For cylindrical cells, Positive Temperature Coefficient (PTC) device and Current Interrupt Device (CID) device are used to manage safety concerns. PTC is used to prevent high currents inside the cell. CID is used to manage cell over-charge by opening the cell circuitry when the internal pressure increases. For pouch cells, there is no safety control device inside installed. Therefore, external fuse and battery management system is integrated between positive and negative terminals, protecting a pouch cell from undesired conditions. When gas is generated inside a cylindrical cell, it can release these gases by CID and keep its original form by its hard steel housing, while a pouch cell retains these gases and keeps the inner pressure by its soft aluminum laminated film pouch, resulting in a swollen form. Consequently, pouch cells are frequently being found swollen in End-of-Life waste and recycling stream.

(a)

(b)

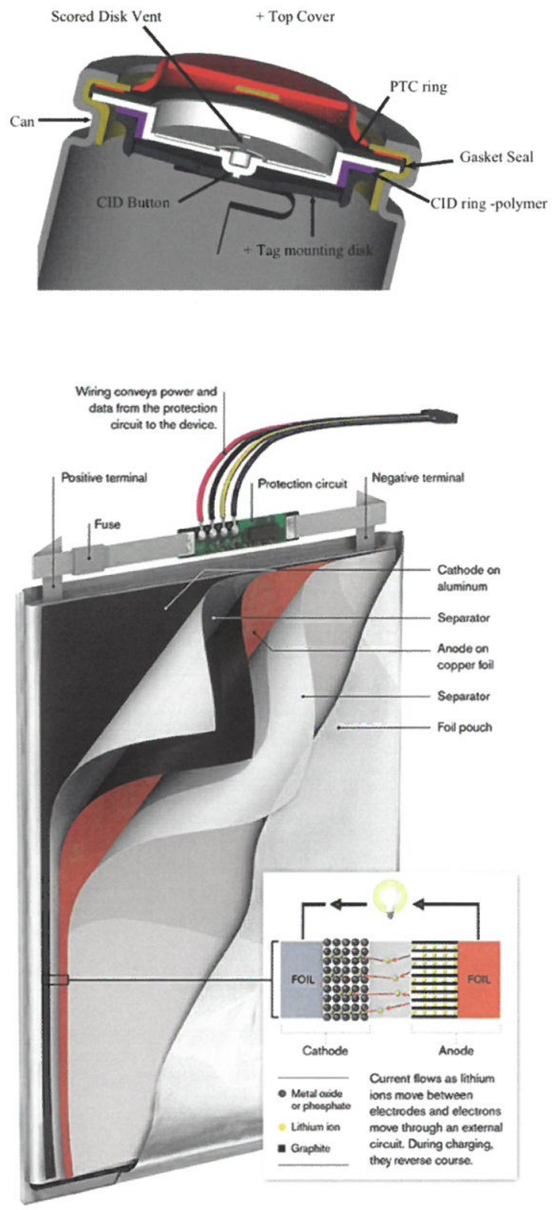



**Figure 2. Internal construction of typical (a) cylindrical cell [2] and (b) pouch cell [3]**

After reaching End-of-Life, Li-ion batteries mainly from consumer applications are first being collected, mostly mixed with other consumer cells (Alkaline, Ni-MH, Ni-Cd etc.), then they are transported to consolidation points, forwarded to sorting plants, sorted out, and packed as Li-ion battery fraction, before finally being sent to recycling facilities. These batteries are commonly transported several hundred kilometers throughout Europe, exposed to mechanical abuse in an uncontrolled environment. Practical experience show, that Lithium batteries are commonly not packaged according their potential risk. Therefore, a critical mechanical damage of these thin aluminum laminated film pouch is not unlikely.

## Li-ion batteries in correlation to transport regulations

Li-ion batteries are classified as dangerous goods (UN3480), in general imposing special provisions (SP) and defined packaging instructions (P909 etc.). These provisions have been developed over decades and lead in most cases to controlled and safe transportation of batteries.

To enable a cost efficiency in consumer End-of-Life battery household collection including Li-batteries, several legal ADR [4] exemptions and facilitations are in place. The most important exemption, SP636, allows a transportation of maximum 333kg of Li-batteries without particular protection of Lithium batteries. Herewith, regulator had originally intended to enable the collection of appr. 10 tons of mixed household batteries (mostly alkaline), which contain max. 333kg equally distributed Lithium batteries. Due to a lack of explicit explanation, this SP is regularly interpreted in a way, that waste owners could send up to 333kg of sole, non-isolated, uninsulated Li-batteries. Accordingly, an increasing frequency of severe fires take place during transportation and storage. Commonly Li-ion pouch cells are involved because of its thin aluminum laminated film pouch, uninsulated electrode tags and lacking safety installations.

## Handling of End-of-Life Li-ion batteries and its contribution to fire incidents

As Li-ion batteries are dominating the rechargeable battery market for already a few years, more and more of these batteries return to waste stream. Figure 3 shows the frequency of reported waste & recycling facility fire incidents in US and Canada from 2016 to 2019. The report indicates an average increase of 14% fire incidents from 2016 to 2018 due to improper handling of Li-ion batteries. With continuous market growth of Li-ion batteries, it is expected that more Li-ion batteries will be disposed of in the near future, resulting in significant increase of number of incidents. Therefore, it is essential to understand how dangerous the SPC´s (swollen pouch cells) are and how to handle these cells in a safe manner.

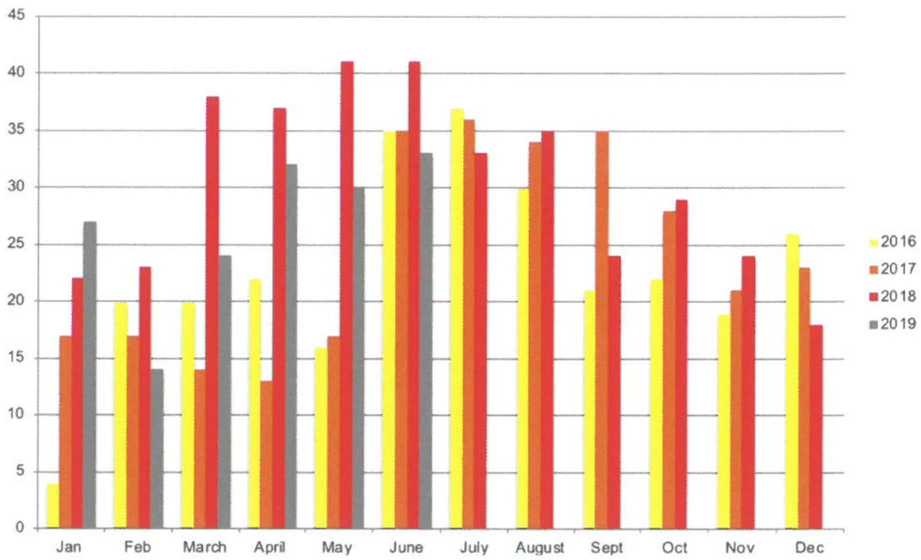



**Figure 3. Reported waste & recycling facility fires in US/CAN from 2016 - 2019 [5]**

## Previous classification of SPC´s and motivation

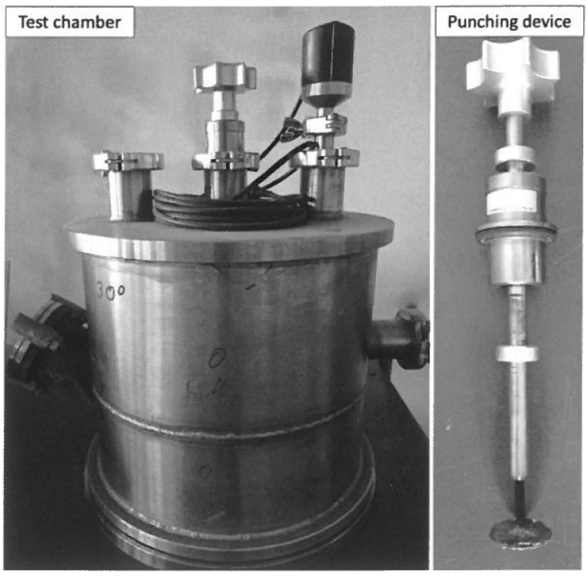
To tackle the above described fire risk of End-of-Life Li-ion batteries, stakeholders began to discuss risk classifications, and to identify a "most dangerous battery group". This group has been implemented legally at ADR-regulation by special provision SP376, which differentiates damaged (physically deformed) and critical (tends to thermal runaway TR) batteries. Furthermore, it defines more specific, strict packaging instructions (P908), labeling, documentation and transportation rules.

Practice has shown that the classification "critical" is hard to determine, as the inner structure of a Li-ion battery and its pending sudden thermal decomposition is not predictable and technically nearly impossible to detect from outside. It is a matter of fact that only swollen Li-ion pouch batteries can be identified visually from outside as a battery which had inner abnormal reaction. As Figure 2 shows, pouch cell structure consists of electrode/separator stacks encapsulated by aluminum laminated film pouch with a thickness of ~100µm. In case of inner abnormal reaction such as electrolyte decomposition, electrode oxidation and other degradation reactions due to undesired conditions e.g., overcharging, deep-discharging or unusual operation temperature, the generated as swells the soft aluminum laminated film pouch. Mostly the pouch retains the gases and resists the increased inner pressure, so that the swollen battery can be easily identified in a battery sorting process. Sorters extract these swollen cells typically, presuming that further, even critical reactions can still occur and consequently package these "critical" batteries according SP376.

A steadily increasing End-of-Life Lithium battery waste stream and thus increasing number of SPC´s has led to uncertainty at untrained collection points, increasing packaging demands and cost for responsible collection schemes, respective producers. But the criticality of storage and handling of SPC´s had also triggered an internal discussion at ACCUREC´s Li-ion recycling facility. The mechanism of gas evolution and swelling effect in pouch cell with different conditions has been unclear, and scientific investigations of the safety of SPC´s are rare. As a consequence, this study had been conducted and focus on safety assessment of SPC´s and their scientific explanation.

## 02. **Investigation**

According to UNECE, respective ADR regulation, End-of-Life Li-ion batteries have to be packed for transportation with isolation material in proven, strong packaging like steel drums. The required non-combustible, non-conducting isolation material could be dry sand, vermiculite, or others. Li-ion batteries are packed in bulk, so that SPC´s - especially those packed at the bottom of drums - can be stressed by bulk material. Additionally, vibration induces material movement in drum which results in compress force variation during transportation. This might result in penetration of aluminum laminated film pouch by sharp metal, or external short circuit by connection of electrode tabs. Consequently, safety assessment investigations were separated into mechanical external and electrical abuse test.




### 02.1 **Mechanical test**

#### 02.1.1 **Punching test**

In total 40 swollen pouch single cells with broad varieties of different types (size, voltage, capacity etc.) were selected for punching test. Punching test was carried out in a cylindrical steel chamber with an observation window and a pressure sensor. Detailed setup is shown in Figure 4. The punching device is a metal stick with a metal pad (diameter 40mm) at the bottom. The system pressure in the chamber was controlled at around 600 mbar before punching, in order to reduce the influence of sudden pressure increase due to possible gas release during punching test. Then the metal pad was punched against the pouch cell by mechanical shock created by a 3kg hammer until aluminum laminated film pouch was opened. During punching, the cells were observed through observation window and the pressure change in the chamber was recorded by pressure sensor. After punching test, the chamber was evacuated below 50 mbar for 10 seconds in order to evacuate possible toxic gases which might be generated during and after punching test.

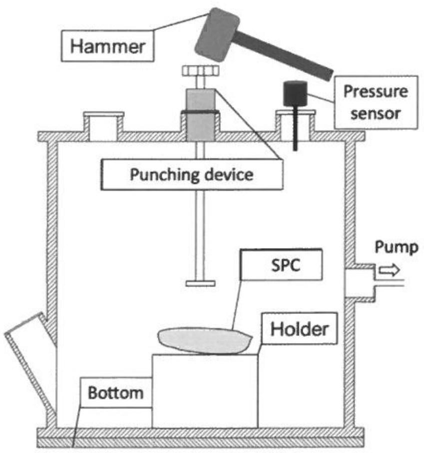



**Figure 4. Setup of punching test**

### 02.1.2 **Penetration test**

110 swollen pouch single cells with broad varieties of different types (size, voltage, capacity etc.) were selected for penetration tests by nail. The nail with 1 mm diameter was penetrated into the pouch cells by pneumatic strip framing nailer which provides similar forces in each test. After evacuation of gases, venting and opening the chamber, the penetrated cells were placed above sand in a plastic container for better observation. Temperature variation of cells were observed and documented by an infrared-thermal camera for 1 hour.

## 02.2 **External short-circuit test**

60 swollen pouch single cells with broad varieties of different types (size, voltage, capacity etc.) were selected for external short-circuit test. Positive and negative poles were directly connected by an amperemeter with measurement range up to 10 A. Poles were connected for 30 seconds and the maximum measured current was recorded as maximum discharge current. Temperature evolution of cells was also observed by an infrared-thermal camera.

## 03. **Test Results**

### 03.1 **Punching Tests**

40 SPCs were punched until their aluminum laminated film pouch was opened. It has been observed that the pressure in the chamber increased up to 10 mbar after opening a cell. This indicates that gas was released from SPC, balancing the pressure difference inside and outside of the SPC before punching. Neither fire nor explosion has been observed during punching test. The cells were opened smoothly at different casing spots, e.g., edge, near punching spot etc (Figure 5). All electrode material was still inside the casing after punching test, confirming no explosion occurred. The smell of the electrolyte was perceptible after the punching test, indicating that the SPC`s still contain a certain amount of electrolyte. However, no fume was observed from SPC which means punching test did not lead to uncontrollable thermal activity i.e., thermal runaway.

**Figure 5. Pouch cells after punching test**

## 03.2 **Penetration test**

In total 110 SPC´s were penetrated by nails and placed on a sand bed for observation (Figure 6a). Neither explosion nor thermal runaway event could be observed. Fire and smoke were also not observed. Only 8 out of 110 cells have showed significant temperature increase during 1 hour observation. The highest temperature that has been reached by the 8 cells was 81.5°C (Figure 6b). Most of the maximum reached temperatures were below 50°C. The remaining 102 cells showed no temperature change during the observation period. There was no evidence that the initial voltage has an influence on the thermal behavior of the penetration tests.



**Figure 6. (a) penetrated SPC above sand and (b) maximum observed temperature**

## 03.3 **External Short-Circuit Tests**

The positive and negative poles of each 60 SPC´s were directly connected to an amperemeter with a measurement range between 0-10 A. The short-circuit current with respect to initial voltage is shown in Figure 7. It can be seen that the external short-circuit current of most cells was lower than 2 A. Figure 7 also shows a tendency of high discharge current with high initial voltage, especially above 2 V. The external short-circuit of normal pouch cells can reach discharge current spikes of 50 A with continuedly discharge current of 18 A which has been reported by [6]. The external short-circuit discharge current of normal pouch cells is at least 3 times higher than SPC. For the connecting moment, no spark was recognized in SPC´s. During the short-circuit period, no temperature increase was recognized, and cells are not swelling furthermore.

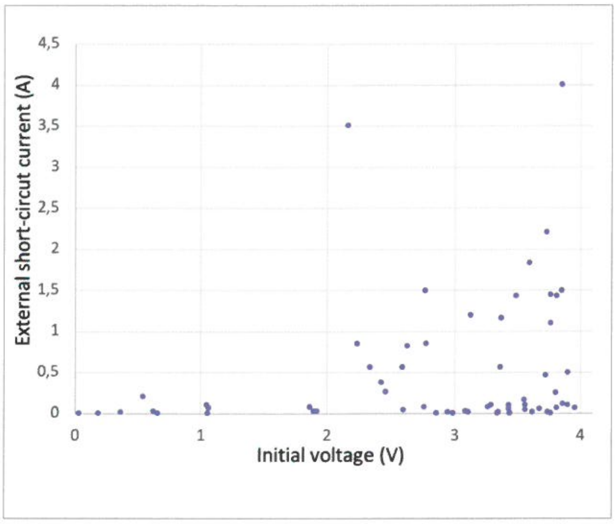



**Figure 7. external short-circuit current with respect to initial voltage**

## 04. **Discussion**

In current waste management practice, the SPC´s are usually classified as "critical" by end consumers, professionals or collecting schemes due to a lack of knowledge. However, the tests here indicate that SPC´s behaves moderate under external abuse conditions. This moderate behavior can be explained by several physical and chemical mechanism.
When a pouch cell starts to swell, it is suspected that abnormal reaction takes place and gas generation inside the pouch occurs. Reference [7] has summarized mainly 4 reasons for gas generation which are:

**1) Formation**

During the first charge/discharge cycles, also called formation cycle, the solid electrolyte interphase (SEI) is formed to prevent further decomposition of electrolyte at the anode surface. At the cathode surface, a similar passivation layer is formed, which is called the cathode electrolyte interphase (CEI). The formation of SEI and CEI consumes electrolyte and electrode material which generate gases.

**2) Cyclic Aging**

A Li-ion battery has only limited cycle and lifetime due to aging effects i.e., degradation process of materials over time and operation. Due to the complexity of the Li-ion battery structure, numerous aging mechanisms have been suggested which can be related to the interactive reactions of those constituents. For example, the lithium salt (LiPF6) is both chemically and thermally unstable and it has the tendency to react with traces of moisture and organic solvents (electrolyte). Even at room temperature, LiPF6 in solution is in a thermal equilibrium with PF5 and LiF. Due to the high reactivity of PF5, this equilibrium causes decomposition and conversion of electrolyte. The reactions can lead to hydrolysis, organophosphate- and organofluorophosphate based aging products inside the electrolyte which generates gases. Furthermore, under electrochemical operation conditions, a ring opening reaction of the cyclic ethylene carbonate can occur; subsequent reactions also in the electrolyte present linear carbonates form oligomeric decomposition species. To sum-up, cyclic aging might be caused by different components but leads to reactions and decomposition of electrolyte which generates gases.

**3) Overcharging**

Overcharge takes place when the charging current is not cut-off after Li-ion battery is fully charged. The principle of charging is providing a driving force to Li-ions to move from cathode to anode. During overcharging, the driving force still exist, even there are no more available Li-ions to be moved. As a result, the driving force acts on the electrode material resulting in oxidation and decomposition of cathode and dendrite formation in anode. The oxidation and decomposition of cathode material generate gases while dendrite formation in anode can result in internal short-circuit of Li-ion batteries.

**4) External abuse of the cells ultimately leading to thermal runaway**

The last reason for gas formation is the thermal runaway event induced by external abuse conditions. For example, external short-circuit, high operation temperature etc. Those conditions will ultimately lead to thermal runaway events which generate gases.

Therefore, it is believed that SPC´s in waste have experienced an abnormal malfunction. Consequently, non-technicians expect that these cells may tend to further abnormal reactions, resulting in explosion, gas venting and/or flames etc.

Both effects, reaction of electrolyte and electrode material, lead to deterioration of electrical properties of a cell. Specifically, reaction of electrolyte consumes Li-ions transportation media, reducing mobility of Li-ions between electrodes and increasing internal resistance. Reactions of the electrode material consume available Li-ion lithiation/delithiation sites, leading to capacity fade.

In order to prove this inner evolution of pouch cells, ACCUREC has set up a test series to investigate the technical status of swollen cells. These tests included a reactivation test by injecting fresh electrolyte into a SPC.

This verification test consists of several subsequent steps:

1. select SPCs with high voltage (>3.7V), as high voltage indicates a high SOC and possibility of po tential TR
2. discharge cells by resistance, and record discharge voltage and current, respective capacity
3. release inner pressure and gases from pouch cells
4. compress pouch cell (electrode stack) and record discharge voltage and current
5. inject virgin electrolyte (DMC … etc.) and record discharge voltage and current

Effects are described exemplary with a SPC of initial 3.97 V and nominal capacity of 4100mAh. It has been connected to a 50 W electric appliance for discharging. For a clear explanation, the test process has been divided into 3 phases which are direct discharging (phase 1), discharging after compression (phase 2) and discharging after injecting virgin electrolyte (phase3). The initial recorded discharge current was around 1 A for the connecting moment (starting of phase 1), however, discharge current drops rapidly down to below 0.2 A, as well as discharging voltage. A hole was made on the aluminum laminated film pouch by a needle (starting of phase 2), the gas was released, and the pouch cell stack was compressed to its original geometry. Discharging voltage and current recovered partly, and minor additional capacity was recorded until current undercuts 0.2 A. After that, 3 ml fresh electrolyte was injected into the pouch cell (starting of phase 3). Discharging voltage and current increased immediately and significantly. Now, discharging process was sustainable with relevant capacity for over 1 hour. The recorded voltage and current from the beginning are exemplary shown in Figure 8.

The test sequences verify that SPC suffers under massive inability to release their energy due to decomposed electrolyte, resulting in lower Li-ion mobility in electrolyte and higher internal resistance of a SPC. The electrochemical energy (i.e., SOC) is still stored in electrodes but cannot be properly released. This technical fact avoids the risky decomposition of the cell (i.e., TR), even if it has still a high SOC and is mechanically or electrically abused.

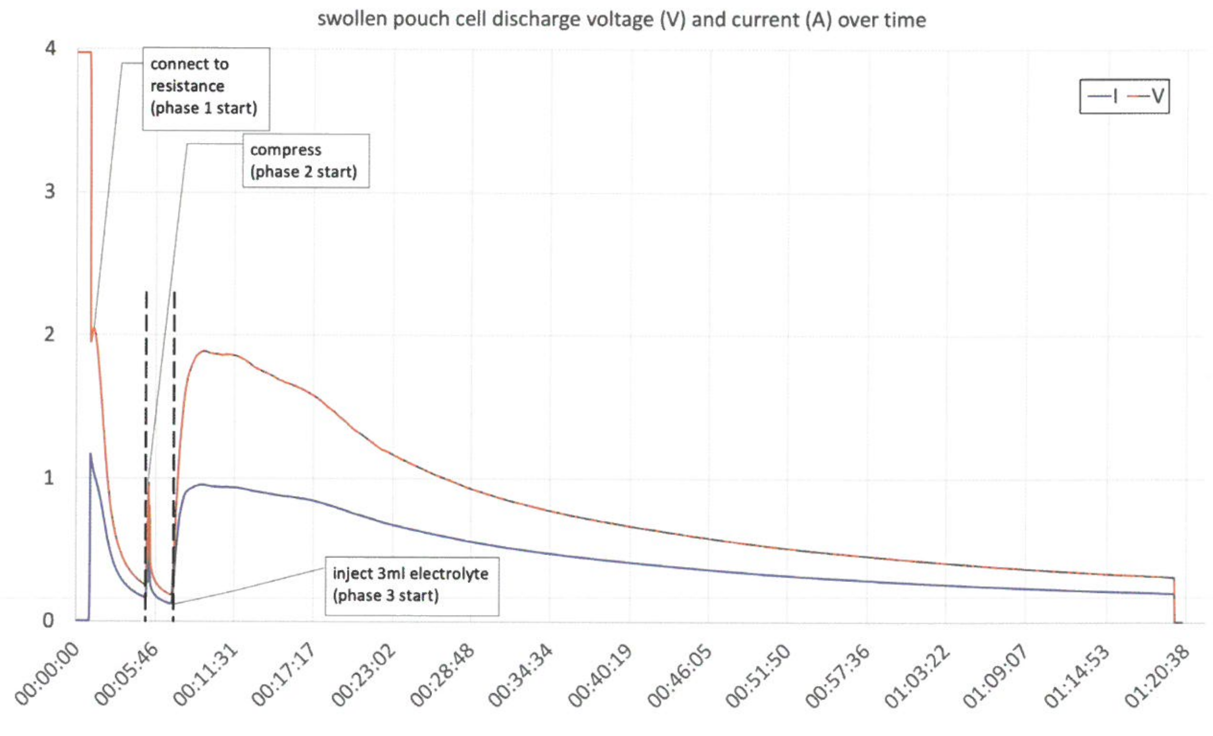



**Figure 8. voltage and current of a SPC in reactivation test**

To underline these results by key parameters, the discharging capacity has been calculated by mathematic integration of Figure 8 curve. The capacity release of the pouch cell in phase 1, 2 and 3 are 0.8%, 0.2% and 13.8% respectively to its nominal capacity. It is assumed this pouch cell has still a capacity of 15% - 20% before test which is sufficient to supply material and energy for a thermal runaway event.
From a practical viewpoint, it should be also stressed here that pouch cells commonly appear in waste stream as cell packs. Even if one or more cells are swollen, this pack usually contains several "OK"-cells with high SOC. In that case, the whole pack has still a considerable risk of heat propagation or thermal runaway event und abuse conditions.

## 05. **Conclusion**

Based on above investigation, the following conclusions can be made.

1. SPC´s indicate the electrolyte is partly decom posed.
2. SPC´s do not indicate an additional risk for potential TR.
3. The decomposition of electrolyte results in severe decline of Li-ion mobility and increase of internal resistance.
4. SPC´s can still have a significant SOC.
5. Although SPC´s can contain high SOC, the multi plicated internal resistance avoids rapid tempe rature increase and/or thermal runaway event even under electrical or mechanical abuse test conditions.

## Reference

[1] C. PILLOT, „Impact of the xEV Market groth on Lithium-ion batteries and Raw materials supply 2018-2030“.
[2] J. Jeevarajan, „Safety Limitations Associated with Commercial 18650 Lithium-ion Cells“.
[3] K. Bullis. [Online]. Available: https://www.technologyreview.com/s/428155/lithium-ion-battery/. [Zugriff am 20 8 2019].
[4] M. Krautwurst, ADR 2019 - 2. Auflage.
[5] R. Fogelman. [Online]. Available: https://recyclinginternational.com/business/fire-recycling-site/26760/. [Zugriff am 20 8 2019].
[6] J. A. Jeevarajan und T. Inoue, „A Novel Lithium-ion Laminated Pouch Cell Tested For Performance And Safety“.
[7] Y. P. Stenzel, F. Horsthemke, M. Winter und S. Nowak, „Chromatographic Techniques in the Research Area of Lithium Ion Batteries: Current State-of-the-Art“.