

WHITE PAPER

**ELECTROLYTE
TRACING AS AN
EFFECTIVE LEAK
TESTING METHOD
FOR BATTERY
CELLS QUALITY
CONTROL**



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ABSTRACT

Rechargeable batteries offer a smart and efficient solution for storing electrical power, making them indispensable in modern technology. They are now ubiquitous, powering everything from smartphones and wearables to the automotive industry and medical devices.

However, no product is without potential defects. To ensure the highest quality of battery cells, new testing strategies and specialized instrumentation are essential. This paper briefly presents the risks associated with sealing defects in battery cells, the potential consequences of these defects on the final product, and the methods to detect them before faulty goods reach the market.

The most frequently used methods for leak testing of battery cells in mass production can be applied before sealing and are therefore suitable for process control but not for the quality check at the end of the line. On the other hand, the testing technologies available for leak testing of totally sealed components are not suitable for effective application on battery cells.

Core of this paper is the description of a reliable and effective method expressly developed for End-of-Line leak testing of Li-ion battery cells.

INTRODUCTION

In the last decades, the battery market is experiencing a huge growth in a multitude of applications like consumer electronics, portable, wearable or medical devices and in new emerging markets such as the automotive industry following the advent of electric vehicles.

Particularly in this last context, a lot of effort is paid not only to improve the battery performance (such as energy density and cycle life), but also in the optimization of battery production process, in terms of efficiency, affordability and safety. Among them, the latter is a fundamental aspect related to the choice of the materials that compose the battery itself, up to the inspection controls integrated in the production processes, that ensure the commercialization of a safe and reliable product ready for use.

The performance of a battery depends entirely on its constituent parts. In the state-of-the-art, commercialized lithium-ion batteries which are basically composed of individual electrochemical cells connected in series, each one constituted by anode, cathode, separator and the electrolyte.

The anode and cathode active materials are generally chosen in the range of the so-called *insertion/de-insertion* materials. One of the most common anode materials is graphite, whereas lithium iron phosphate (LFP) is an example of a possible cathode material. The separator is chosen to be a porous layer, electronically insulating to prevent electrical short circuit between anode and cathode and wetted with the electrolyte, which guarantees ions mobility during charge/discharge cycles.

A simplified description of an electrochemical cell can be found in Figure 1. [1]

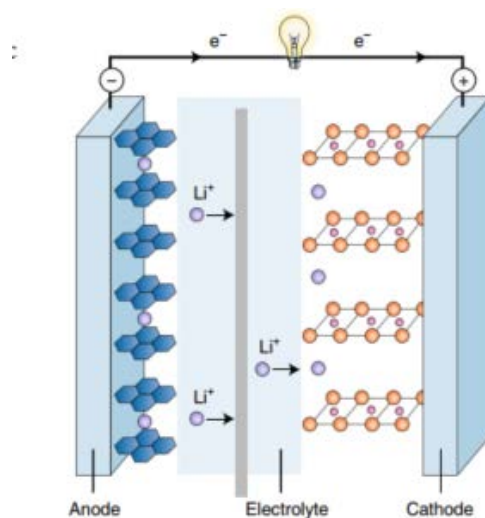


Figure 1. Schematic representation of an electrochemical cell for Li-ion battery. [1]

In the state-of-the-art Li-ion batteries, the liquid electrolyte is a mixture of lithium salts dissolved in a mixture of organic solvents.

The lithium salt (or a mixture of them) is chosen to have the best ion mobility, thus providing the least resistance to ion transport during charge/discharge cycles of the battery. The choice of organic solvents relies on ensuring the proper viscosity and solvation effect of the ions dissolved. Among the most used lithium salts, fluorinated compounds with a large sized counter-anion are preferred; on the other hand, Solvents usually are chosen to be organic compounds, mostly carbonate-based ones. [2]

An example of salts and solvents representing the electrolyte state-of-the-art is reported in Figure 2.

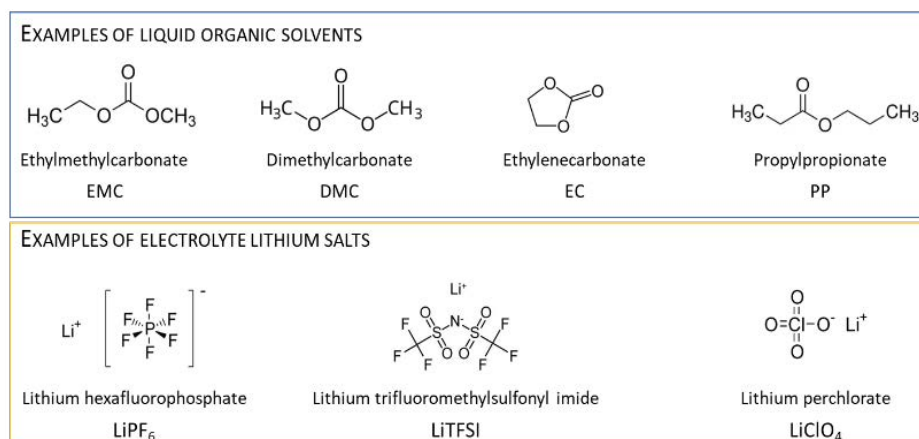


Figure 2. Examples of liquid organic solvents and lithium salts for Li-ion battery electrolyte.

Among the different challenges in battery design, the electrolyte stability represents a critical one, which can be addressed inherently when its components are selected or during battery production process to ensure safety against external contaminants.

Each molecular species has a proper reduction potential, which is directly related to the energy required to reduce (or, indeed, oxidize) the species itself. In an electrochemical cell, the electrolyte components undergo a series of degradation reactions at electrodes potentials that overcome the redox potentials of each of the species involved. This limit identifies the electrochemical stability window of each component. The product of those reactions is the formation of a protective layer called **solid electrolyte interphase** (SEI). Its role is of primary importance for the health of the battery, increasing the battery life by preventing detrimental phenomena such as self-discharge or lithium dendrite growth, which may eventually lead to internal short-circuit. [3]

Electrolyte stability in Li-ion battery is also a topic related to battery safety [4]. In presence of water contamination [5, 6], for example, the electrolyte would be interested by degradation due to several undesired reactions. Among them, gas generation reactions can occur related to electrochemical water decomposition and consequent hydrogen and oxygen evolution reactions or by evolution of gaseous acidic species as product from the interaction of water with lithium salts. As a consequence, battery life and safety are strongly affected, leading in the worst cases to battery swelling, electrodes misalignment and internal short circuit. [7]

In this context, it is widely recognized the importance of ensuring a reliable production process that leads to a final product for which safety of use is guaranteed. Quality control processes are integrated throughout the entire production line, from raw material quality assessment to end-of-line testing [8]. In the latter, particular importance is given to the leak test of both battery housing and finished battery.

This work gives a review of the possible methods to perform in-line leak tests on completely sealed battery cells based on known technologies, analysing the advantages and critical aspects of each of the presented techniques. Moreover, it is presented in details a new method for leak detection, called **electrolyte tracing**. In this regard, it is shown how the Marposs leak test solution can afford to ensure reliable and repeatable results, offering multiple solutions according to the specificity of each production environment and of the battery that is under investigation, being it pouch, button, prismatic

or cylindrical cell of any dimension.

LEAK TESTING OF THE OPEN CELL IN THE MANUFACTURING LINE

Before going through the details about end of the line leak testing of completely sealed battery cells, it must be underlined that checking the cell case is still a fundamental part of the quality assessment of the product.

Usually, these kinds of tests are performed in vacuum before electrolyte filling. The first step is to insert helium at a known pressure into the battery case through an aperture, typically the electrolyte filling opening (Figure 3). This hole is kept sealed during testing while helium is fed to the cell, the test chamber is evacuated and the presence of helium into the test chamber is monitored. If a defect is present on the battery case, it can be detected through a signal increase registered by a Helium mass spectrometer and if the signal goes above a certain threshold the case is discarded.

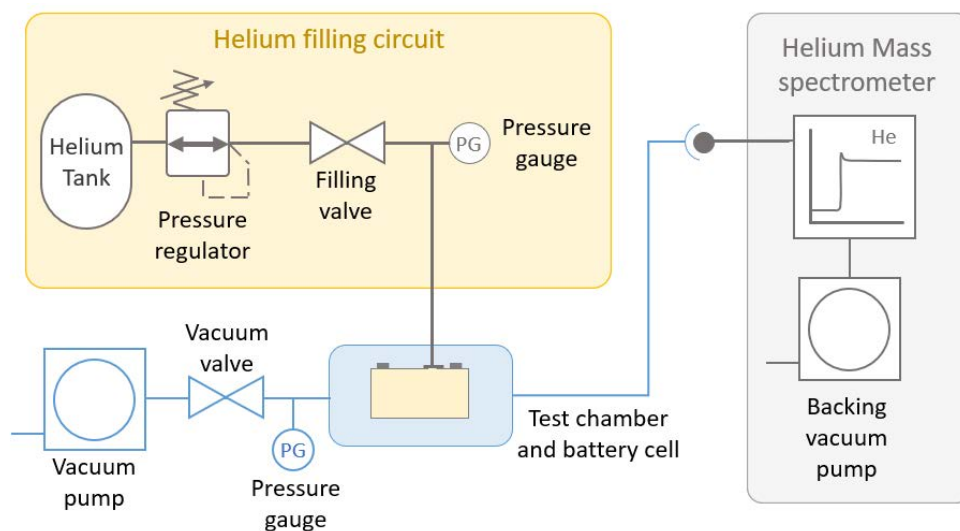


Figure 3 - Example of a battery case leak test setup

The test assures the integrity of the case before fundamental production steps like filling, formation, degassing and aging where not knowing the presence of a defective part can produce costly consequences.

Anyway However, open cell tests as such are not enough to assure leak proofness of the completely sealed cell at the end of the line, after all the additional production steps. From a leak testing only perspective, however, they can open the possibility of focusing the end of the line test only on the final sealing area, potentially shortening the time taken for the final test.

CONVENTIONAL METHODS FOR LEAK TESTING OF SEALED COMPONENTS

As already stated, assuring the leak proofness of a battery cell is essential to improve its quality, safety and life span. Leak testing, however, comprehend a vast number of techniques [9], each with different objectives and sensitivities, and not every one of them is applicable to check batteries.

Dealing with cells, in fact, immediately excludes all the techniques where high pressures are mandatory to make the system perform properly and all the methods in which the object is immersed in or sprayed with a liquid of some sort. Moreover, as said before, open cell tests are not enough to fully check the

leak proofness of the battery.

For the specific scenario described in this paper the selection must continue though. In fact, the objective is to test a finished and completely sealed battery, hence the tracer needs to be already inside the battery or the check must be done indirectly, checking the pressure variation of a test chamber which houses the cell. Another important piece of information is to determine where the possible defect may be located on the battery, mainly in order have a starting point to understand how it can form, how wide it can be and in which conditions the test can be performed. This means knowing how the battery is sealed and where the final sealing occurs. As can be seen in **Table 1** this can depend strongly on the cell format.

Format	Typical sealing method	Defect	Location
Pouch cells	Vacuum sealing through ultrasonic bonding or laser welding of the pouch film	Pouch deformation during sealing	All sealed sides of the battery, Electrical contacts area, areas near bends
Button / coin cells	Crimping	Deformation during crimping	Near the crimped area
Cylindrical cells	Gasket/seal rings and crimping	Dimensional defects on the gasket or the seal rings, deformation during crimping	Top of the cylindrical battery, near the sealing/
Prismatic cells	Laser welding, crimping	Welding defects, deformation during crimping	Electrolyte filling hole area

Table 1 - Sealing defects for different cell formats.

At the end, to check effectively sealed objects such as battery cells, the technique selection is reduced to pressure decay (or mass flow) methods performed with nitrogen (or dry air) to limit contamination from moisture or, as an alternative, helium injection or helium bombing methods.

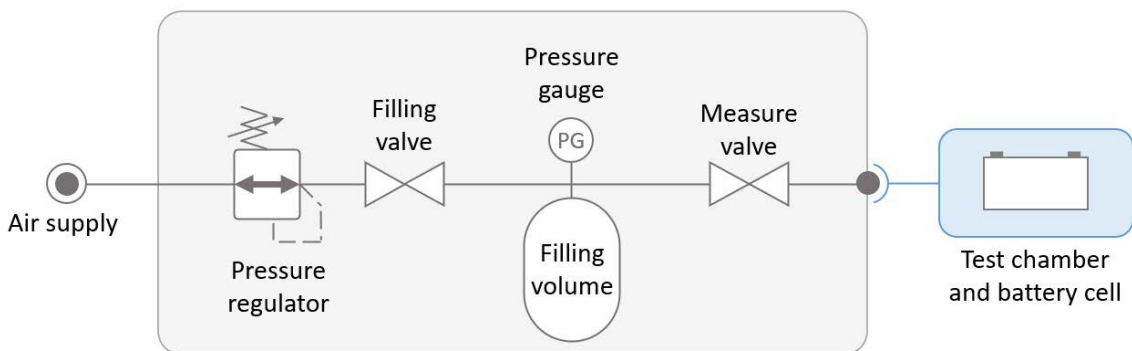


Figure 4 - Example of a pressure decay leak test setup

Taking Figure 4 as an example, in order to perform a pressure decay test, the first step is to fill a reference volume with gas like N2 or dry air until a target pressure is reached. When the filling volume

is ready, the measure valve opens and a certain amount of time is then dedicated to stabilize the pressure, after that the measure phase begins. If a pressure decrease is registered in the filling filled volume, the leak rate can be esteemed calculated. Usually, on the battery side, the test chamber volume is minimized for optimization purposes. Theoretically speaking, pressure decay leak testing could be applied to fully sealed pieces as battery cells; however, several considerations must be addressed.

First of all, in the thoughtless case in which air is used for testing, it needs to be at least dry air, completely clean from humidity residues. Generally speaking, using N2 would be preferable because, as already stated, air may have interactions with the cell internal components, causing instabilities into the cell itself.

Additionally, due to design optimization, the free volume inside a battery cell (or in the proximity of the sealing zone for certain designs), is typically very small and often unevenly distributed. In the case of a significant defect, it is possible that the filling process is going to be too quick, causing the pressure inside the battery to stabilize immediately and potentially giving “false good” results. As can be seen in Figure 5, at first the leak rate increases the larger the volume but when the orifice diameter passes a certain value, then the leak rate starts to decrease.

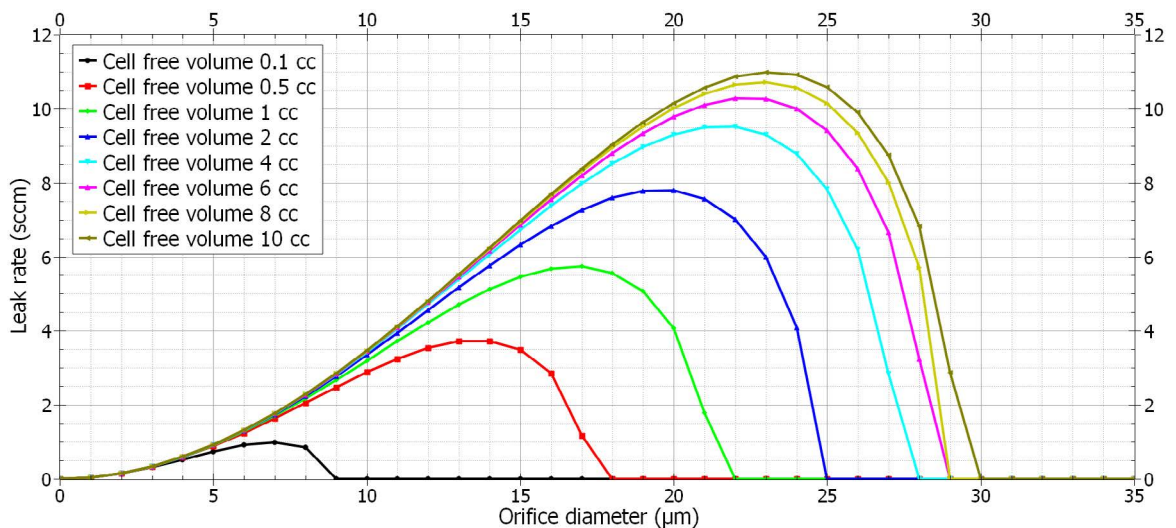


Figure 5 - Theoretical behaviour for leaks for different pinholes, each curve represents a different free volume inside the battery cell. The inlet pressure is fixed.

A first consequence that can always be reached is a condition in which two pinholes with a wide diameter difference may measure the same leak rate. Further to this, above a set dimension, the leak rate becomes zero, because the internal volume of the battery is filled completely and the pressure difference between the defective battery and the filling volume becomes zero (see Leaks dynamics and calibration, eq. 1). This can be somewhat intercepted during the test by selecting specific filling procedures and controls but, in any case, the residual volume and its distribution remain a “hard limit” on the application feasibility.

Finally, in order to be able to reliably detect small leaks it can be esteemed that pressures of at least 6 bar_{Rel} are required to perform the test (Figure 6).

This aspect, of course, is connected to the mechanical characteristics of each cell, and may vary for each format and for every manufacturer.

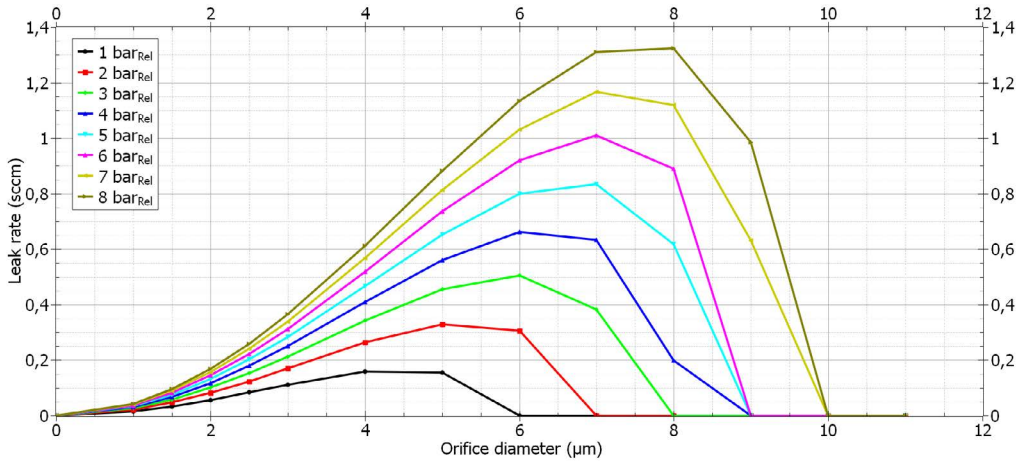


Figure 6 - Theoretical leaks for different pinholes at various inlet pressures, residual volume of the sealed object is fixed at 0.1 CC

For the sake of completeness, it would be also possible to conceive a test in which the battery is inserted in a vacuum test chamber and the pressure rise from the mixture of gas exiting from the leaking cell is detected. In this case, the setup needs to change, as shown in Figure 7.

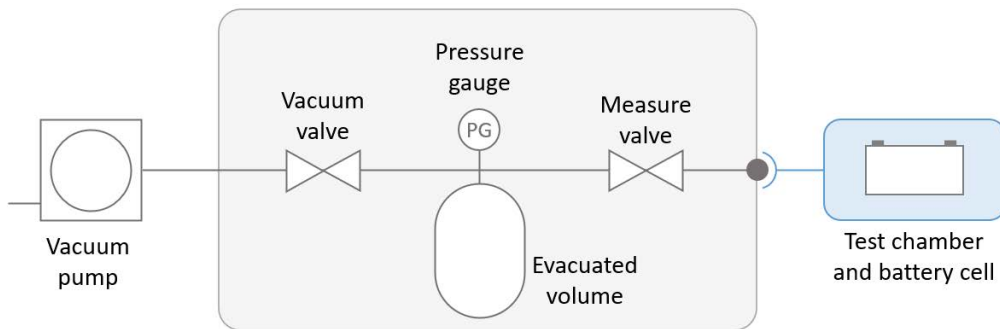


Figure 7 - Example of a vacuum test setup, and the process needs to be adjusted accordingly.

In a more realistic condition, the issue here is that the pressure difference is going to be at best 1 bar and the degas process from the test chamber itself is going to mask smaller leaks. Another important matter issue is that the battery does not provide a reliable source of gas in time, and leaks above a certain dimension are going to influence the internal pressure, decreasing the leak rate during the measure process.

Considering the difficulties, also this method is usually excluded, leaving pressure (or vacuum) decay to different application such as battery pack leak testing.

Now, also helium leak testing can be evaluated as a viable alternative. The technique is quite widespread and it is also possible to evaluate different measurement approach, like sniffing or partial flow, even

though usually the complete cell is tested in vacuum.

The main point in order to apply helium leak testing, however, is to insert the trace gas into the battery cell. In time, two possible options have been suggested.

1. Helium injection during electrolyte filling. The idea behind this method is to provide the trace gas by injecting a finite amount of helium into the battery during the electrolyte filling process.

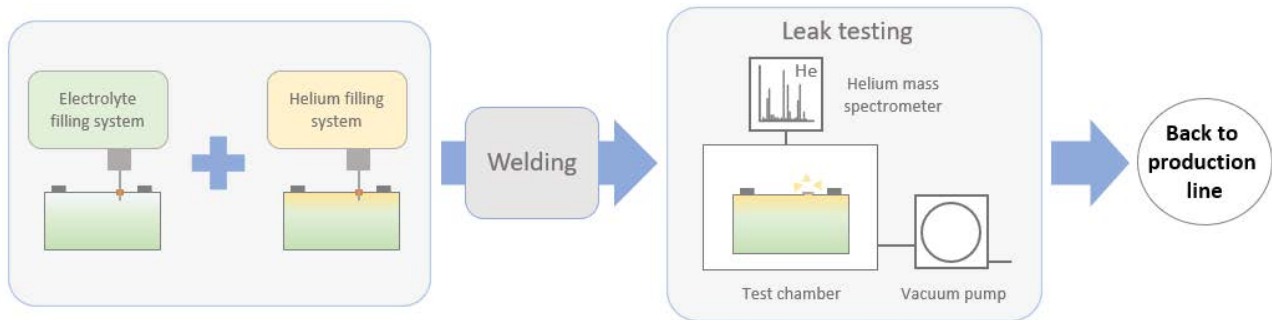


Figure 8 – Simplified scheme for the Helium injection process

Without considering the need to modify of the existing production line, the limited quantity of helium injected already introduces issues with repeatability and consistency in leak measurements. When this aspect is combined with the potential for large leaks, where most of the helium may escape, or with delays between battery production and leak testing, the most realistic conclusion is that the reliability of the method is undermined and the risk of producing “false good” results is too high to consider this a good testing procedure.

2. Helium bombing. In this method, the sealed battery is placed in a chamber filled with high-pressure helium, this forces the gas to permeate through any defects present on the cell. The battery is then extracted from the filling chamber and transferred into the test chamber.

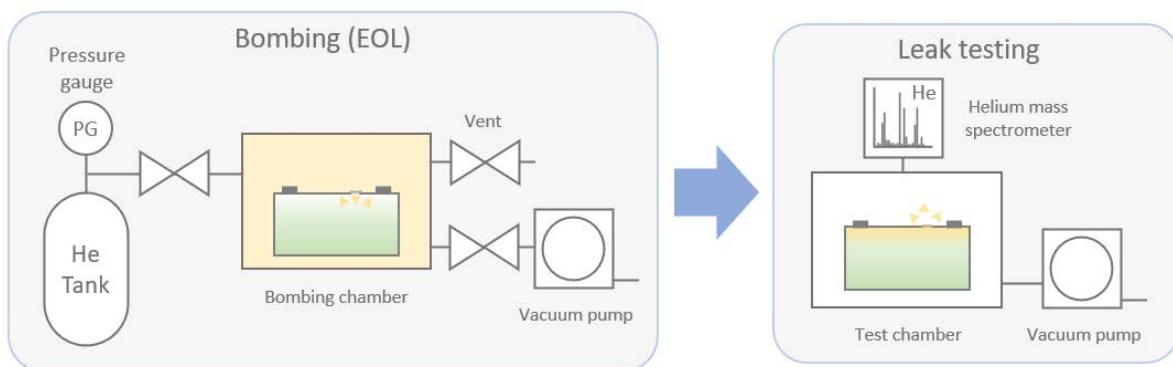


Figure 9 – Simplified scheme for the end of the line Helium bombing process

The main concerns with helium bombing are, first of all, the fixed time needed to assure consistent filling of the cell, especially if a very small leak has to be detected, secondly it is necessary to consider the fact that a significant amount of helium can escape through large defects, making it difficult to quantify the leak accurately. Although the time issue can be mitigated by optimizing the testing line timings or conducting the filling at high pressure, the method is affected by various issues in terms of behaviour of the leak in respect of the filling pressure, residual volume, quantity of the trace gas present into the cell and distribution of the tracer inside the battery.

An additional aspect, derived from experience in Helium leak testing, is the fact that, due to the increasing cost of this gas [10, 11], often clients advance requests for testing with diluted helium, for the implementation of helium recovery systems or even for the possibility to use alternative tracers. Additionally, thanks to the increase in utilization in various applications, is often considered also a critical resource in terms of supplying and processing [12, 13].

Summing up all of the challenges posed by the different approaches, none of them can assure a fully reliable measurement of the leak so the only possible conclusion was to develop a new specific testing technique to address the needs of battery cells leak testing.

ELECTROLYTE TRACING

To clearly summarize the points made so far, electrolyte tracing wants to provide a reliable test for checking battery cells that have been filled with electrolyte and fully sealed, without requiring significant modifications to the production line or in the battery structure.

The initial phase of development involves selecting a viable tracer for detection and identifying suitable instrumentation, with this objective in mind, the focus naturally shifts to the substances already present in the cell.

Among the various components of a battery cell, electrolyte solvents can be identified as the most suitable option for leak detection due to their inherent volatility. This characteristic is particularly advantageous because it enables the solvents to readily generate vapours that can easily diffuse into the surrounding environment or within a test chamber. In the latter scenario, the process can be further optimized by placing the cell under vacuum conditions. This approach not only forces the evaporation of the solvent but also accelerates the diffusion and transfer process, thereby enhancing the detection signal associated with any potential leaks.

Mass spectrometry can be identified as the right analytical technique for this kind of application and RGA (residual gas analysis) quadrupole mass spectrometers offer promising performance, compactness and affordability in respect to other known technologies.

Also, these kind of instruments can be installed into testing machines, but it is also necessary to consider that this integration can be more complex in respect to the typical helium leak test, particularly when dealing with process optimization.

Marposs developed two different setups from commercial RGA products and applied various degrees of personalization. The first one is the "Heated Capillary" (HC) system, while the second one is identified as the "Direct Vacuum" (DV) system. Each setup implements the leak test in its own specific manner, with different peculiarities, advantages and disadvantages.

The HC system is based on an already available commercial quadrupole mass spectrometer gas analysis system and the main personalization is on the measure process side (patented, see [14,15]).

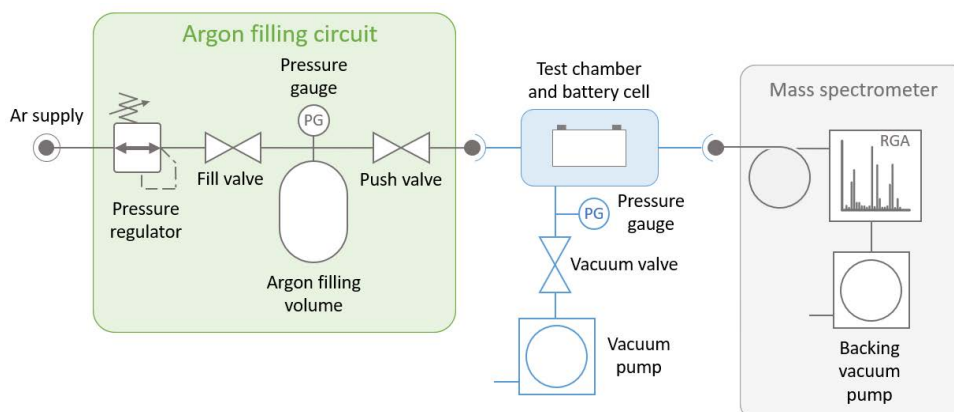


Figure 10 – Example of "Heated capillary" system scheme

This setup is focused on assuring quick cycle times and low requirements in terms of vacuum level into the test chamber. The measuring process is divided into three phases: Vacuum, Stabilization and Acceleration.

The first step is to reach low vacuum into the test chamber while the Argon filling volume is saturated, then the chamber is isolated in order to stabilize the pressure and let the tracer accumulate. This last phase is the one that takes up most of the time during the measurement process. Finally, the Push valve is opened and the Argon rapidly expands into the test chamber, increasing the pressure and forcing the tracer to transfer into the mass spectrometer heated capillary (hence the name of the system) and measured.

The measure is registered as a quick signal impulse after the Argon is accelerated into the test chamber. Even though this means that the system can be used only for go/no-go machines, it can perform a test with a cycle time as low as 8 s, depending on the setup, without requiring costly high-performance pumps. Thanks to the Argon impulse and proper test chamber structure the system can also be cleaned quite effectively from solvent residues. Moreover, with specific setups, having the mass spectrometer always connected to the vacuum chamber during the test made possible to intercept big leaks already in stabilization phase, allowing to preventively open up the chamber and make the cleaning process quicker. This adds up to already existing methods to intercept gross leaks and heavy contaminations through VOC sensors and pressure checks.

The main disadvantage is sensitivity, limited to a leak with 10 μm diameter as a standard.

The DV system introduces an additional level of customization and integration in the development of electrolyte tracing systems. This setup does not require a carrier gas and the mass spectrometer is connected to the test chamber through a specially designed inlet. The instrument remains disconnected from the test chamber until the final phase of the testing process, which is divided into three main

stages: Vacuum, Stabilization, and Measure.

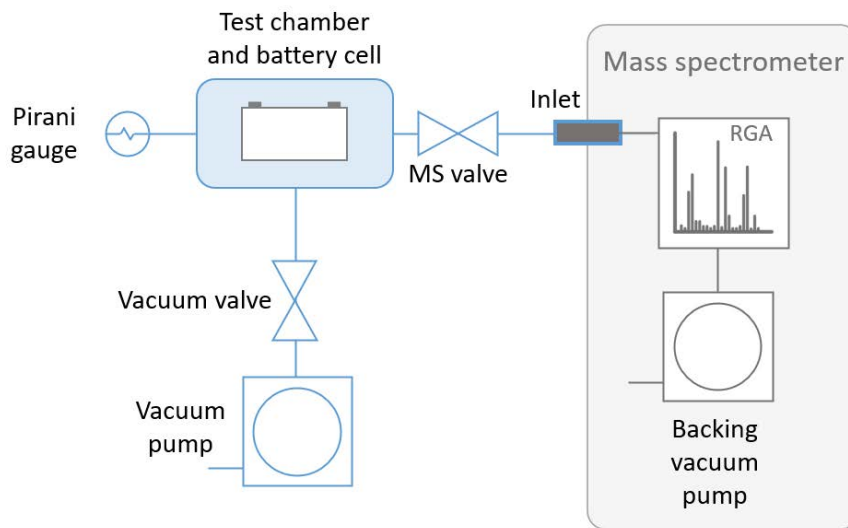


Figure 11 – Example of “Direct vacuum” system scheme

This setup requires to take the test chamber to a higher vacuum and needs a tighter control over it, but improves sensitivity and control over the measured signal, opening the possibility of proper calibration of the system.

In terms of timing, the measure process is strictly bounded to the vacuum phase. The Stabilization phase is usually much shorter in respect to the HC system, taking a minimum of two seconds, but can be tuned differently depending on the request. Same can be said for the Measure phase, which is usually four seconds `long.

The DV system also introduced an additional step to further enhance and personalize Electrolyte tracing technology. This, combined with the experience gained from the use of Heated Capillary systems on fully automated machines, contributed to the existing internal knowledge in mass spectrometry implementation and calibrated leak development.

To sum up the two options, Heated capillary systems can be a valid option for pilot lines where the entity of the defect is unknown and the need is to perform a first quality assessment phase for new sealing techniques that may give big defects. This system can be also applied to go/no-go production lines where the need is to have quick evaluation of defect above 10 µm without necessarily integrating costly pumping systems.

The Direct vacuum system, instead, is focused on semi-automated pilot projects and fully automated production lines. It provides the possibility to obtain a quantification of the leak through calibration and better sensitivity. Additionally, it also opens up the possibility for gauge capability studies. However, in order to maintain short cycle timings, it needs pumps with higher performances and a more specific selection for the materials constituting the test chamber in order to limit disturbance from outgassing.

QUADRUPOLE MASS SPECTROMETERS

The mass spectrometers selected for Electrolyte tracing consists of three main components: the ion source, the analyser, and the detector [16]. The detection process typically involves the following steps:

1. Introduction of Analyte Gas through an inlet.
2. Ionization of the gas molecules through the ion source.
3. Separation and selection of the ionized molecules through the analyser.
4. Detection of the selected ion through its interaction with the detector surface and consequent charge transfer.

In quadrupole mass spectrometers any substance going into the system is bombarded with 70 eV electrons and splits into ionized fragments as a consequence. The mass filter selects the ions and the detector gives a signal proportional to the quantity of the ionized fragment present. The signals obtained are then elaborated through software and ordered by atomic mass unit (a.m.u.), i.e. the mass of the ion.

The signal is typically displayed on a graph showing the atomic masses versus the intensity of the signal for each mass, generating a mass spectrum. Each substance can be identified by its unique mass spectrum, characterized by the presence of only certain fragments each one with typical intensities. Of course, when dealing with mixtures of gases it is possible that multiple signals superpose, which can make the interpretation of the spectrum a complicated matter.

If the intent is to detect a known specific tracer, it is possible to focus the measure on a specific mass, typical of the compound that needs to be detected. This second measuring mode is typically used in tracing techniques, and displays the change of the signal intensity of the selected peak in time.

Even though for certain tracers is easy to understand which is the best possible peak to be selected, electrolyte tracing deals with more complex molecules and choosing the right peak is fundamental to ensure strong and clean signals.

A TAILOR-MADE SETUP

As mentioned, the chosen tracer for Electrolyte tracing is the solvent evaporated by a leaking battery. Typically, inside the cell is not present a single solvent but a mixture of different components, each added in a specific quantity. In order to establish which is the best signal to use for detection, a couple of different approaches can be put into place.

The most complex case is when an unknown mixture needs to be analysed. When this occurs a complete mass scan needs to be performed in order to determine which substances are emitted from a cell. This usually implies to be able to create at least a controlled defect on the battery and properly being able to manipulate it. After acquiring the complete spectrum, it needs to be studied in order to understand which compounds are present into the mixture and, between them, determine possible candidates for detection. If the interpretation is done correctly, the tracer is then selected and a specific peak is chosen to identify it during tests. Practical trials with controlled leaks follow the process in order to verify the result and understand the system response.

A second option is to already know the electrolyte formula from the client, or at least have a list of possible tracer candidates, and then focus the measurement on a specific marker associated with the spectrum of the substance.

Ideally, having the complete formulation quickens the process, but that can be a sensitive information

for a manufacturer, providing fundamental details about the product. The request can be limited to at least the main volatile solvent present in the client's electrolyte and, if possible, some information on the percentage of the solvent within the mixture in order to have more accurate quantification.

Focusing on the selection of the right marker, the most important information is that each molecule has its own specific spectrum, like a fingerprint, but not every peak will be suitable for detection. For example, a first obstacle are the signals associated to residue signals of moisture and atmospheric air (N_2 , O_2 , CO_2 , Ar, etc.) remaining after evacuation of the test chamber. As a general rule, the selected marker needs to be as far away to these signals as possible in order to minimize interferences with the detection of the solvent.

As an example, Figure 12 shows a mass spectrum of Dimethyl Carbonate (DMC) sampled using Marposs' system. The darker peaks represent the normalized residue signals of atmospheric contaminants within the test chamber.

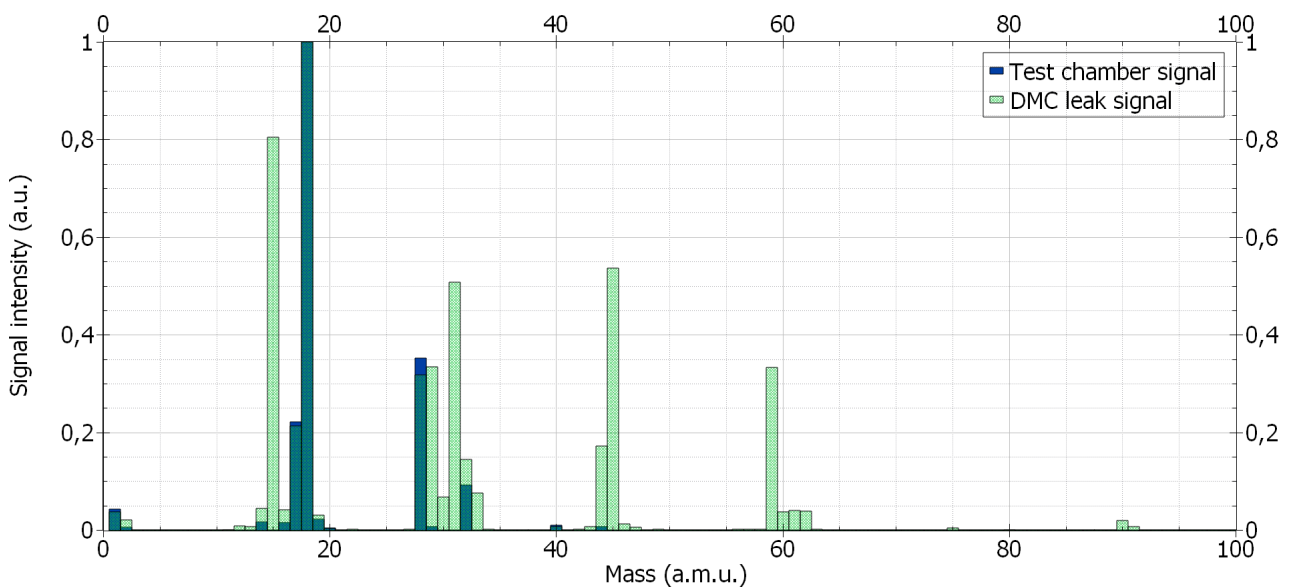


Figure 12 - Comparison between test chamber signal and a DMC leak signal (normalized peaks)

Once the peak is selected, the instrument is set to read only that specific signal.

Even though these processes can be standardized to a certain degree, when all the necessary data are obtained and the appropriate marker has been selected, the system needs to be fully validated and everything need to be tailored in order to meet the specific needs of the client.

The first matter to consider is that different solvents vary in behaviour and signal intensity, so is preferable to perform specific tests and to have proper communication with the clients to fine-tune the system for each application before installing the instrumentation into automatic machines. This involves not only optimizing the test chamber in terms of materials and design, but also selecting suitable vacuum pumps, integrating cleaning methods to prevent contamination, ensure quick recovery after high signals and understanding how the system responds to solvents under varying conditions.

In order to do this, the possibility to have at hand a variety of controlled leaks is of utter importance both for studying the measure limit for each solvent and the system reaction to them.

LEAK DYNAMICS AND CALIBRATION

As already clarified, the solvents are part of a mixture in liquid state and are typically almost entirely absorbed within the separator. This fact alone differentiates the technique in respect to typical tracing techniques.

Usually, classical leak tests deal only with gases and, from a pure theoretical and modelling point of view, the leak value depends from the geometry of the leak channel itself and is influenced by pressure or, more precisely, by the thermodynamic state of the substance (i.e. also from temperature and volume).

This is still completely valid also for Electrolyte tracing, so the starting point in order to analyse any leak is that it always involves transferring the mass (or volume) of a substance through a channel (geometrically modelled as a capillary, a pinhole, a porous material, etc.). The transport process is always influenced by the pressure at the heads of the leak, and strictly depends on the geometric structure, as can be seen from eq. (1) [\[17\]](#).

$$Q = C(p_{in} - p_{out}) \quad (1)$$

Where C (m³/s) is the conductance and depends on the geometry of the leak, p_{out} and p_{in} are the pressures in Pa. Generally speaking, if the pressure difference between the two heads of a defect is low, the flow rate is going to be small, while the increasing of this pressure variation is going to make the leak increase accordingly.

In Electrolyte tracing, because the solvent is absorbed into the separator, it is not possible to inject the tracer at a certain constant pressure, so this parameter cannot be tuned and controlled like in helium leak tracing, for example. Additionally, the only option to evidence the presence a solvent leak is to enhance the leakage process by putting the battery into a vacuum and accelerate the evaporation of the solvent itself.

An additional issue is posed by the fact that the solvent does not necessarily come in contact with the defect in liquid or in gaseous form. The electrolyte, in fact, is injected into the battery cell as a liquid mixture of solvents, lithium salts and additives, then it is imbued into the separator. This means that the solvents can be present into the battery both in liquid form, if a certain quantity of the electrolyte is not fully absorbed, and in gaseous form, owing to the fact that they tend to evaporate quite easily.

The physical state in which the solvent interacts with the defect depends on the battery's structural design and, in some cases, the positioning during testing process.

For example, with button, prismatic and cylindrical cells, the structure of the cell itself implies that residues of liquid electrolyte are going to deposit on the bottom of the cell and all the free volume is going to be saturated with solvent gases. In other cases, for example pouch cells, the situation is uncertain owing to the nearly zero free volume and the specific sealing technique.

In any case, considering both options and eq. (1), the tracer pressure inside the battery is going to be the vapour pressure of the evaporated solvent or the total pressure inside the cell in case of liquid leaks.

Studying the leak behaviour and understanding its mechanics allows to create controlled tests to properly simulate solvent leaks inside the measurement systems, providing information on how the leak is going to change in function of different parameters and giving the possibility to create solid

calibration procedures and dedicated master leaks to calibrate the system.

As stated previously, the basic parameters to study the leak behaviour in electrolyte tracing are mainly two: the physical state of the solvent and the geometry of the leak.

If the geometry of the defect is exactly the same, the main difference between liquid and gaseous leaks lies within the quantity of solvent passing through a defect itself, giving different results also in terms of registered signal intensity.

If the simulated leak is build using a capillary or the real defect can be approximated as a capillary, Hagen-Poiseuille equation [18] can be used to provide a proper evaluation of the volume of liquid passing through the channel. In order to use this approach, also all the boundary conditions of Hagen-Poiseuille law need to be respected. So, the flow must be laminar and the fluid must be Newtonian and incompressible. Note that is not strictly necessary that the pipe cross section is circular, but this choice is usually done to ease the operation. For the same reason, only a pure liquid is considered.

If a solvent in liquid state is going through such a leak, the equation describing the volumetric flow rate is:

$$\dot{V}_L = \frac{\pi r^4}{8\eta_L l} (p_{in} - p_{out}) \quad (2)$$

Where \dot{V}_L is the volumetric flow rate, r is the radius of the channel, p_{out} and p_{in} are the pressure at the heads of the channel, η_L is the viscosity of the fluid and l is the length of the channel.

For what concerns the case where only evaporated gas is in contact with the defect, we need to draw an approximation in which the gas is in near ideal conditions and at a temperature is in equilibrium with the ambient [18, 17]. Moreover, the local pressure gradient must be small enough to ignore compression effects. The volumetric flow rate at the outlet hence becomes:

$$\dot{V}_G = \frac{\pi r^4}{16\eta_G l} \frac{(p_{in}^2 - p_{out}^2)}{p_{out}} \quad (3)$$

From eq. (3) the leak rate is easily obtained just by multiplying the outlet pressure .

$$Q_G = \frac{\pi r^4}{16\eta_G l} (p_{in}^2 - p_{out}^2) \quad (4)$$

In eq. (3) and (4) however, two parameters may pose some issues. Even though the vapour pressure for many evaporated solvent (i.e. p_{in}) can be extrapolated from literature, the gas viscosity η_G is not as extensively studied.

Additionally, the values obtained are usually associated to specific conditions or derived from purely empirical tests. Finally, the exact conditions inside the cell are not always known and are strictly dependent on the sealing process of the battery producer.

Format	Possible conditions of the cell after final sealing
Pouch cells	Vacuum (ex.: 200 mbar _{abs}), depends on the process
Button / coin cells	Atmospheric pressure, controlled atmosphere
Cylindrical cells	Atmospheric pressure, controlled atmosphere, possible low vacuum
Prismatic cells	Near atmospheric pressure, controlled atmosphere, possible low vacuum

Table 2 - Cell format and expected internal conditions for the battery after sealing

To underline the difference that a change in the leak geometry may pose, we can now consider a leak more similar to a pinhole, a defect with a very short length, approximable to zero. To directly compare the results with eq. (4), let's say that the solvent comes again in contact with the pinhole in gaseous state, then the equation describing the phenomenon is the following:

$$Q_{G,pinhole} = kA(p_{in} - p_{out}) \sqrt{\gamma \frac{RT}{M} \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma+1}{\gamma-1}}} \tag{5}$$

The leak rate in this case depends from the temperature (T), the molar mass of the solvent (M), the specific heat ratio of a gas (γ), the area (A) of the orifice and increases linearly with the pressure difference (p_{in}-p_{out}). To better visualize the difference, it is possible to compare the leak rate of orifices of different radius (length of the channel theoretically zero) with capillaries having, again, different radius and fixed 100 μm length (Figure 13). The length is not casual, but is the average length of the channel of pinholes tested at Marpos's Leak Test Laboratory.

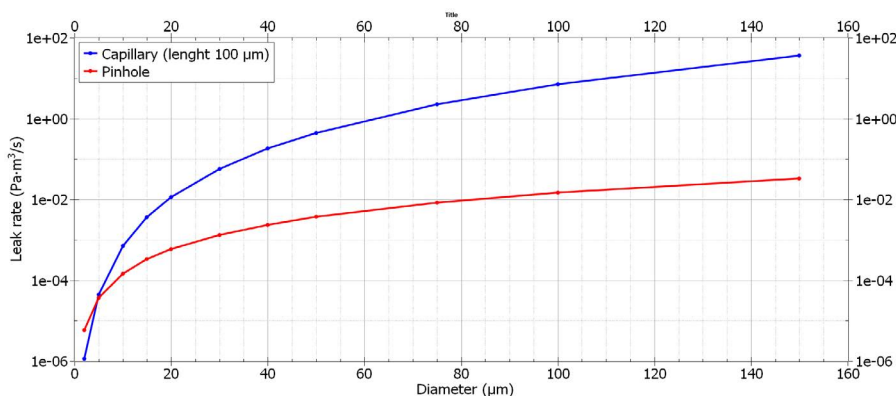


Figure 13 - Comparison between the leak rate equations (4) and (5) in air (pin=1 bar vs vacuum) for capillaries with fixed length (equal to pinhole) and pinholes, Tref = 0 °C.

Now, knowing that the real case scenario can pose a number of complex options, the focus can be shifted on system calibration. In this instance, the leak geometry is known, the tracer (i.e. the solvent)

inserted into the master is controlled (both pure or mixed), and everything can be constructed in such a way that a number of other parameters can be extrapolated by literature or through testing. This means that the physical analysis of this object, even though still complex, poses a lower number of difficulties. Moreover, the behaviour of this object can be studied not only with the Electrolyte tracing system, but also with different techniques. For example, a system to obtain a quantification of the flow rate by measuring the weight loss of a known geometrical defect in a predetermined time span and in controlled conditions can be conceived. This kind of system can be also adapted to analyse controlled leaks with different geometries, independently from the physical state of the solvent in contract with the leak.

Side by side with other instrumentation and with proper time, can also be used to validate the theoretical equations and to potentially extrapolate values for the missing parameters. With a system such as the one described, pinholes or calibrated leaks in contact with evaporated solvent have been characterized, measuring the weight loss in time. These calibrated leaks can then be used to set up the mass spectrometers in Marposs testing equipment.

The following examples (Figure 14 to Figure 17) are data extracted from the test performed in order to certificate Dimethyl Carbonate (DMC) filled masters. In order to determine the behaviour of the leak installed the master has been tested in controlled temperature conditions (Figure 14) and with different levels of vacuum (Figure 15). Then, the master has been measured repeatedly during 15 days to evaluate the stability

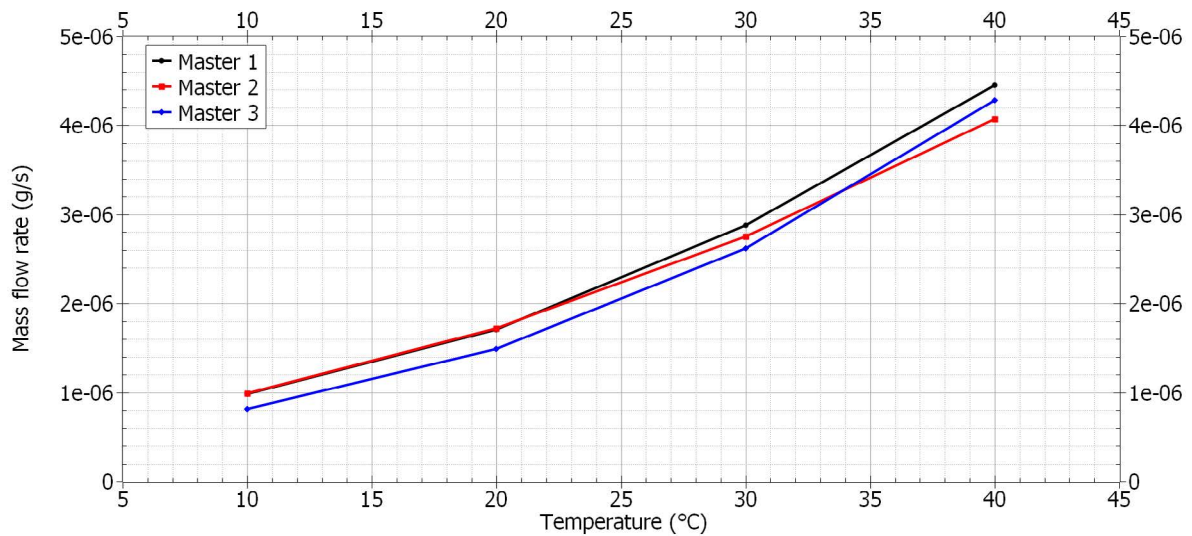


Figure 14 - Example for CL-SOLT master mass flow rate change with temperature

of the leak in time and (Figure 16), finally, into Marposs' leak test system (Figure 17).

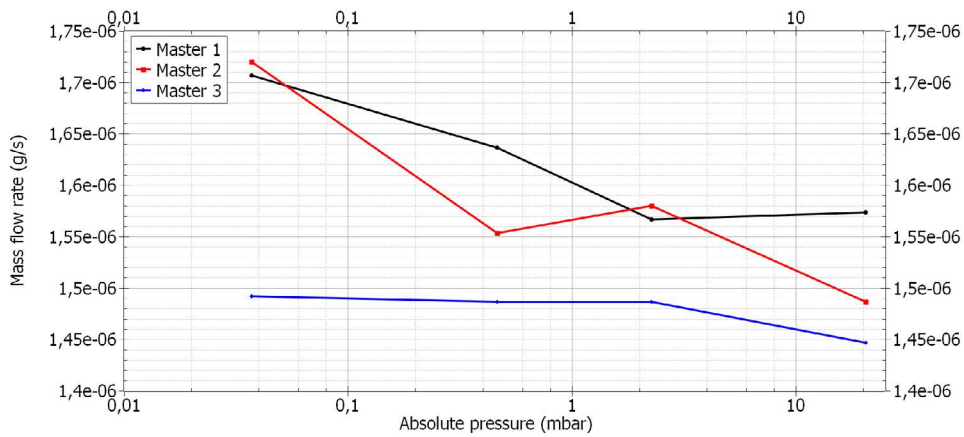


Figure 15 - Example for CL-SOLT master mass flow rate change with test chamber pressure

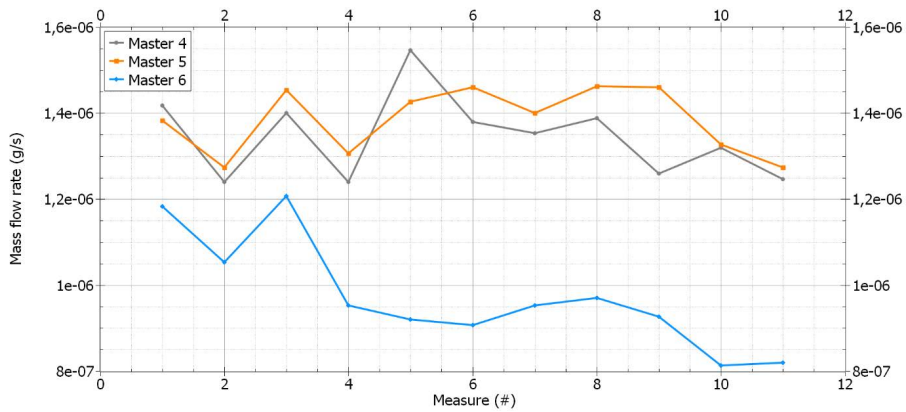


Figure 16 - Example for CL-SOLT master mass flow rate change with time (11 measure set in 15 days)

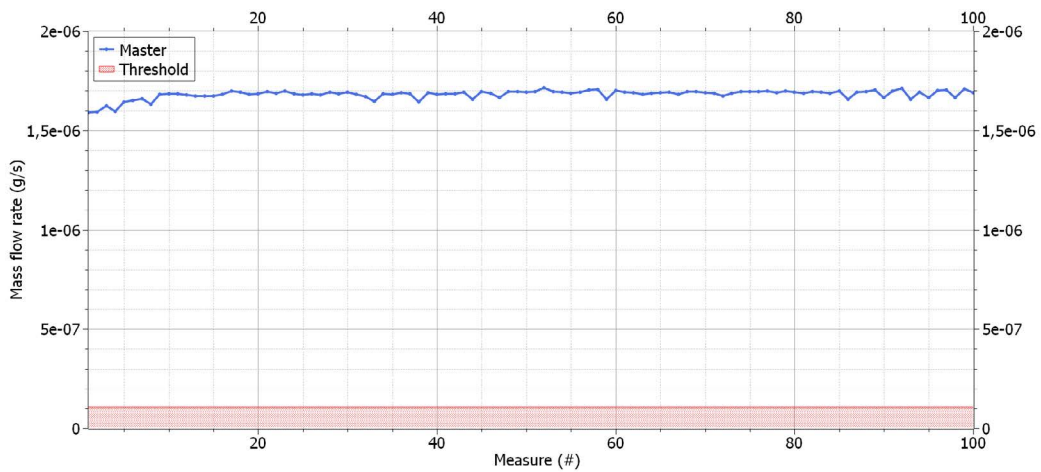


Figure 17 - Example for CL-SOLT master mass flow rate measure after mass spectrometer calibration during 100 consecutive tests.

As can be seen, the masters can be tested in different conditions in order to provide the necessary information to fully comprehend its behaviour. Moreover, all the characterization process remains valid also with different geometries, solvents and solvent mixtures in order to simulate a leak from a battery and understand how the measurement system is going to respond.

The choice to focus on gaseous leaks is driven by their ability to represent the more probable behaviour of a broad range of battery formats, such as coin, cylindrical, and prismatic cells. The leak of pouch cells can be also properly associated to a g/s leak, but with some care (see “Converting the measurement”).

Various defect sizes have been tested, ranging from a diameter as small as 1 µm to several hundred microns. This gives also the possibility to effectively evaluate contamination recovery for the instrument and develop techniques to intercept gross leaks, which have then been implemented into automatic machines used in production lines or pilot projects.

A final aspect to consider is that, thanks to this choice, it has been possible to study from the beginning a more restrictive case in terms of quantity of material emitted from the defect, granting the ability of detecting properly both liquid or gas leaks. In fact, generally speaking, with equal thermodynamic conditions, a solvent gas leak is going to transfer a lower quantity of matter in respect to a liquid leak with the same geometrical characteristics. In a very simplistic way, we can say that this is due to the fact that the evaporated gas inside the residual volume of the cell is much less dense in respect to a liquid, so the interactions between the molecules and the reaction of the fluid to external inputs are going to change accordingly.

For what concerns instead going a step more near to the real case scenario, further studies can be performed in order to understand how the signal is affected by the presence of a mixture of solvents inside the master. This is, in fact, something to take into account when comparing the calibration master with the real cell. Generally speaking, the master is filled with a single solvent, but a real battery is not. A RGA mass spectrometer, however, is set to detect only a single tracer.

One of the consequences of this aspect is that it's likely to register a loss of signal due to the presence of a mixture, thanks to the fact that in absolute terms, a lower quantity of tracer reaches the mass spectrometer.

With this knowledge, however, is possible to include a correction factor during calibration, which is going to give quantitative measures closer to the real leak also while testing a battery cell.

CONVERTING THE MEASURE

In Marposs' specific case, the approach is to measure solvent weight loss over time, i.e. mass flow rate (g/s), for a master in a vacuum, containing only the tracer rather than a mixture (although this is possible).

A typical conversion is usually to pass from mass flow rate (\dot{m}) to volumetric flow rate (\dot{V}), this can be done relatively easy using the solvent density (ρ) [18].

$$\dot{V} = \dot{m} \cdot \rho \quad (7)$$

The only precaution here is to consider that, if the solvent is in gas phase, then the vapor density needs to be calculated, the vapour pressure of the solvent and the temperature need to be known.

If the leak rate is needed, working under the approximation that the solvent is transferred in gas phase and is rarefied enough to be considered an ideal gas, the conversion can be done through equation (8).

$$Q_G = \frac{\dot{m}}{M}RT \quad (8)$$

Where \dot{m} is the mass flow rate, R the ideal gas constant, T the temperature in K and M the solvent molar mass.

For what concerns the Marposs approach, the choice is to express the measure in g/s or in mbarL/s of solvent, applying the equation above. The only limitation to this conversion is for pouch cells, for which may be difficult to choose "a priori" if the leak comes always in contact with solvents in liquid or gaseous phase. In many instances both cases may be potentially present in different parts of the sealing surface. In this specific case, only the g/s value is going to be used because both the calibration process of the master and the measure of the mass spectrometer are blind to differences such as geometry of the leak or the solvent phase inside of the battery. So, if all the other thermodynamic conditions (mainly temperature) are stable, then the measure obtained is a signal directly connected to the quantity of the solvent escaped from the defective battery and evaporated into the test chamber.

CONCLUSION

Leak detection is essential to improve safety, reliability and quality of battery cells. The need to find a solution to this challenge sparked the development of Electrolyte Tracing, which has the potential to emerge as a new testing solution dedicated to this market.

Even though the sensitivity of the technique is not yet on par with helium, the selection of appropriate markers for detection, coupled with an understanding of leak dynamics and the calibration of measurement systems, can enable reliable quantification of leaks in various battery formats.

As the technology continues to evolve, it will likely become an essential tool for battery manufacturers striving to meet the highest standards of quality and safety.

As explained in this paper, the verification of the perfect sealing of battery cells is not only necessary to prevent leaks of electrolyte, but also serves to limit the entry of contaminants into the cell and therefore to guarantee its correct functioning over time. For this purpose, the method presented allows the accurate measurement of the smallest leakage levels of battery cells once sealed and is therefore a fundamental operation in the quality control at the end of the line.

It should be emphasized that this test operation is not necessarily an alternative to the test performed on open cells, using helium as a tracer gas in a vacuum chamber. When applicable, a leak test before electrolyte filling would be advisable, both for process control and possible feedback on previous operations, and to avoid sending rejected cells to the subsequent formation and aging operations. However, the verification of the perfect sealing through electrolyte tracing at the end of the line represents a fundamental quality gate, which should always be part of the product quality certification process.

REFERENCES

[1]	J. B. Goodenough, «How we made the Li-ion rechargeable battery,» <i>Nature Electronics</i> , vol. 1, n. 204, March 2018.
[2]	K. Y. Goodenough J. B., «Challenges for Rechargeable Li Batteries,» <i>Chem. Mater.</i> , vol. 22, pp. 587-603, 2010.
[3]	M. P. N. P. Verma P., «A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries,» <i>Electrochimica Acta</i> , vol. 55, pp. 6332-6341, 2010.
[4]	E. P. Roth e C. J. Orendorff, «How electrolytes influence battery safety,» <i>The Electrochemical Society Interface</i> , vol. 21, 2012.
[5]	D. Aurbach, I. Weisseman, A. Zaban e P. Dan, «On the role of water contamination in rechargeable Li batteries,» <i>Electrochimica Acta</i> , pp. 1135-1140, 1999.
[6]	H. Zhou, Y. Xie, X. Gao, Z. Chen, H. Jiang, Y. Tong, X. Fan, Y. Lai e Z. Zhang, «The influence of water in electrodes on the solid electrolyte interphase film of micro lithium-ion batteries for the wireless headphone,» <i>Journal of Colloid and Interface Science</i> , n. 606, 2022.
[7]	K. K. L. Y. C. N. Han J., «Scavenging materials to stabilize LiFP6-containing carbonate-based electrolytes for Li-ion batteries,» <i>Adv. Mater.</i> , p. 1804822, 2018.
[8]	G. Quian, F. Monaco, D. Meng, S. Lee, G. Zan, J. Li, D. Karpov, S. Gul, B. Stripe, D. Vine, J. Zhang, J. Lee, Z. Ma, W. Yun, P. Pianetta, X. Yu, L. Li, P. Cloeten e Y. Liu, «The role of structural defects in commercial lithium-ion batteries,» <i>Cell Reports Physical Science</i> , vol. 2, 2021.
[9]	R. S. Bhosale, P. P. Kumbhar, K. S. Mahajan, A. K. Yachkal e A. Katarkar, «Study on Leak Testing Methods,» <i>IJSRD - International Journal for Scientific Research & Development</i> , vol. 5, n. 1, 2017.
[10]	A. Nordrum, «The era of cheap Helium is over - and that's already causing problems,» <i>MIT Technology Review</i> , 25 Feb. 2024.
[11]	D. Kramer, «Helium prices surge to record levels as shortage continues,» <i>Physics Today</i> , vol. 76, n. 9, 1 Sep. 2023.
[12]	M. Grohol e C. Veeh, «Study for the Critical raw materials for the EU,» DG Grow, European Commisison, 2023.
[13]	USGS, «U.S. Geological Survey, Mineral Commodity Summaries,» 2024.
[14]	E. Cohen e G. Vollaro, «Method for leak testing a battery cell». EU Brevetto EP 3 736 903 B1, 11 November 2020.
[15]	E. Cohen e G. Vollaro, «Method for leak testing a battery cell». US Brevetto US20230253632A1, 15 July 2020.
[16]	J. H. Gross, <i>Mass Spectrometry, A Textbook</i> , Springer, 2004.
[17]	J. H. O'Hanlon, <i>A User's Guide to Vacuum Technology</i> , John Wiley & Sons, Inc., 2003.
[18]	M. Bergoglio e A. Calcatelli, «Rivelazione e misurazione delle fughe,» <i>Il Giornale delle Prove non Distruttive Monitoraggio Diagnostica</i> , vol. 3, 2007.
[19]	D. Wang e Y. Zhang, «Research on Structural Design of New Type Buttoned Lithium Battery,» <i>IJRES</i> , 2017.

[20]	R. Fang, P. Dong, H. Ge, J. Fu, Z. Li e J. Zhang, «Capacity plunge of lithium-ion batteries induced by electrolyte drying-out: Experimental and Modeling Study,» <i>Journal of Energy Storage</i> , vol. 42, 2021.
[21]	G. Gachot, S. Grugeon, M. Armand, S. Pilard, P. Guenot, J. Tarascon e S. Laruelle, «Deciphering the multi-step degradation mechanisms of carbonate-based electrolyte in Li batteries,» <i>Jurnal of Power Sources</i> , vol. 178, pp. 409-421, 2008.
[22]	F. J. Günter, C. Burgstaller, F. Konwitschny e G. Reinhart, «Influence of the Electrolyte Quantity on Lithium-Ion Cells,» <i>Jurnal of The Electrochemical Society</i> , vol. 166, 2019.
[23]	M. Wiedenbeck, R. Bugoi, M. J. M. Duke, T. J. Dunai, J. Enzweiler, M. F. Horan, K. P. Jochum, K. L. Linge, J. Košler, S. Merchel, L. F. G. Morales, L. Nasdala, R. Stalder, P. J. Sylvester, U. Weis e A. Zoubir, «GGR Biennial Critical Review: Analytical Developments Since 2010,» <i>Geostandards and Geoanalytical Research</i> , 2012.
[24]	M. Grützke, V. Kraft, B. Hoffmann, S. Klamor, J. Diekmann, A. Kwade, M. Winter e S. Novak, «Aging investigations of a lithium-ion battery electrolyte from a field-tested hybrid electric vehicle,» <i>Journal of Power Sources</i> , pp. 83-88, 2015.
[25]	S. A. Kozlova, V. N. Emel'yanenko, M. Georgieva, S. P. Verevkin, Y. Chernyak, B. Schäffner e A. Börner, «Vapour pressure and enthalpy of vaporization of aliphatic dialkyl carbonates,» <i>The Journal of Chemical Thermodynamics</i> , vol. 40, pp. 1136-1140, 2008.
[26]	S. Maddipatla, L. Kong e M. Pecht, «Electrolyte Leakage in Cylindrical Lithium-Ion Batteries Subjected to Temperature Cylcing,» <i>Energies</i> , vol. 17, 2024.
[27]	R. Borah, F. R. Hughson, J. Johnston e T. Nann, «On Battery materials and methods,» <i>Materials Today Advances</i> , vol. 6, 2020.
[28]	Y. Wang, C. Zhang, J. Hu, P. Zhang, L. Zhang e L. Lao, «Investigation on calendar experiment and failure mechanism of lithium-ion battery electrolyte leakage,» <i>Journal of Energy Storage</i> , vol. 54, 2022.

PARTNER

Marposs was founded in 1952 and Mr. Stefano Possati is the President of the Group; it provides shop-floor solutions for measurement, inspection and testing in the production environment.

Leading supplier to the main automotive and aerospace manufacturers, Marposs is widening its offer towards the biomedical industry, by combining measurement accuracy and compliance with standards. It includes dimensional and functional controls as well as leak, flow, burst tests customized to the various types of biomedical components and their machining process. Thanks to this large portfolio, Marposs fulfills user-specific requirements in terms of measuring methods (tactile vs contactless) of repeatability, of robustness within machine tools, by a complete project engineering from the use case to training and maintenance.

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