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NEW REQUIREMENTS FOR QUALITY AND IN-PROCESS CONTROLS OF NEXT-
GENERATION BATTERIES

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List of Acronyms

AAC	Average article citations
AAM	Anode active material
ALS	Asymmetric least-square algorithm
CAM	Cathode active material
CEI	Cathode electrolyte interface
CI	Chemical ionization
CSE	Composite solid-state electrolyte
DC	Direct current
DMC	Dimethyl carbonate
EC	Ethylene carbonate
EI	Electron ionization
EPO	European patent office
EV	Electric vehicle
FD	Field desorption
FI	Field ionization
GPE	Gel polymer electrolyte
ICE	Internal combustion engine
ISE	Inorganic solid electrolyte
IT	Information Technology
LFP	LiFePO_4
LISICON	Lithium super ionic conductor
LLZO	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$
LOD	Limit of detection
LPSBr	$\text{Li}_6\text{PS}_5\text{Br}$
LPSCl	$\text{Li}_6\text{PS}_5\text{Cl}$
LPSI	$\text{Li}_6\text{PS}_5\text{I}$
MALDI	Matrix-assisted laser desorption/ionization
MS	Mass spectroscopy
MW	Molecular weight
NASICON	Sodium super ionic conductor
NiCd	Nichel-Cadmium
NiMH	Nichel-Metal hydride
OEM	Original equipment manufacturer
PAN	Poly-acrylonitrile
PEO	Poly-ethylene oxide
PMMA	Poly-methyl methacrylate
PVDF	Poly-vinylidene fluoride
R&D	Research and development
RF	Radio-frequency

SEI	Solid electrolyte interface
SEM	Secondary electron multiplier
SHE	Standard hydrogen electrode
SPE	Solid polymer electrolyte
SSB	Solid-state battery
SSE or SE	Solid-state electrolyte
TC	Total citations
TOF	Time-of-flight

Abstract

The fight against climate change has deeply influenced the transportation sector, which is gradually moving away from internal combustion engines and toward widespread electrification. The increasing demand for batteries has pushed many players, both within and beyond the automotive industry, to explore new cell chemistries, especially to meet the stringent requirements of the automotive sector. At the same time, efforts are being made to reduce dependence on Asian countries, which currently dominate the global battery market. The emerging European battery industry therefore represents both an opportunity and a challenge, not only for battery manufacturers but also for companies whose mission is to ensure process quality and reliability, even in highly innovative production environments.

This industrial thesis aims to study and analyse the critical aspects that next-generation battery chemistries may encounter during the scale-up process from laboratory to industrial production. The work, carried out at MG SpA (Marposs group, Travagliato BS) and Marposs SpA (Bentivoglio, BO), represents an early stage in the design of new instrumentation and/or the adaptation of existing systems for process and quality control of next-generation chemistries. The ultimate goal is to facilitate efficient and reliable technology transfer from R&D laboratories to production lines.

Section 1 introduces the key challenges faced by the European battery market. It gives a brief overview of electrochemical cell operation and the main parameters affecting performance for all that is considered state-of-the-art at the time of writing this thesis. Moreover, it also explores the new trends on innovative battery chemistries, such as solid-state battery systems and related materials, among the most cited in relation with the emerging electric vehicle industry.

In Section 2, a detailed market analysis is presented with the objective of building a business plan to maximize the impact of Marposs research and development investments. The results of the research highlight the efforts of the European market players on exploring new chemistries and innovative production technologies to compete with the actual Asian market.

Section 3 introduces the theory behind leak testing techniques, which play a crucial role within any battery manufacturing process. Leak tests provide essential information not only on process robustness and reliability but also on product safety for end users. Indeed, air infiltration into a battery cell can cause swelling due to the formation of gaseous species, among which corrosive and harmful acids, and, in the most severe cases, leads to thermal runaway.

Section 4 presents leak testing techniques applied to sealed batteries and on the exploration of air reactivity in novel solid-state electrolytes, that build the experimental activities carried out in this thesis work. In this section, three methods are presented.

The theoretical optimization of test parameters for the so-called helium bombing test is first illustrated. The parametrization of the test was then experimentally validated through the design of a custom “master leak” model reproducing the internal volume specifications of a battery cell provided by the customer.

Subsequently, a leak testing approach based on electrolyte tracing in sealed pouch cells is presented, including the design of the testing apparatus, optimization of experimental parameters, calibration and repeatability validation of the test bench, and application to customer cells.

Finally, the reactivity study of a next-generation electrolyte belonging to the sulphide family (among the most promising candidates for solid-state battery applications in the automotive sector) is described. The work investigates the sulphide’s behaviour under atmospheres with different moisture contents, given its well-known tendency to react with water and generate hydrogen sulphide gas.

Additionally, the thesis presents, in Section 6, the design and validation of an innovative dilatometry (M-EET), capable of operando monitoring of electrode thickness variations under controlled mechanical load. The system has been engineered to enable both two- and three-electrode testing configurations, with the aim of quantifying chemo-mechanical deformation mechanisms relevant to advanced battery chemistries. Although further improvements are required to achieve full electrochemical reliability, this development marks an essential step toward integrating mechanochemical diagnostics into the workflows of next-generation cell characterization.

The overall goal of this thesis is to provide Marposs with experimental insights and methodological tools to support the development of in-house technologies capable of anticipating the needs of future clients currently engaged in the research and development of next-generation battery chemistries. By understanding both the analytical requirements and the production challenges of such systems, the company will be better positioned to design reliable testing and quality control solutions that will remain relevant as these new chemistries move from laboratory to industrial scale.

1. Introduction

In this chapter the reader can firstly find a brief introduction on the European battery scenario and the goals that the European commission poses to this emerging industry in the old continent, together with the motivations that lead to the revolution of the energy industry, all of them discussed in Section 1.1.

Section 1.2 will briefly describe the theoretical basis for energy conversion and storage in batteries, before dealing more in details with the different generations of battery technologies that are currently under investigation and that will shape the future of European battery industry.

Section 1.3 briefly describes the chemistry behind state-of-the-art Li-ion batteries and the most promising research trends in this field.

Section 1.4 presents the challenges associated with the use of a solid matrix for the conduction of Li-ions in next-generation solid-state batteries, with particular attention to polymer and ceramic-based solid-state electrolytes.

1.1. The European battery scenario

The reduction of greenhouse gas (GHG) emission is not a recent topic: this journey started in 1997 with the ratification of the Kyoto protocol, when 192 Parties signed the agreement to reduce the GHG emissions to levels that prevent catastrophic consequences on climate change [1]. Since then, Europe has put lots of effort in this direction, with initial proposals such as RED I directive in 2009 [2] and the 2030 Climate and Energy strategic plan in 2014 [3], that established the pillars for a more sustainable country, up to regulations that established restrictions on energy production, for example the Paris Agreement in 2015 and its adoption by the EU in 2016 [4], [5]. From 2018 onwards, the interest grew so fast that a new regulation was published basically each year until this 2025. In this scenario, batteries were recognized to play a crucial role, especially in what is known as electrification of transportation, thus decreasing the pollution coming from fossil fuel used in common internal combustion engines. Several initiatives pose the basis for promoting green transport, clean energy and achieving climate neutrality until 2050, the most important being the European Green Deal in 2020 [6] and the European Battery Regulation [7]. This growing interest and spread of applications for rechargeable batteries is driving research fast, demanding for higher energy density batteries that can be adopted in the automotive sector, granting for longer driving range, long-enough life span and increased safety. If, on one hand, state-of-the-art lithium-ion batteries demonstrated very high performance, with some of the solutions that have reached a mature stage of production, it is clear that for application in the automotive sector the current Li-ion chemistry is not enough. This demand from a nascent commercial sector started the second battery revolution. As a matter of fact, the story of the first rechargeable Li-ion battery started with a demand for the emerging market of the consumer electronics. The information technologies (IT) were developing smaller and lighter electronic devices, which required lighter but still powerful batteries to be powered. Primary batteries were light enough, but they could not be recharged; on the other hand, secondary batteries were only lead-acid and NiCd or NiMH ones, which, relying on aqueous electrolytes, posed several challenges to be scaled down in size and maintain high energy density. In this context, at the beginning of the 1980's, there were plenty of research institutions in the world studying for the adoption of liquid organic solvent-based electrolytes, the most important pillars graphically showed in Figure 1.1.

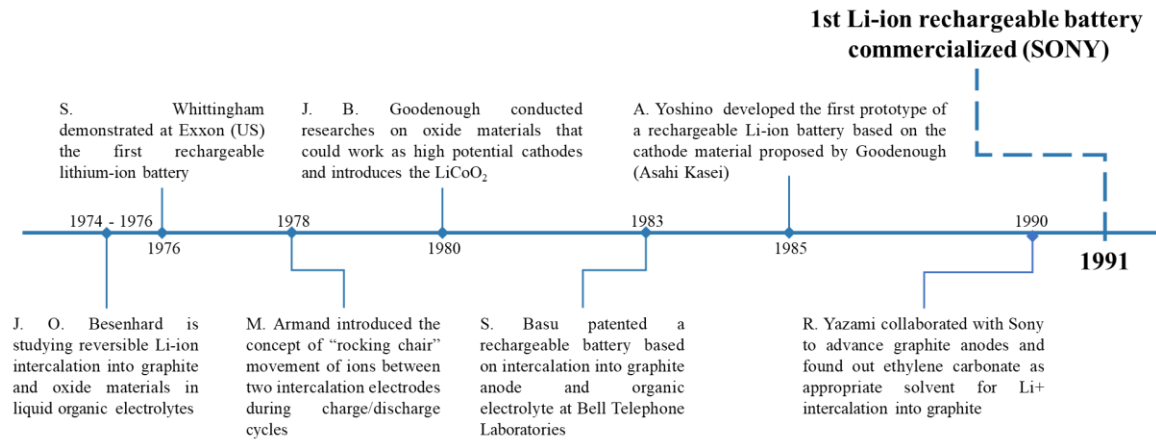


Figure 1.1. References for the researches and events can be found in [8], [9], [10].

As illustrated in Figure 1.1, battery research was an active area of interest for academia in both Europe and Asia from the beginning. However, the connection between academic institutions and industry was notably faster and stronger in Asia, particularly in Japan. Here, companies like Sony, Sanyo, and Matsushita (now Panasonic) engaged in robust collaboration with universities, often accelerated by governmental financial grants. This synergy allowed Japanese companies to establish and maintain a dominant position in both the battery market and further research throughout the latter half of the 20th century. This superiority began to shift in the early 21st century with the emergence of a new major player: China. Recognizing the immense potential of electric vehicles (EVs) at a time when competition in the conventional internal combustion engine (ICE) automotive market was mainly dominated by established European companies, Chinese industries and the government made significant strategic investments, fundamentally altering the global battery landscape. A series of policies played a crucial role in this regard, such as the "Made in China 2025" strategy and the "Battery Whitelist". They promoted the development of battery technologies and, most of all, technologies for scaling up the production with exceptional cost-effectiveness, limiting at the same time the importation of batteries from countries outside China. In this way, the production efficiency of this country increased rapidly, overcoming in short time the production pace of Japan too, thanks to the joint action of governmental fundings and fast academia to industry scale-up. Furthermore, Chinese banks, working closely with the government, facilitated access to raw materials for battery production by investing in mines and processing facilities globally. By 2015, China surpassed Japan and Korea as the larger exporter of lithium batteries.

The consumer electronic industry has been dominated by the use of Chinese batteries since more than 10 years. Nowadays, the emerging EV sector is posing some challenges to the reliability on the sole Chinese market for a component (the battery) that constitute the core of an electric vehicle. The phenomenon that is currently affecting the European industry is the institution of R&D centre for alternative battery chemistries, capable to increase battery endurance on the longest possible range of driving with decreasing the cost, from raw materials to the production ones. Indeed, at the same time, companies always involved in building manufacturing machines (like Coesia Group, Sovema group or CMWTEC) are now broadening their interest in battery manufacturing machineries, with competitive cost and increased efficiencies. The European Union is thus trying to promote the transfer of knowledge from academia to industry by getting access to financial programs, which has granted more than €10 billion in the last 5 years (2020-2025). This financial program aims to provide an energy revolution for a greener economy, ending up with the abandon of the reliance on fossil fuels to focus on more sustainable technology. To accomplish this, several aspects must be taken into consideration. The race to increase energy density of electrochemical devices is strongly linked to their reduction in production costs, and the overall research is looking into this direction. Indeed, the following sections aims to give a general understanding of what an electrochemical device is and how it stores and converts chemical to electrical energy. Then, a review of the current technologies adopted for the state-of-the-art Li-ion chemistries based on liquid organic electrolyte will be addressed, before exploring new trends in the more innovative solid-state batteries.

1.2. Electrochemical energy storage and conversion

In electrochemical devices, energy is stored as chemical energy and converted to electrical energy by transfer of charges (electrons) from an electronic conductor to a chemical species. In secondary batteries, this transferring is reversible, meaning that when all the chemical energy is released as electric energy, the electrons can be forced to invert their pathway by applying electric energy to restore the reactants, which are the source of chemical energy. These *faradaic processes* occur within the active materials of the electrodes, where chemical species undergo reduction or oxidation at well-defined potentials during charge and discharge. Nowadays, the most used electrode active materials for Li-ion batteries are intercalation materials (like graphite) for the anode side and insertion materials (like transition metal oxides) for the cathode side. Figure 1.2-a shows

the typical structure of olivine-like LiFePO_4 and the insertion of lithium ions into the crystal lattice, while Figure 1.2-b shows the intercalation of lithium ions into the graphite layered structure.

The lithium ions diffuse through a solution called electrolyte; when an electric field is applied at the electrodes, anions and cations migrate from their equilibrium position close to the electrode surface [11]. Here, the electrolyte can be reduced (or oxidized) to form the solid electrolyte interface (SEI) [12]. This nanometric thin layer, if properly engineered, can protect the electrode surface from degradation when long cycle life is expected. Liquid electrolytes are soaked into a porous thin membrane, the separator, which also electrically isolates anode and cathode, preventing cell short circuit.

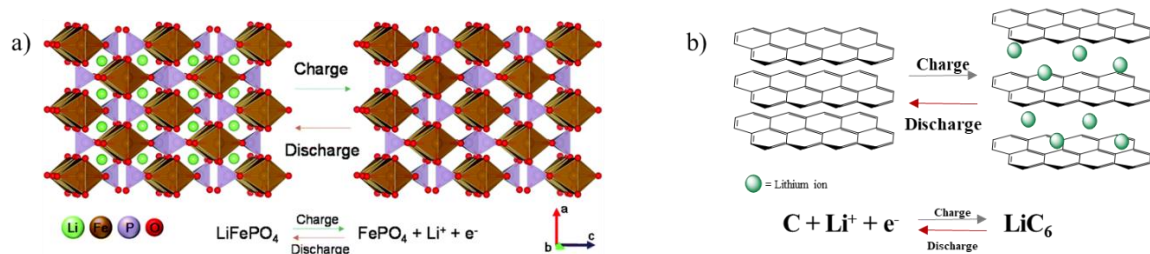


Figure 1.2. a) Insertion/de-insertion of Li-ions into the olivine-like structure of LiFePO_4 (reprinted with permission from [13]); b) intercalation/de-intercalation of Li-ions into the graphite layers.

In contrast to liquid electrolyte, a solid-state electrolyte is an ionically conductive, electronically insulating solid material that replaces the liquid components as well as the separator in a battery. In case of a solid matrix the ion transport is mainly due to collective jumps and lattice vibrations through defects or vacancies, in case of crystalline matrices [13], or movement through molecular motions of polymer chains in polymer matrices [14] (Figure 1.3).

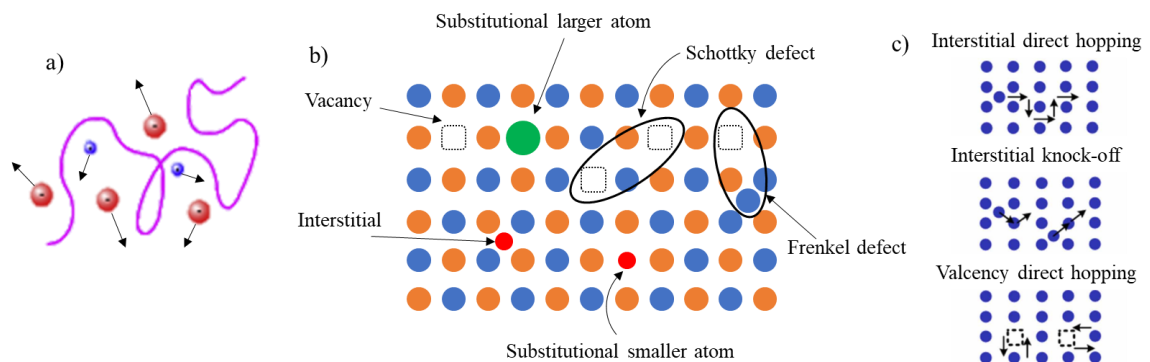


Figure 1.3. a) Ion motion through molecular chains of polymer matrix (modified from [14]); b) schematic illustration of defects in a crystal lattice; c) ion diffusion types in inorganic solid-electrolytes. b) and c) modified from [13]

The choice between a liquid or solid-state electrolyte depends on multiple factors. Although many argue that liquid electrolytes are less safe, research on this field has brought to important advancements that make this technology widespread in all the consumer electronics and in the automotive sector. On the other hand, solid-electrolytes can have important implications in their use with electrode active materials with high specific capacity and voltage, for example when coupled with metallic lithium as anode material, substituting graphite-based anodes. The use of lithium metal will enlarge dramatically the energy density of batteries, but its high reactivity poses severe safety concerns. A fundamental issue is related to the formation of dendrites that can break the separator and short circuit the cell when coming in contact with the cathode surface, thus leading not only to cell fail, but most importantly to thermal runaway effects. Solid-state electrolytes have been recognized for their ability to suppress dendrites growth, thus opening the possibility to use lithium metal in future generation batteries.

1.3. The chemistry of Li-ion batteries

Since the first Li-ion battery was commercialized by Sony in 1991, progresses have been made to adapt this technology to different application fields. Consumer electronics, for example, requires batteries to be smaller in size and, at the same time, safer and with a relatively long cycle life. On the other hand, the emerging electric vehicle industry requires higher energy densities for increasing the driving autonomy to hundreds of kilometres with a single charge. Therefore, the research on this topic is nothing but exhausted, with thousands of papers and patents being published every year.

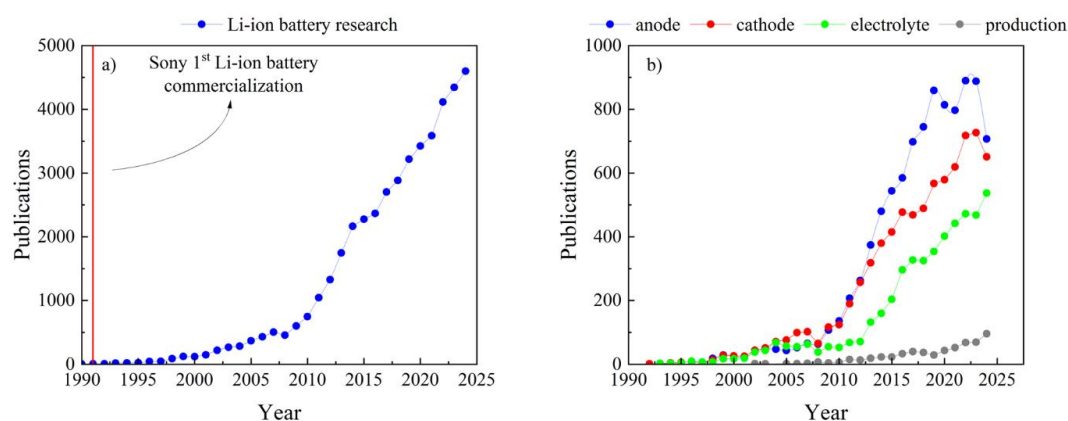


Figure 1.4. a) Number of publications that are related to progresses in the research on Li-ion batteries with liquid electrolytes. Book, book chapters and reviews do not count; b) Number of publications divided by specific topics regarding anode, cathode, electrolyte or production-related articles.

As can be seen from Figure 1.4, advancements in Li-ion chemistry that exploit liquid electrolytes are still a hot research topic. In the latest 5 five years, much effort is paid to reduce cost at the pack level below 100 US\$ kWh⁻¹ and increase the specific energy at cell level up to 500 Wh kg⁻¹, which is the holy grail for Li-ion batteries suitable for automotive applications. In this regard, the use of metallic lithium as anode material is a promising alternative to the common graphite-based one, with a theoretical specific capacity of 3860 mAh g⁻¹ compared to the 372 mAh g⁻¹ of natural graphite and a standard electrochemical reduction potential of -3.04 V vs SHE [15]. The use of metallic lithium poses different challenges, such that its implementation will be linked to developments in the materials that constitute both the electrolyte (through the formation of a stable SEI) and the separator, in order to suppress the lithium dendrite growth. The high reactivity of lithium metal is also affecting the way its production can be scaled up to mass production. Common roll-to-roll processes can be used and different strategies to adapt them to the challenges that lithium metal poses are under investigation, such as protecting lithium to avoid its passivation in contact with air or protecting the rolling machineries with a polymeric layer that also reduces the risk of lithium adhesion to the roller themselves [16], [17], [18]. Minimal defects on the lithium surface can, indeed, favour the dendrites growth. Nevertheless, the roll-to-roll process can have limitations when trying to achieve very thin lithium layers (e.g. < 30 μm). To this purpose, other techniques can be used, such as vacuum thermal evaporation technique recently developed by CSEM [19].

A valuable alternative to lithium metal for improving energy density in a relatively faster time scale is silicon (alloy-type anode), with a theoretical capacity of 4200 mAh g⁻¹. Its abundance and low cost make this material very attractive for application in Li-ion batteries, but its use as primary electrode active materials faced some difficulties. Silicon is indeed known to experience a severe volume expansion during charge, which strongly affects its mechanical stability and the overall cycle life of the final device [20].

On the cathode side, high voltage Ni-rich LiNi_xM_{1-x}O₂ (with $x \geq 0.6$ and M = Mn, Co) are the most attractive active materials, with a capacity up to roughly 200 mAh g⁻¹ and an operating voltage of about 3.8 V vs Li⁺/Li [21]. In this field, most attention is paid to reduce the cobalt content in the active material formulation in order to reduce raw material cost. Ni-rich cathodes, such as NMC811, are generally preferred due to their specific capacity and potential; however, ongoing efforts are focused on improving their safety and thermal stability [22], [23].

The research on novel materials is strictly related to their performance assessments, which not only regards higher specific capacity but also safety, which is even more important when transferring this knowledge to the real-world applications.

1.4. Solid-state batteries

The gain in both safety and energy density is driving the shift towards novel chemistries and, in this regard, solid-state batteries give a broad range of possibilities. A solid-state battery works the same as a liquid-electrolyte battery, but with a solid matrix between the electrodes that is both a good ionic conductor and an electronically insulating material. They show improved safety when coupled with materials like lithium metal as anode, as their stiffness is helping reduce the risk for dendrite growth, thus significantly reducing the probability for short circuit and thermal runaway. Indeed, they show promising applications in industries such as the automotive, where the use of more materials with higher specific capacity and potential could lead to specific energy density up to 350 kWh kg⁻¹. Nevertheless, the use of a solid phase between the two electrodes poses several challenges. First of all, the adhesion and physical contact at the solid electrolyte/electrode interface are worst compared to a cell with liquid electrolyte. This leads not only to an increase of the interface resistance, but also affects the cell stability during prolonged cycling. The electrodes swelling during charge/discharge cycles affects the physical contact of the electrode with the electrolyte surface, thus leading to the formation of defects that are indeed good sites for the formation and growth of lithium dendrite (in combination with lithium metal) or electrode fracture and disaggregation (in combination with silicon-anode). To reduce the risk of contact loss, high stack pressure needs to be applied on cells during cycling, up to tents of MPa, which strongly limits their application [24]. Moreover, solid-electrolytes need to be manufactured in dense and thin layer to have good ionic conductivity and increase the overall energy density of the cell. When dealing with hard and brittle materials, this requirement is difficult to achieve and manufacturing cost increases rapidly.

At present, the exploration of new materials for solid-state battery is an active research field and there is not a single chemistry or formulation that is currently winning over. As shown in Figure 1.5-a, solid-state battery research is engaging the scientific community half-way than the Li-ion research with liquid electrolyte, the reason why could find several explanations, from the novelty of the field to the need of specific instrumentations to

assemble and test solid-state cells. The trend, indeed, shows an increased in publications for solid-state around 2015, compared to the rise in scientific publications around 2008 for Li-ion with liquid electrolyte. As mentioned, the solid-state electrolyte research is wide and explores several different chemistry solutions. Figure 1.5-b shows the words occurrence in the author's keywords among all the publications. It gives a clear indication on which are the research trends among different research groups.

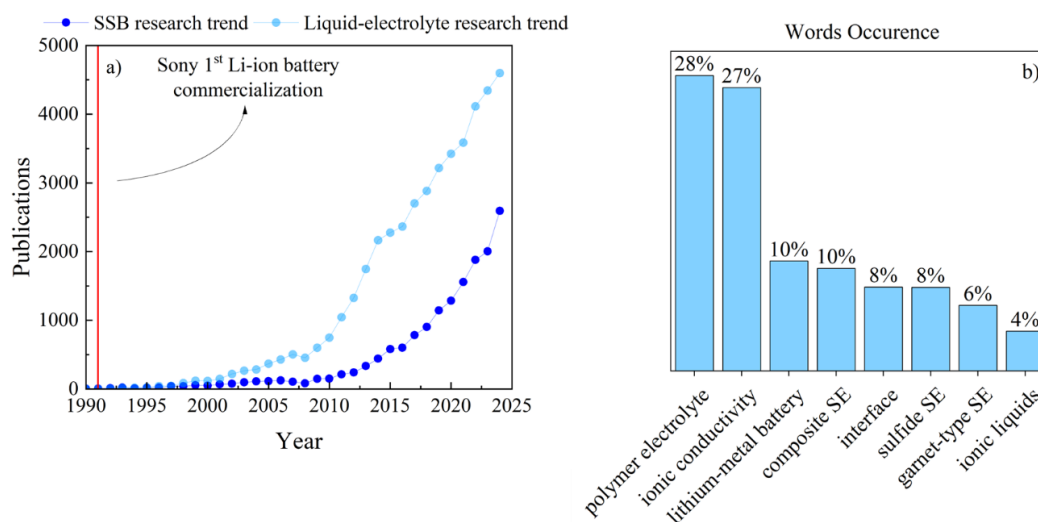


Figure 1.5. a) Number of publications that are specifically related to applications for solid-state batteries, compared to research publications specifically concerning liquid electrolyte-based batteries. Book, book chapters and reviews do not count for the total; b) Percentage of word occurrence in the author's keyword fields of solid-state related publications.

Organic solid-state electrolytes, which falls into the category of *polymer electrolyte*, have received much more attention, compared to inorganic electrolytes, like *sulphide* or *garnet*-based systems. Between these categories falls the family of *composite* solid-state electrolytes, which generally comprise a polymeric organic matrix with inorganic fillers. Figure 1.5-b also reveals that, a part from specific research on the material side, much importance is given to the understanding of the ionic conduction mechanism in solid-state matrices, as well as to the electrode/electrolyte interface, which play a fundamental role in solid-state battery safety and performance, as previously mentioned. Nonetheless, solid-state chemistries are very often associated to the use lithium metal as anode materials.

1.4.1. Organic polymer electrolytes

As stated in Section 1.4, organic polymer electrolytes are among the most studied in the solid-state battery research scenario. They are made of a polymeric matrix in which a Li-salt is dissolved. They can be completely solvent-free, thus called solid-polymer electrolyte

(SPE), or they can contain a certain amount of organic solvent, incorporated into the polymeric structure to form a gel, thus called gel-polymer electrolytes (GPE) [25].

The ion transport properties of the polymer matrix depend on the mobility of the polymeric chains; therefore, polymer electrolytes work well at temperatures higher than their glass transition temperature. In general, polymer electrolytes do not require high stack pressures to operate and the electrode/electrolyte interfaces are less critical than in inorganic solid electrolytes [26].

To date, the most investigated and discussed solid-electrolytes have a polymeric matrix made of poly-ethylene oxide (PEO), poly-acrylonitrile (PAN), poly-methyl methacrylate (PMMA), poly-vinylidene fluoride (PVDF) and co-polymers of them [27].

1.4.2. Inorganic electrolytes

The alternative to polymer solid-state electrolytes is the use of inorganic solid-electrolytes (ISE), among which the most promising for almost-ready market application are categorized into oxides and sulphides. Compared to organic polymer electrolytes, these materials have higher mechanical and thermal stability as well as high ionic conductivity at room temperature, but face several challenges in electrode/electrolyte interfacial contact and stability with electrodes. Therefore, in order to reach the target energy densities, these systems require high stack pressure both in the sample preparation stage and during cycling, to avoid contact loss at the electrode/electrolyte interface. Contact loss is also a consequence of the volume variation of electrode at each charge/discharge cycles, that also causes electrode particles cracking and loss of transport pathways for the lithium ions.

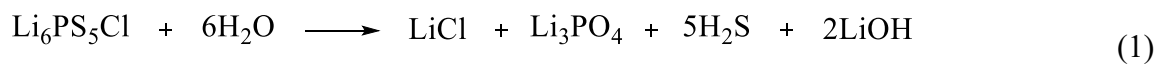
Oxide-based electrolytes include perovskite, garnet, NASICON and LISICON structures. Overall, they exhibit ionic conductivity at room temperature lower than sulphide ISEs and a high Young's modulus. Therefore, these materials usually require high sintering temperatures and high stack pressure to improve the interfacial contacts and thus cycling performance and stability.

Sulphide ISEs show the best ionic conductivity at room temperature and better mechanical performances compared to oxide-type ISEs. In this class falls glass-ceramic $\text{Li}_2\text{S-P}_2\text{S}_5$, argyrodite-type $\text{Li}_6\text{PS}_5\text{X}$ (with $\text{X} = \text{I, Br, Cl}$) and those that exploit the tetragonal unit cell structure of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ with substitutions of germanium (mainly due to the relatively low abundance and high cost of germanium). Argyrodite-type ISEs are attracting much

attention due to their relatively large stability window, other than their high ionic conductivity at room temperature. Despite their similar crystalline structure, $\text{Li}_6\text{PS}_5\text{I}$ (LPSI), $\text{Li}_6\text{PS}_5\text{Br}$ (LPSBr) and $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) show different ionic conductivities, with the LPSCl showing the best performances at room temperature [28], [29].

Among the main challenges associated with this kind of material, their high reactivity towards water to produce hazardous H_2S strongly affects the control of environmental conditions in the production facilities, thus increasing the overall production cost [30].

The degradation of LPSCl involves a multi-step cascade of reactions that begins at the material's surface. First-principles calculations give some insights into the pathways of degradation, whose full chemical formula is shown in (1) [31]. The initial step involves the adsorption of water molecules onto the sulphur-rich (111) surface of the electrolyte. This adsorption weakens the phosphorus-sulphur (P-S) bonds within the crystal lattice, favouring the substitution of sulphur atoms with oxygen atoms. The newly incorporated oxygen atoms migrate into the subsurface layers of the electrolyte, leading to the formation of a porous, oxygen-enriched layer with a composition similar to $\text{Li}_6\text{PO}_5\text{Cl}$. Being porous, this layer does not prevent further moisture diffusion, leading to propagation of degradation in the bulk of the solid-electrolyte [32], [33], [34].



As anticipated, although the challenges associated with their harmful reactivity with moisture, which also requires the production process environment to be highly moisture-free, this class of materials are still the most attractive for most applications, such as implementation in EV industry. Therefore, most of the current research direction is to exploit argyrodite-type materials to reach the goal of high energy density (up to 500 Wh kg^{-1}) demanded by most automotive applications and long cycling life.

In this regard, pressed sulphide SSEs have shown low cycling stability in combination with lithium metal electrode due to the easy appearance of micro-cracks during lithium plating/stripping cycles that favours the growth of lithium dendrite, leading to premature short circuiting. The appearance of these preferred paths for lithium dendrite growth is not directly associated with interface instability. For example, $\text{Li}_6\text{PS}_5\text{Cl}$ is known to form a stable SEI in contact with lithium metal and the formation of cracking regions has been associated to its rigidity [35]. Therefore, in order to mitigate this phenomenon and provide

long cycle life, different strategies have been proposed. One way to avoid fast cracks propagation could be increasing the electrolyte thickness, but it dramatically reduces the overall energy density of the cell. Recently, much research is focusing on the study of composite solid-state electrolytes (CSE) in which a slurry of the sulphur-based electrolyte is casted on a highly porous polymeric scaffold. This solution has been demonstrated to provide optimal electrochemical performances with high ionic conductivities, long cycle life and good mechanical properties in electrolyte layers with thicknesses up to 30-40 μm [36], [37].

The use of lithium metal still poses several challenges and a valuable alternative is the use of silicon as anode active material, as mentioned in Section 1.3. The cell architecture in this case must take into account the dramatic volume change of silicon during charge/discharge cycles, which affects the SEI stability in liquid electrolyte-based cells [38]. Therefore, the use of silicon anode in combination with solid-state electrolyte has been widely investigated. Powder-pressed silicon composite anodes, fabricated by mixing silicon powder, solid electrolyte and conductive carbon followed by pressing with solid-electrolyte layer at high pressure show good electrochemical performances, but their production is generally limited to small pellet-type cells and poses important challenges for the scale-up of larger format cells. In this sense, sheet-type silicon composite anodes obtained by tape casting, in which a slurry composed of anode active material, binder, conductive additive and solid-electrolyte particles is casted on the current collector and dried, are more suitable for scale-up of mass production. Nevertheless, the utilization of composite-type anodes limits the specific capacity of these materials, which remains lower than the theoretical specific capacity of pure silicon [39], [40]. The energy density of silicon-based cells still remains lower than their equivalent cells using lithium metal instead. The thickness of the solid electrolyte layer and the silicon mass loading of the anode are crucial parameters that need to be addressed to reach the desired energy density of at least 300 Wh kg^{-1} for automotive application [41]. An example of how the synergistic effect of thinner electrolyte layer and high silicon mass loading can lead to superior performances was given by Neumann et al., in which a $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte layer of roughly 30 μm coupled with an electrolyte-free silicon anode processed with aqueous-based slurry could provide a valuable way for cost reduction and high sustainability without paying the way for energy density and cycle stability [42].

In this work, the $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte layer provided by Fraunhofer ISE (Freiburg im Breisgau, Germany) was subjected to different moisture-content atmosphere in order to investigate its stability towards different dew points of a dry-room production environment. This will evaluate its cost affordability in the scale-up of the production process. In order to accomplish this scope, the electrolyte was placed in a test chamber connected to an air treatment group for moisture content regulation. The H_2S production was monitored via mass spectrometry. The performance of cells built using air-treated solid-state electrolytes were assessed through electrochemical cycling protocols described in Section 4.3. This study not only provides valuable insights for the setting up of a production environment, like dry-room condition, but can also be used as a starting point to design quality controls, like battery leak test described in the following sections.

2. Europe market analysis

This section provides a general understanding of the current research topics in Europe and overseas, together with a detailed market analysis on how the previously cited technologies are prioritized across countries and regions. Specifically, it summarizes the most relevant scientific directions emerging from academic literature, highlighting regional priorities and differences in R&D strategies. In parallel, industrial signals from companies, patent filings, and market reports are examined to clarify which technologies are closest to commercialization (particularly in the automotive sector), and what technological, economic, or regulatory barriers still need to be overcome. Overall, this combined perspective enables a more accurate view of the present innovation landscape and the maturity of solid-state battery solutions for future large-scale deployment.

A fundamental prerequisite for any industry seeking to sustain innovation and maintain a competitive edge is a deep market analysis to accurately drive its research and development (R&D) efforts and strategically allocate investment capital. This principle is particularly critical in rapidly evolving technological landscapes. The scenario surrounding battery technology is a prime example; the field is currently very dynamic, observing new advancements virtually every day, with the emergence of nascent companies across the globe, especially given the enormous demand and innovation stimulated by the automotive sector's transition to electrification. Therefore, a deep understanding of market needs, promising technological trajectories, and the competitive landscape is not just beneficial, but essential for defining a clear, impactful strategy. This project directly addresses this need by focusing on the prospects for next-generation battery development.

The market analysis aims to achieve the following specific objectives:

- Identify the most promising solutions in next-generation battery technology, with a specific focus on solid-state batteries, that have a high likelihood of successfully scaling up to mass production for application in the automotive industry.
- Evaluate development needs across Marposs existing products and applications to ensure they can be effectively adapted to the next generation of battery technology.

The market analysis was performed by collecting information from different sources, briefly summarized in Figure 2.1.

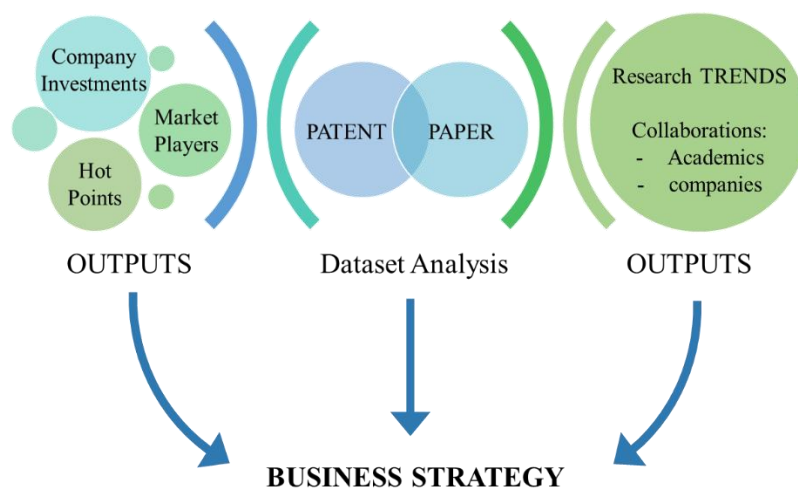


Figure 2.1. Summary of the strategies to perform a market analysis and the specific outputs expected in order to build up a business strategy.

Company investments and market players were carefully analysed from the information provided on companies' web profiles (like websites, LinkedIn and others), newspaper specifically focused on battery topics (like batterynews.com, vaielettrico.it, and so on) and reports taken from sources like marketandmarket.com and Shmuel De-Leon Energy Ltd (www.sdle.co.il). The specific references will be cited throughout this chapter if necessary for exemplary purpose only, since the intention is to give an overall representation of the main challenges and technology updates.

The analysis of scientific publications was conducted through a keyword-based bibliographic search in the Scopus database (Elsevier), and the results were subsequently analysed using the web interface Biblioshiny, a tool from the Bibliometrix package in R (provided by K-Synth Srl, Academic Spin-Off of the University of Naples Federico II), run on RStudio. The keyword-based bibliographic research included articles published from 1990 to 2024, with research fields that embrace solid- or semi- or quasi- solid-state chemistries centred in the area of lithium-ion batteries (avoiding including other chemistries like sodium-ion or potassium-ion batteries, which are not always correlated to the automotive industry). The keywords were chosen so as to isolate, as much as possible, articles specifically addressing the design and characterization of solid-state electrolytes, while avoiding the inclusion of publications focusing primarily on electrodes or other battery components. For example, works centred on anodes or cathodes were excluded even if they mention their application in combination with solid-state electrolytes, since the electrolyte was not the main subject of investigation. By applying these selection criteria, the dataset was refined to a total of 9096 documents. A close view is dedicated to the latest years, running from 2020 to 2024. The analysis aimed to point out the most studied chemistries, in order to define priorities for Marposs equipment's development, together with the network of collaborations among countries and affiliations, that can provide suggestion on possible beta-tests for developments of new quality and in-process controls.

The paper analysis was discussed in close correlation with the patent analysis. Intellectual properties represent an important asset for companies, as they can be seen as a form of capital and evidence of active research efforts within specific fields. They highlight which companies invest most in research and development, making them natural candidates for collaboration or dialogue. This becomes particularly relevant when working on new products that need to be tested, validated, or introduced to the market. The patent analysis

was carried out using Espacenet, the public patent database provided by the European Patent Office (EPO).

The next-generation battery market is a landscape of intense competition and strategic partnerships, primarily driven by two core revolutionary pathways: the electrolyte, leading to solid-state electrolytes, and the anode materials, leading to lithium metal. Major legacy automakers (VolksWagen, Ford, BMW, GM, Hyundai, Mercedes-Benz) are aggressively investing in or forming joint ventures with specialized battery startups to secure exclusive access to next-generation technology. Chinese giants like CATL and BYD continue to dominate the conventional lithium-ion market but are also pioneering the mass production of cost-effective alternatives like sodium-ion batteries (Na-ion). In the attempt to improve energy density and safety with next-generation battery chemistries, companies like Welion (a China-based company) and SES (an US-based company) are investing on semi-solid-state batteries, which are more affordable for scale-up production in terms of cost and equipment availability (thanks to the possibility of adapting the current established Li-ion battery production process) compared to the more complex all-solid-state technology. On the other hand, players like Factorial Energy (an US-based company), QuantumScape (an US-based company) and SolidPower have accepted the bet and aim to provide the automotive industry with all-solid-state batteries. QuantumScape is currently declaring a specific energy density of 301 Wh kg^{-1} for its lithium-metal solid-state battery with a charging time lower than 15 minutes [43]. At IAA mobility 2025, they debuted with PowerCo (the battery company of VolksWagen) in powering a Ducati's motorcycle in a live demonstration with their lithium-metal ASSB devices; at the same event, VW announced the new generation of all-solid-state batteries by PowerCo will power their city cars (like Polo) [44], [45]. In response to that, Mercedes-Benz announced their first on-the-road test with a lithium-metal solid-state battery, the FEST[®] (Factorial Electrolyte System Technology), provided by Factorial Energy, with which the company collaborates since 2021 [46]. Factorial Energy is indeed sponsoring two cell chemistries: FEST[®], based on the use of lithium-metal in combination with quasi-solid polymer electrolyte, and Solstice[™], an all-solid-state battery that exploit a sulphide-based all-solid-state electrolyte [47]. Another automotive company that is betting on solid state technology is BMW, collaborating with SolidPower to power vehicles in prototypes, such as the BMW i7 announced on May 2025 [48]. In 2020, a joint venture between Stellantis group, TotalEnergies and Mercedes-Benz gave birth to Automotive Cell Company (ACC). Even

though they are not specifically focused on battery chemistries that make use of solid-electrolytes, they can be cited among those companies that are putting effort in the new born of a European battery market, with a focus on cathode materials for high energy density devices [49]. These evidences are in good agreement with the battery roadmap presented by Fraunhofer ISI in 2022 [50]. SSB market is expected to growth up to tens of GWh of annual production up to 2035, while LIB market is expected to reach up to several TWh, as summarized in Figure 2.2.

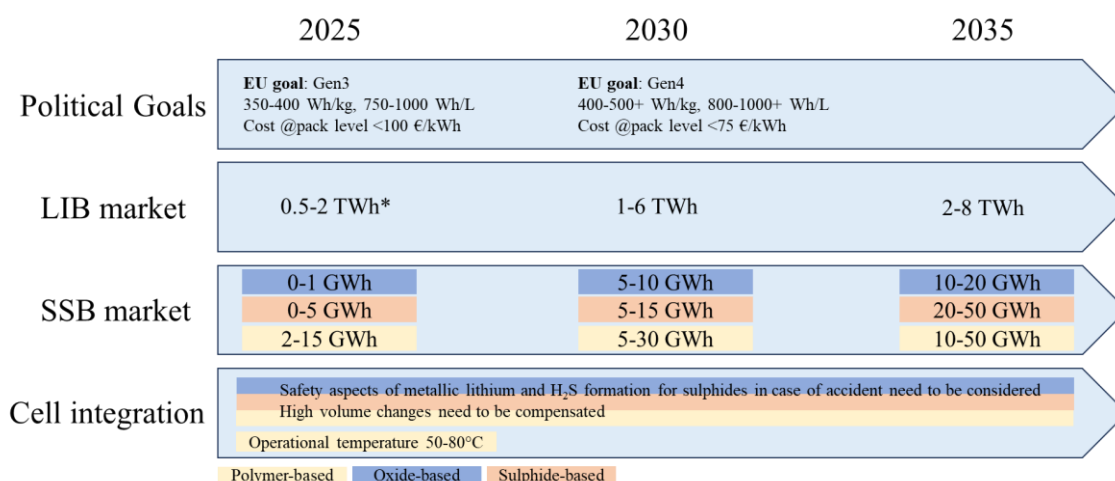


Figure 2.2. European battery roadmap as described by Fraunhofer ISI in the 2022 market report. Modified from [50]. *Annual LIB production as attested by [51] is 190 GWh y⁻¹

The polymer SSB cell concept consisting of a lithium anode, one or more polymer electrolyte layers and LFP as the cathode active material has already been on the market for several years, with Blue Solutions being one of the pioneering since 2011. Nevertheless, their relatively high operational temperature and low charging rate make them less attractive for automotive applications. In this sense, batteries based on sulphide or oxide solid-electrolytes are preferred, even though the former suffer from reactivity with air to produce harmful hydrogen sulphide (H₂S), while the latter still require high external pressure to overcome high cell resistance due to poor electrode/electrolyte interface contact.

From an OEM perspective, the most demanding investments are those involving the introduction of new production processes to the market, which require the development and validation of new instrumentation. For this reason, much of the current research effort is focused on electrolytes. While new chemistries continue to evolve for cathode active materials or for metallic lithium and silicon anodes, the quality control requirements for

these components are not expected to differ significantly from those already in place for current LIB generations. By contrast, changing the nature of the electrolyte, such as moving to solid-state electrolytes, shifts the focus to new parameters that must be monitored and controlled during production. Therefore, in order to anticipate the incoming upscale production of a new technology, it is crucial to investigate where the research is focusing on.

From the academic research, solid-state battery related topics are a hot field. Figure 2.3-a shows the first five country ranking for scientific production from 2020 to 2024. Although China, the USA, and Japan still occupy leading positions in the battery sector, Germany emerges as a country with a vibrant research activity, comparable to South Korea, which is home to major battery companies such as LG Energy Solution and Samsung SDI. Although this is true, the analysis of the total number of citations versus the average articles citations reveals an interesting scenario. The total number of citations (TC) is calculated on the sum of the citations obtained by the complete set of articles of a country (Equation 1). On the other hand, the average articles citation (AAC) is the average impact an article has on the scientific community, calculated as the ratio of total citations divided by the number of articles a country has published (Equation 2).

$$TC = \sum_{N_{articles}} citations \quad \text{Eq. 1}$$

$$AAC = \frac{\sum citations}{N_{articles}} \quad \text{Eq. 2}$$

Therefore, the AAC factor is an estimation of the quality of published papers and it is more representative on the impact they had on the scientific community. Figure 2.3-b shows how the high scientific production not necessarily means more advanced or impactful research progresses. Indeed, France appears as the country with the highest AAC factor, meaning that it is a fertile ground for advanced research in the emerging solid-state battery field.

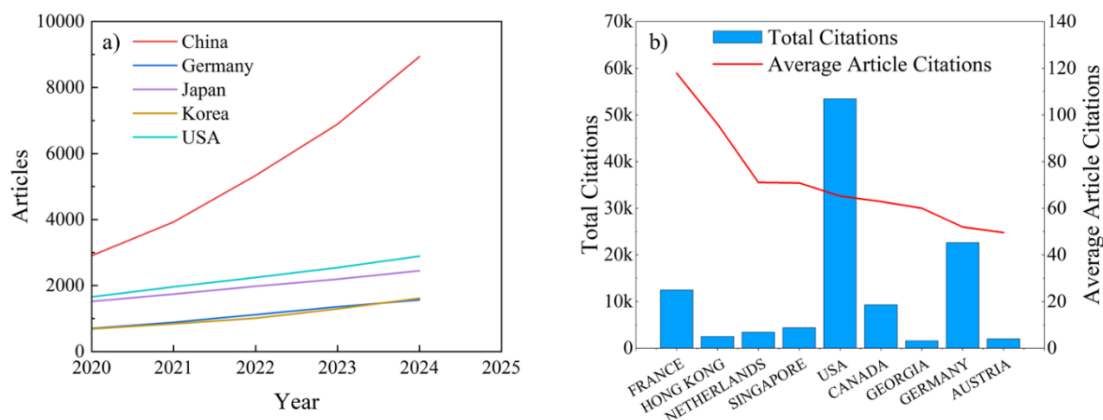


Figure 2.3. a) Ranking of the first five countries for total number of articles published on SSB field; b) Total citation index versus Average Article citation index of the first ten countries on the ranking

As shown in Figure 2.3-a, China, the United States, and Japan still maintain a clear leadership in terms of the number of publications on next-generation batteries, even in innovative areas such as solid-state electrolytes. Nevertheless, Germany appears among the top five countries worldwide, together with South Korea. This is a remarkable result, as it indicates that European countries, driven by the policies discussed in Section 1.1, are intensifying their efforts to compete with the global leaders in the sector in a field such as solid-state electrolytes, which represents a relatively new research domain for all countries. Germany's achievement of a research activity level comparable to South Korea suggests the existence of a dynamic and well-stimulated R&D environment, reflecting Europe's increasing strategic commitment to strengthening its position in the global battery landscape. Considering the top ten countries ranked by citation count shown in Figure 2.3-b, Germany and France follow the United States, which indicates that research outputs from these countries are widely acknowledged within the scientific community. Moreover, when looking at the average number of citations per article, France ranks first overall. This suggests that, although France and Germany cannot yet compete with larger players such as the USA and China in terms of publication volume, their research stands out for its high quality. It also highlights that the research centres producing these results are among the most advanced in the field of solid-state electrolytes. For this reason, following this evidence, the author's keywords of articles with French and German affiliations were analysed. It is important to note, however, that this does not imply a restriction to research carried out exclusively within France or Germany, as many of these works are conducted in collaboration with institutions worldwide. The results can be found in Figure 2.4 where Germany and France are also compared with the results obtained from the same research

worldwide. In order to classify solid-state electrolytes, a set of exclusion criteria was first applied to the keyword search, removing generic terms such as “lithium-ion batteries” or “solid-state electrolytes”. Among the 50 most frequent keywords, the remaining terms were then grouped into broader families. For example, keywords such as “PEO” and “poly(ethylene oxide)” were assigned to the solid polymer electrolyte category, while terms like “LLZO” or “garnets” were grouped under oxide-based electrolytes, and so forth.

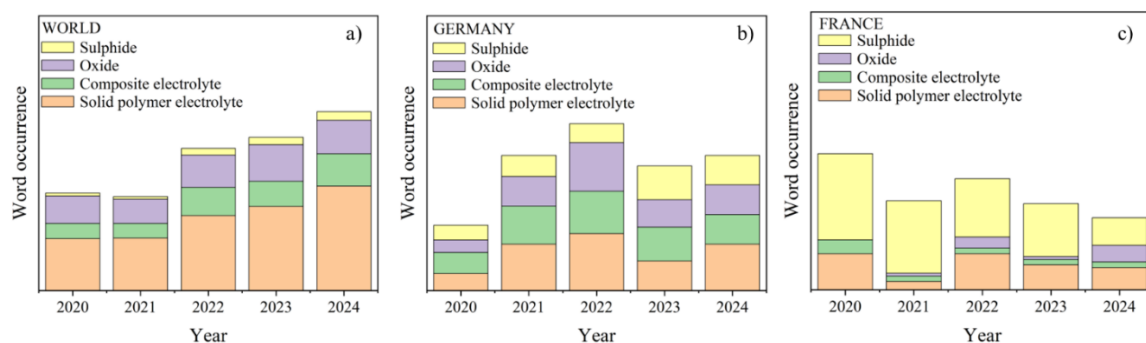


Figure 2.4. Occurrences of author's keywords, categorised into sulphide, oxide, composite and solid-polymer based electrolytes for bibliographic search of articles counting for a) world, b) Germany and c) France.

From this analysis, and as shown in Figure 2.4-a, polymer-based solid electrolytes appear to be the most widely studied category. While this is generally true, it is particularly useful to focus the investigation on European countries, such as Germany and France already cited, which, as highlighted, have proven to be especially active and impactful in terms of research quality. This focus is also strategically relevant for a company such as Marposs (headquartered in Italy), since collaborations with geographically and culturally closer countries are more convenient to establish. Figure 2.4-b and Figure 2.4-c confirm that interest in polymer electrolytes remains significant within Europe, although it is not as dominant as in the global statistics shown in Figure 2.4-a. On one hand, this is understandable because, as mentioned in Section 1.4, polymer electrolytes require less complex instrumentation for synthesis and electrochemical testing. On the other hand, European research also shows a strong engagement with sulphide-based electrolytes, which, as demonstrated by the analysis of company investments and market players, are currently among the most promising technologies for automotive applications.

As anticipated, in such a fast-evolving field, it is particularly insightful to correlate academic research trends with patent analysis, in order to identify the major applicants in each of the solid-state electrolyte categories discussed above. When considering patent data, it is important to clarify the terminology: the inventor refers to the individuals who

contributed to the claimed invention, regardless of whether they hold any legal rights over the patent. The assignee designates the organization or individuals holding ownership rights to the patent, often the employer of the inventor; this entity may change over time, and in some cases, there may be no assignee at all. Finally, the applicant is the organization or individual who files the patent application, which may be the original inventor or the assignee. The patent search was carried out by filtering for documents directly related to solid-state battery devices. In this case, unlike the bibliometric analysis of scientific publications, the focus was not limited to patents dealing exclusively with the formulation or design of solid-state electrolytes. Instead, patents were considered whenever they specifically addressed the use of solid-state electrolytes, ranging from their formulation to their application in devices, as well as innovative synthesis processes or instrumentation for production lines and quality control. The dataset was then refined to obtain the same categorization of electrolyte families used in the publication analysis, namely polymer-based, oxide-based, and sulphide-based electrolytes. On this basis, a ranking of the top 50 applicants worldwide was compiled. Table 1 shows the first 20 positions and the number of documents submitted by each of the applicants.

Table 1. Ranking of applicants based on number of patents submitted between 2020 and 2024. Automotive companies are highlighted in bold.

POLYMER RELATED PATENTS		OXIDE RELATED PATENTS		SULPHIDE RELATED PATENTS	
APPLICANTS	N° of doc.	APPLICANTS	N° of doc.	APPLICANTS	N° of doc.
TOYOTA MOTOR CORP	327	TOYOTA MOTOR CORP	93	TOYOTA MOTOR CORP	122
TOYOTA MOTOR CO LTD	173	TOYOTA MOTOR CO LTD	49	TOYOTA MOTOR CO LTD	60
KOLON INC	161	HONDA MOTOR CO LTD	29	HONDA MOTOR CO LTD	35
HONDA MOTOR CO LTD	140	PANASONIC IP MAN CO LTD	25	SAMSUNG SDI CO LTD	25
HYUNDAI MOTOR CO LTD	108	BLOOM ENERGY CORP	21	IDEMITSU KOSAN CO	22
KIA CORP	106	SAMSUNG ELECTRONICS CO LTD	17	PANASONIC IP MAN CO LTD	22
LG ENERGY SOLUTION LTD	83	GEN ELECTRIC	13	AGC INC	17
PANASONIC IP MAN CO LTD	45	AGC INC	12	SAMSUNG ELECTRONICS CO LTD	15
KIA MOTORS CORP	41	UNIV XI AN JIAOTONG	12	PANASONIC HOLDINGS CORP	12
UNIV HUAZHONG SCIENCE TECH	39	ZHUHAI COSMX BATTERY CO LTD	11	SHANGHAI YILI NEW ENERGY TECH CO LTED	11
SAMSUNG SDI CO LTD	35	KOREA ELECTRONICS TECHNOLOGY	10	KOREA ELECTRONICS TECHNOLOGY	10
BOSCH GMBH ROBERT	34	MITSUBISHI GAS CHEMICAL CO	10	MITSUBISHI GAS CHEMICAL CO	10
TOSHIBA ENERGY SYSTEM & SOLUTION CORP	34	FDK CORP	8	NISSAN MOTOR	10
TOSHIBA CORP	33	LG ENERGY SOLUTION LTD	8	TIANMU LAKE INST OF ADV ENERGY STORAGE TECH	9
TOYOTA CENTRAL RES & DEV	33	NISSAN MOTOR	8	PANASONIC HOLDINGS CO LTD	8
KYOCERA CORP	31	PANASONIC HOLDINGS CORP	8	SVOLT ENERGY TECH CO LTD	8
UNIV SOUTH CHINA TECH	29	UNIV CENTRAL SOUTH	7	INST PHYSICS CAS	7
PRIME PLANET ENERGY & SOLUTIONS INC	28	UNIV HUAZHONG SCIENCE TECH	7	MITSUBISHI MATERIAL CORP	7
PANASONIC IP MAN CORP	25	UNIV TSINGHUA	7	RENAULT SAS	7
UNIV CENTRAL SOUTH	25	DENSO CORP	6	UNIV CENTRAL SOUTH	7

Overall, the largest number of patents falls within the “polymer” category. Nevertheless, a substantial number of documents have also been filed in the “oxide” and “sulphide” categories. Toyota Motor consistently appears at the top of all three rankings, which is highly significant as it clearly reflects how the drive toward transportation electrification is strongly pursued on a global scale. Toyota and, to a somewhat lesser but still considerable

extent, Honda Motor, are evidently working to build internal know-how in order to deliver products fully tailored to the requirements of electric vehicles. Beyond these two leaders, several other automotive companies also appear among the top 20 applicants, including Hyundai Motor, KIA Motors, Nissan Motor, and the European OEM Renault SAS, as highlighted in bold in Table 1. Among the automotive companies included in the top 50 applicants, GM Global Tech Operations LLC, the R&D subsidiary of General Motors (USA), appears in 39th position within the polymer-related patent ranking. It is also worth noting that position 42 in the sulphide-related ranking is occupied by SolidPower, which, as previously discussed, collaborates with automotive companies such as BMW.

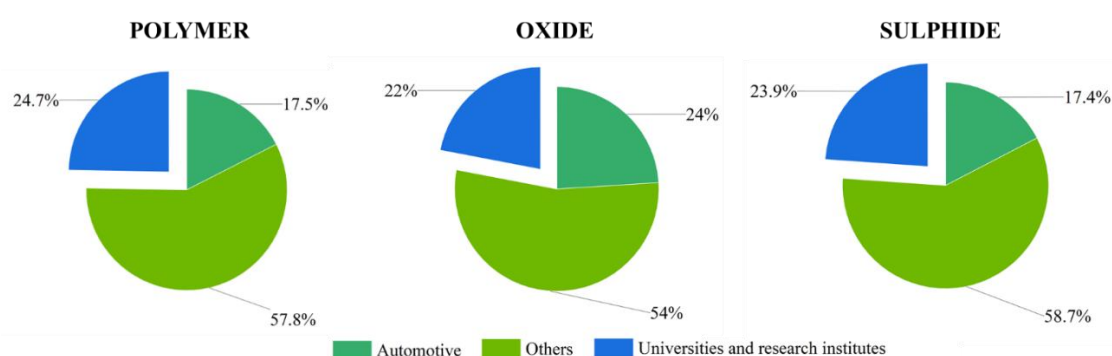


Figure 2.5. Pie charts representing the percentage of applicants belonging to academic research institutions or industries. The latter were divided into automotive and others, which includes battery makers, electronics and semiconductor industries or general chemicals.

In general, when considering patents, the percentage of those filed by companies is higher than those filed by universities and research centres, as highlighted in Figure 2.5. This can be interpreted in several ways. First, it reflects the inherently application-oriented nature of patenting: companies have a direct interest in protecting intellectual property to secure competitive advantages and strengthen their market position. Second, it highlights the scale of industrial R&D investments, showing how companies are actively seeking to consolidate know-how in the solid-state battery sector through intellectual property protection. By contrast, universities and public research centres play a fundamental role in the early, exploratory phases of research and in generating scientific knowledge, but their output is more frequently disseminated through publications rather than patents. In many cases, the transfer of knowledge from academia to industry occurs later, either through collaborations, licensing agreements, or the creation of spin-offs. Among the companies, a significant share belongs to the automotive sector, which once again reflects and confirms the strong interest of these firms in developing in-house technologies to better address the challenges posed by the electrification of transportation.

From the combined analysis of patents and scientific publications, it emerges that at the global level there is a strong interest in the most challenging chemistries, such as oxides and sulphides, particularly among automotive companies. In Europe, the share of patent ownership, both within and outside the automotive sector, remains comparatively limited, although academic research efforts are intense and often directed toward these challenging chemistries. Germany stands out in this regard, not only because of its well-established automotive industry, but also for its active research across all major electrolyte families, showing a balanced focus on polymers, oxides, and sulphides based solid-state electrolytes. Nevertheless, for the reasons discussed in Section 1.4 and in the review of market players' strategies at the beginning of this chapter, polymers are unlikely to represent the most suitable choice for powering electric vehicles. The strategic choice of a company like Marposs, however, would be reasonable to be exploring the R&D activities of both research centres and companies focusing on these chemistries. One possible strategy would be to analyse the current battery manufacturing processes and identify how they could be adapted to meet the requirements of next-generation chemistries. Table 2 and Table 3 show an example of possible quality and in-process controls that can be adapted from the already consolidated Li-ion battery manufacturing with liquid electrolytes to the new generation of battery chemistries.

It is reasonable to assume that the conventional coating processes currently applied to electrode materials will remain suitable for next-generation chemistries that make use of slurries deposited on current collectors. On the other hand, processing steps may differ in the case of metallic lithium anodes. Nevertheless, key quality control parameters, such as thickness uniformity and surface homogeneity, remain relevant even for lithium metal electrodes.

With respect to solid electrolyte manufacturing, considerable attention is being directed toward adapting coating processes for these materials as well, instead of relying on the more traditional laboratory-scale approach of cold or hot-pressing powders into pellets. Coating is inherently more scalable and industrially practicable, whereas pressing would require the design of new equipment and significant additional investments to optimize inline parameters. Moreover, coating enables the production of thin layers that would be difficult to achieve through pressing. Coating techniques currently used for sulphide-based solid-electrolytes include infiltration or tape casting of the electrolyte onto a scaffold polymeric structure like nonwoven materials [52], [53], [54], [55].

Specifically for polymer electrolytes, another promising approach involves handling the monomers and initiator in solution and introducing them during a filling step, much like liquid electrolytes. Polymerization could then be triggered after cell sealing, either thermally or electrochemically [56].

Processes such as slitting, stacking, and final sealing are primarily determined by the cell format rather than the cell chemistry. It could be argued that, for certain chemistries more tolerant to air exposure, leak testing of sealed cells might be considered less critical. However, external contamination is almost never neutral or beneficial to cell performance, which makes leak testing a highly advisable step across all chemistries.

Table 2. Key process parameters and corresponding inline/in-process quality control methods for electrode and cell-stack manufacturing steps (coating, calendaring, slitting, stacking).

PRODUCTION PROCESS – CELL LEVEL						
	COATING and CALENDERING		SLITTING		STACKING	
	Parameters	Controls	Parameters	Controls	Parameters	Controls
GAUGING	Thickness Basis weight Width Profile (edges)	Confocal sensors Ultrasonic dampening Line camera Laser scanner	Foil width and overall dimension	Laser micrometer	Overall dimension Thickness	2D camera Laser scanner Contact gauging
INSPECTION	Surface homogeneity	Vision line camera	Burrs	Vision line camera	Crack detection Surface homogeneity	Vision and 2D camera (AI assisted)
MONITORING	Web tension Roll wear	Force/torque sensor Confocal sensor Laser scanner	Cutting tool Web tension	Vision 2D camera Force/torque sensor	Alignment	Vision and 2D camera
TESTING						

Table 3. Critical quality attributes and associated inspection techniques for cell assembly and cell-finishing operations (tab welding, sealing, electrolyte filling, formation and end-of-line testing).

PRODUCTION PROCESS – BATTERY LEVEL						
	TAB WELDING		SEALING		END OF LINE FORMATION/AGING	
	Parameters	Controls	Parameters	Controls	Parameters	Controls
GAUGING	Overall dimension	Line and 2D camera	Thickness of weld beads	Interferometric sensors		
INSPECTION	Welding defect	Vision and 2D camera (AI assisted)	Welding defect	Vision and 2D camera (AI assisted)		
MONITORING	Process	Acoustic/light emission	Alignment	Vision and 2D camera		
TESTING			Cell tightness	Leak test	Cell tightness Electrical testing	Leak test OCV Internal Resistance

3. Battery leak test

This section presents the theory of leak testing, spanning the discussion from helium leak testing techniques that can be implemented on a battery production line, to the more advanced electrolyte tracing technique for the end-of-line testing of sealed battery cells.

Fundamental concepts such as leak rate definitions, detection thresholds, and the influence of test environment and pressure differentials are introduced to establish a common framework. Industrially relevant methods are described in terms of their applicability and sensitivity.

Finally, the section highlights electrolyte tracing as an emerging solution specifically tailored for sealed cells.

Together, these elements provide a comprehensive overview of leak detection strategies for in-line battery quality control.

Battery leak testing is a fundamental step in production line quality control. Batteries are generally sealed under vacuum to provide the best performance and longevity. However, even the presence of a fine leak can negatively affect battery performance, as it allows a slow ingress of air over time, ultimately leading to premature cell degradation. While large leaks (commonly referred to as “gross leaks”) are relatively easy to detect, identifying exceptionally fine leaks requires high-performance instrumentation, such as those described in this chapter.

The presence of trace water inside a lithium-ion battery strongly affects battery performances. As a first straightforward consequence, water hydrolysis generates gaseous H_2 . Gas generation in a closed battery system is detrimental for the battery performances and safety, leading to pressure accumulation inside the cell (cell swelling), electrode contact loss and thermal runaway events.

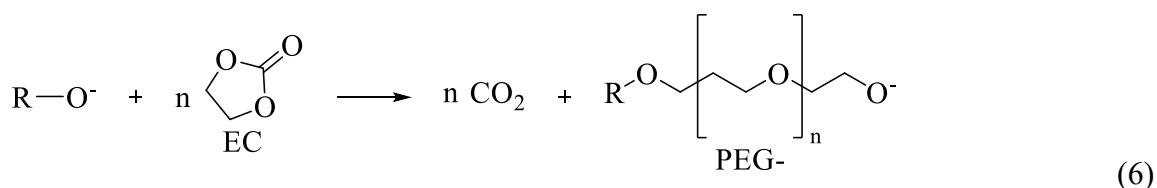
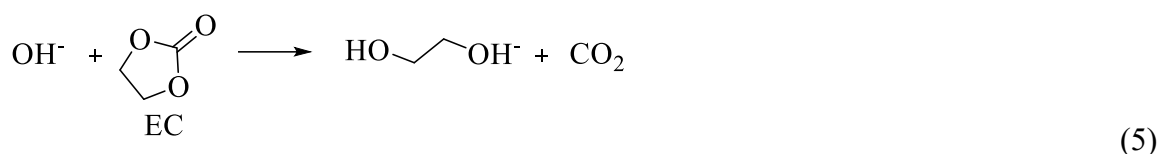
The electrolyte commonly used in current commercial Li-batteries can degrade in presence of water contaminations. $LiPF_6$ is widely known for its reactivity to water and formation of toxic HF. This lithium salt dissociates in its ionic products and, in a lesser extent, in its molecular dissociation products, as indicated in (2) and (3) respectively, and consequently reacts with water according to (4).

This reaction kinetics was observed to be relatively fast in organic liquid electrolyte compared to water-based solutions, given to the better dissociation of $LiPF_6$ in water and consequently a lower concentration of PF_5 is formed. The hydrolysis of this lithium salt continues in a multi-step process that further produces HF [57], [58], [59].

Apart from the detrimental consumption of fresh electrolyte from the hydrolysis, this phenomenon also contributes to gas generation and cell pressure buildup.



Water impurities also affect the solvent stability and interfere with the SEI formation during the first charge/discharge cycles. It has been demonstrated that carbonates like ethylene carbonate (EC) and dimethyl carbonate (DMC), vastly used in commercial Li-ion batteries, are also decomposed by water traces. For example, EC undergo fast nucleophilic attack by hydroxide ions to form alkoxide and carbon dioxide according to (5). The alkoxide species can further react with EC (6) [60].



The formation of poly-ethyleneglycol oligomeric and then polymeric units increase the electrolyte viscosity and can further precipitate at the anode/electrolyte interface.

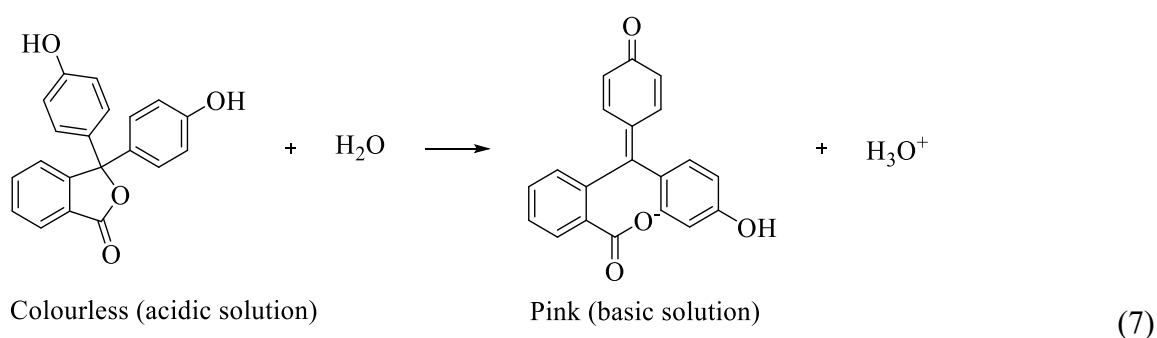
The so-formed carbon dioxide can not necessarily lead to gas evolution and pressure buildup, but rather can react with hydroxide anions or alkoxides and further affect the SEI structure.

Cathode active materials are also sensible to water impurities. Several studies reported transition metal dissolution in materials like NMC or LiCO_2 through in-situ and post-mortem analysis, which irreversibly leads to performance degradation of battery cell [61], [62], [63], [64], [65].

Having established that water contamination is detrimental for battery performances, most efforts are paid to avoid water contamination over a certain ppm level in battery production process, mostly in the cutting, stacking and sealing process, and to control the correct sealing of the battery cell after electrolyte filling, prior to perform formation and ageing of

the cell. While the former scenario is accomplished by placing those production steps in a dry room environment, the latter is attained by performing battery leak test quality controls.

Early leak test detection methods were documented in the 1960s for testing the sealing of Nickel-Cadmium (Ni-Cd) alkaline rechargeable batteries used in aerospace applications for storing the energy accumulated by solar panels installed on satellites [66]. At that time, there were two methods for identifying a leaking defect: pH indicators and helium mass spectrometry. The electrolyte in a Ni-Cd battery, providing the best diffusion of hydroxide anions, is an aqueous solution containing from 30% to 40% w/w of potassium hydroxide (KOH). The final battery is generally sealed in cylindrical or prismatic housings. Because the alkaline solutions used as electrolyte has a $\text{pH} > 14$, one of the methods used to check cell integrity and electrolyte leakage was local pH monitoring by using a pH indicator. A pH indicator is indeed a molecule that, added in small amount to a solution, changes its photophysical properties according to the pH of the solution, so that an indication of the acidity (or basicity) can be done by spectroscopic methods or simply by observation. Indeed, this method only resulted in qualitative analysis, but it was cheap and fast, thus used by the majority. To monitor the pH locally close to the battery case welding, a solution containing phenolphthalein in a mixture of ethyl alcohol and water was used as indicator. Phenolphthalein is colourless in solutions at $\text{pH} < 8$ and becomes pink at $\text{pH} > 8-10$ (7) [67].



Although this method can provide good qualitative results, more accurate and quantitative methods are required to assess the quality of the production process.

3.1. Helium leak test

A leakage is defined as the accidental admission or escape of a liquid or a gas through a hole or a crack. A method to identify a leak could be, for instance, given a sealed test object (defined as a “closed system”) inside a test chamber that is subsequently evacuated to a

pressure lower than ambient, monitoring the pressure within the chamber over time. If the object is truly hermetic, no variation in the chamber pressure should be observed, as no gas can escape from the object into the surrounding vacuum. Conversely, if the chamber pressure gradually increases, it indicates that gas is leaking out of the object under test, revealing the presence of a leak (see green and black lines in Figure 3.1).

This definition is representative of most cases in the battery field, where cells are sealed with an internal pressure close to, but slightly lower than, atmospheric pressure. It should be noted, however, that leakage can still occur even when the pressure difference across a defect is minimal. In such conditions, gas transport is primarily governed by molecular diffusion rather than by a pressure-driven flow.

Pressure rise of an evacuated system is therefore one of the methods used to detect leakage. The test object is thus placed in a vacuum chamber and the pressure inside the chamber is brought to few mbar_{ABS} (absolute milli-bar) and monitored in time (green line of Figure 3.1).

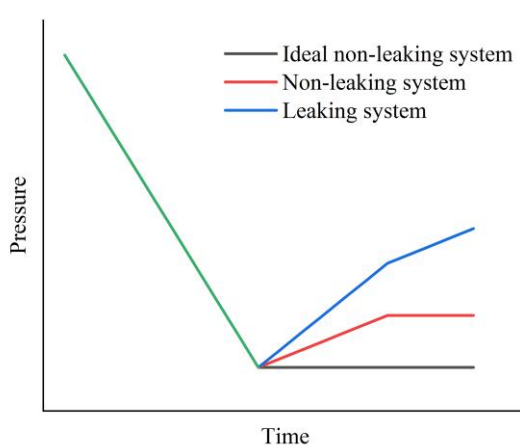


Figure 3.1. Measure of pressure variation in an ideally closed system (black line), real closed system (red line) and leaking system (blue line). The green line represents the pressure drop due to evacuation of the test object.

In an ideally sealed system, no pressure variation should be observed over time. However, in practice, a gradual increase in pressure is always detected. This phenomenon, known as outgassing, arises from the physical desorption of gaseous molecules from the surfaces of both the test object and the vacuum chamber. Outgassing is a transient process that continues until the equilibrium vapor pressure of the released gases is reached within the closed volume. Therefore, in real cases when the test object is, said, perfectly sealed, only

the outgassing from its constituent materials will be observed, and the pressure rises until a new equilibrium is reached. The time needed to reach such equilibrium strongly depends on the type of material the test object is made of and their interactions with the entrapped gases. Conversely, if the test object presents a leakage, the system can no longer be considered closed. In this case, a continuous gas exchange occurs between the interior of the test object and the surrounding environment, leading to a sustained increase in chamber pressure. The rate at which this pressure rises depends primarily on the size of the defect and the pressure differential across the leak, both of which determine the overall leak rate. The leak rate Q , here expressed in mbarLs^{-1} , is determined by the volume V of gas at a certain pressure P that crosses a plane in a given time interval (Equation 3).

$$Q = \frac{\delta(PV)}{\delta t} \quad \text{Eq. 3}$$

For example, a leak rate of 1 mbarLs^{-1} signifies that the pressure in a sealed, evacuated vessel of 1 L rises by 1 mbar every second. This value is not absolute, as it depends on the type of gas, the pressure difference, and the temperature at the leak site.

For many practical applications, it is more intuitive to consider the "mass flow," $\Delta m/\Delta t$, which directly correlates with the mass of material being lost or gained over time. The relationship between the volumetric leak rate Q and the mass flow is derived from the ideal gas law:

$$\frac{\Delta m}{\Delta t} = \frac{Q \times MW}{R \times T} \quad \text{Eq. 4}$$

where MW is the molecular weight of the gas (g mol^{-1}), R is the molar gas constant (here chosen as to be $83.145 \text{ mbarL}(\text{mol K})^{-1}$) and T is the absolute temperature (K).

The behaviour of a fluid flowing through a leak channel is not uniform: it can be categorized into distinct regimes, each governed by different physical principles. The transition between these regimes is primarily determined by the size of the leak opening relative to the fluid's properties and the existing pressure conditions and can be estimated relying on the Reynolds number (Re) and the Knudsen number (Kn). The Reynolds number is the ratio of inertial forces to viscous forces in the fluid, and it is the primary determinant of whether a flow is laminar or turbulent. While the former is characterized by smooth, highly ordered motion, with fluid layers sliding past each other without significant mixing, the latter is a

chaotic motion characterized by velocity fluctuations and enhanced mixing (schematically represented in Figure 3.2-a and Figure 3.2-b). The Knudsen number is the ratio between the mean free path of gas molecules λ and the characteristic dimension of the leak, e.g. the leak diameter d . When this ratio is lower than 1, the flow can no more be described by continuous fluid dynamics but rather by the random motion of individual molecules (Figure 3.2-c).

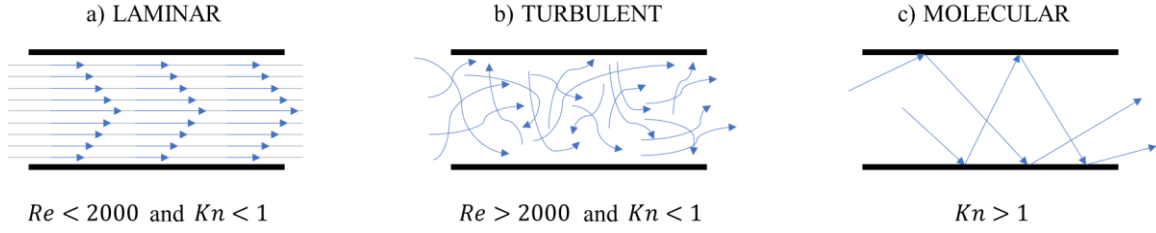


Figure 3.2. Schematic representation of gas flow in the a) laminar regime; b) turbulent regime; c) molecular regime.

The gas flow through a leak can be described by different analytical models based on the idealized geometry of the leak, namely the flow through a capillary or an orifice. In particular, a short, sharp-edged hole where the length (L) is much less than the diameter (d) is treated as an orifice, while a long, narrow channel where $L \gg d$ is treated as a capillary. The flow through a capillary in the laminar regime is often described by the Hagen-Poiseuille law, for which the volumetric flow rate Q is expressed by:

$$Q = \frac{\pi r^4}{16\eta L} (p_1^2 - p_2^2) \quad \text{Eq. 5}$$

where r is the radius and L is the length of the capillary, η is the dynamic viscosity of the gas, and p_1 and p_2 are the pressures at the inlet and outlet, respectively. A significant implication of this equation is the fourth-power dependence of the leak rate on the channel radius. This means a small change in diameter has a dramatic effect on the flow rate; doubling the diameter increases the leak rate by a factor of 16. This highlights how precise control and measurement of microscopic leak geometries can be challenging. The Hagen-Poiseuille law is an effective model for laminar, incompressible flow. However, as pressures increase and gas velocities rise, compressibility effects become significant, and the simpler incompressible model becomes less accurate [68]. The gas flow through leaks that behave like an orifice under high pressure can be considered frictionless and adiabatic and the governing equations can be derived from the principles of energy and continuity,

leading to a critical pressure ratio below which the flow becomes *choked*. Under choked flow conditions, the mass flow Q_m rate is independent of the pressure at the outlet side of the orifice and is instead a function of the upstream pressure P_1 and temperature T_1 (Equation 6).

$$Q_m = C_d A P_1 \sqrt{\frac{\gamma}{RT_1} \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{2(\gamma+1)}}} \quad \text{Eq. 6}$$

In Equation 6, A is the area of the orifice, γ is the ratio of specific heats of the gas, C_d is called *discharge coefficient*, a dimensionless quantity that corrects for losses due to geometry and non-idealities that make the real mass flow rate diverging from the theoretically calculated one.

From the mass flow, the volumetric gas flow can be easily obtained under the assumption of ideal gas flow:

$$Q = \frac{Q_m RT_1}{P_1} \quad \text{Eq. 7}$$

with:

$$Q_n = \frac{Q_m}{MW} \quad \text{Eq. 8}$$

In real scenarios, a leak rarely is described by a perfectly shaped orifice and neither the flux of gases through the orifice can always be said perfectly choked. For these reasons, a semi-empirical model can be applied that make use of the Equation 9 written below for calculation of the mass flow rate of a gas through a pinhole leak [69]:

$$Q_m = k A (p_1 - p_2) \sqrt{\frac{\gamma RT}{MW} \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{\gamma-1}}} \quad \text{Eq. 9}$$

Here, k is an empirical constant used to enclose many of the geometrical parameters of Equation 6, like C_d . Equation 7 can always be used in the approximation of an ideal gas flow to convert from mass flow Q_m to volumetric flow rate Q .

The semi-empirical equation of gas flow through an orifice (Equation 9) can be used to estimate the dimensions of the leak from the measured volumetric gas flow. The same

model is used to design *calibrated leak standards* with specific leak rate for system calibration.

Helium leak detection is an excellent method for battery quality control. Being chemically inert and possessing the smallest atomic radius, helium is able to diffuse through micro-defects that are impermeable to most other gases, making it particularly suitable for high-sensitivity leak detection. The test generally involves two steps: injection of helium inside the test object and subsequent inspection of helium traces from the sealed object. The former phase can be performed through direct injection of the tracer gas before the sealing process or forcing its flow through eventual leaks in a pressurised chamber. In both scenarios, the battery is then placed in a vacuum chamber connected to a mass spectrometer for the detection phase.

Figure 3.3 shows a simple schematic of a leak tests performed by direct injection of helium in the battery before sealing. Figure 3.3-a represent a leak test performed on the battery cell housing. It is filled with helium and then placed in a vacuum chamber after sealing it with dedicated tools. The chamber is then evacuated at a pressure of few tenths of mbar_{ABS} and let communicate with a helium mass spectrometer for gas detection and leak rate estimation. Typical detectable leak rates range from 10^{-5} to 10^{-7} mbarLs⁻¹.

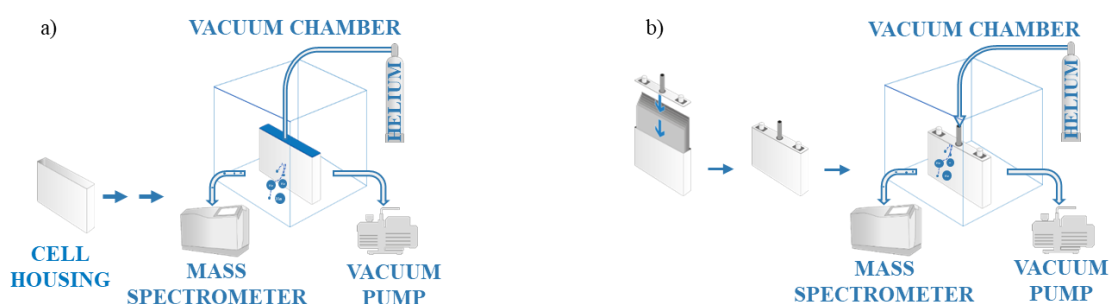


Figure 3.3. Leak test of battery housing using helium as tracer gas. (a) leak test on an empty battery housing performed by injecting helium and appropriately sealing the case before measurement of helium leak rate; (b) leak test on battery filled with jelly roll, prior to electrolyte injection step.

The same method can be used for testing cells after insertion of the electrodes and separator jelly rolls in the battery housing, as depicted in Figure 3.3-b. In 1960s, helium leak test was applied to both empty and full (electrodes + electrolyte) battery cans. However, because the sensitivity of this tracer gas technique proved to be incorrect when the tracer gas was injected in the cell filled with the electrolyte, the pH-indicator method, described in the

introduction of this chapter, turned out to be more effective for complete sealed battery cells early at that time [70].

Helium leak test can also be performed by forcing the helium ingress in the leakage of the battery cell. This kind of test is called *bombing* or *back-pressurising* technique. In this case, the sealed battery cell is firstly placed in a vessel filled with helium at pressure ranging typically from 5 to 10 bar_{ABS}. This step is known as the *bombing* phase and the cell is left at the bombing pressure P_B for a certain time t_B . The pressure differential between the bombing pressure and the internal pressure of the cell is the driving force for helium to enter the cell if a leakage is present. After a certain time (t_{dwell}), the cell is transferred into a vacuum chamber connected to a mass spectrometer to measure the leak rate (R) of the helium eventually present in the internal free volume (V). Figure 3.4 shows a schematic representation of the helium bombing technique and the main parameters associated to each. A fundamental distinction exists between the "equivalent standard leak rate" (L), also called "true leak rate" and the "measured" or "apparent leak rate" (R). The true leak rate is defined as the leak rate when the high-pressure side is at 1 atmosphere and the low-pressure side is at a pressure lower than 0.001 atmosphere (vacuum). This is a characteristic of the package itself, depends only on the geometry of leak opening, and is independent on test parameters. Conversely, the measured leak rate is a function of the test parameters, that is bombing pressure, bombing time, dwell time, and specimen volume, and is the value read by the spectrometer [71].

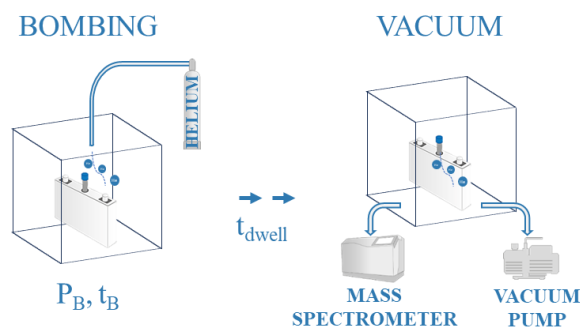


Figure 3.4. Schematic view of the bombing (or back-pressurising) helium leak test with a sealed battery cell

The theoretical basis for the technique was firstly introduced by Howl and Mann, who described the relationships between the equivalent standard leak rate L and the apparent

leak rate R for pure laminar (Equation 10) and pure molecular (Equation 11) flow regimes. Derivation of the formulae is beyond the scope of this work and can be found in ref. [72].

$$R = \frac{P_B - P_0}{P_B} L \left(\frac{1 + Se^{-\frac{2Nt_{dwell}P_0}{V}}}{1 - Se^{-\frac{2Nt_{dwell}P_0}{V}}} \right)^2 \quad \text{Eq. 10}$$

$$R = \frac{LP_B}{P_0} \sqrt{\frac{MW_{air}}{MW_{He}}} \left[1 - e^{-\frac{(Lt_B/P_0V)\sqrt{MW_{air}}}{MW_{He}}} \right] e^{-\frac{(Lt_{dwell}/P_0V)\sqrt{MW_{air}}}{MW_{He}}} \quad \text{Eq. 11}$$

In Equation 10 for the laminar flow regime, S contains information on the pressure inside the cell after the bombing stage, in the form written in Equation 12:

$$S = \frac{P_{cell,B} - P_0}{P_{cell,B} + P_0} \quad \text{Eq. 12}$$

In both Equations, P_0 refers to the atmospheric pressure, while in Equation 11 MW_{air} and MW_{He} are the molecular weight of air (taken to be 30 g mol^{-1}) and helium, respectively.

The effectiveness of the back-pressurising technique is defined by its sensitivity and the range of detectable leaks. These characteristics are direct functions of the test parameters. The product of bombing pressure (P_B) and bombing time (t_B) is a primary factor that determines the minimum detectable leak. Increasing this product increases the amount of tracer gas forced into a fine leak, thereby enhancing the sensitivity of the test for small leaks.

The dwell time, t_{dwell} , between the bombing and the test, also plays a critical role. A longer dwell time allows more tracer gas to escape from the specimen, which significantly reduces the maximum detectable leak. For a very large leak, an extended dwell time can lead to a false negative result, as virtually all the gas may escape before the measurement can be taken.

The internal volume of the specimen, V , is another crucial variable. A smaller volume leads to a faster pressure decay during the dwell period, thereby lowering the maximum detectable leak. This poses a significant challenge for testing small-volume objects like

battery cell with small residual internal free volume, since the detection threshold decreases proportionally with the reduction in internal volume.

In this work, a study has been conducted to find optimized parameters to perform helium bombing test for batteries depending on the residual free volume inside the cell. This study is specifically designed for hard-case batteries, since soft-case pouch cells can swell during the bombing phase, posing a risk to the integrity of the cell itself. The theory has been validated through the use of a simulacrum with calibrated capillary leaks. This study reveals that the variable free internal volume of the cell strongly affects bombing test parameters. Without a proper understanding of this parameter, the testing conditions cannot be adequately optimized on a case-by-case basis, which can ultimately compromise the reliability of the results. For instance, if the actual free internal volume of the battery cell is smaller than the value assumed during calculation, the helium filling during the bombing procedure may be insufficient, potentially leading to a “false good” result. Further details on this aspect are provided in the Experimental Section of this work.

3.2. Electrolyte tracing

Many of the existing methods to perform battery leak test were explained in Section 3.1, where it is also described how different helium leak tests are highly sensible to very small leaks, but either fail to give proper results when applied to a complete and sealed battery cell, such as in the case of helium injection during the electrolyte filling process, or can be rarely applicable to all cell formats, such as the helium bombing technique in the case of soft pouch bags.

A reliable and versatile method to detect battery leakage is the so-called *electrolyte tracing* technique. Unlike conventional tracer gas methods, electrolyte tracing directly detects the leakage of the battery's electrolyte. Common electrolytes for Li-ion batteries are a mixture of organic solvents where a lithium salt is solubilized to provide ionic conduction. The organic solvents can be more or less volatile and are therefore easy to detect with a mass spectrometer in case of leakage from a battery cell [73].

A typical setup to conduct electrolyte tracing is shown in Figure 3.5.

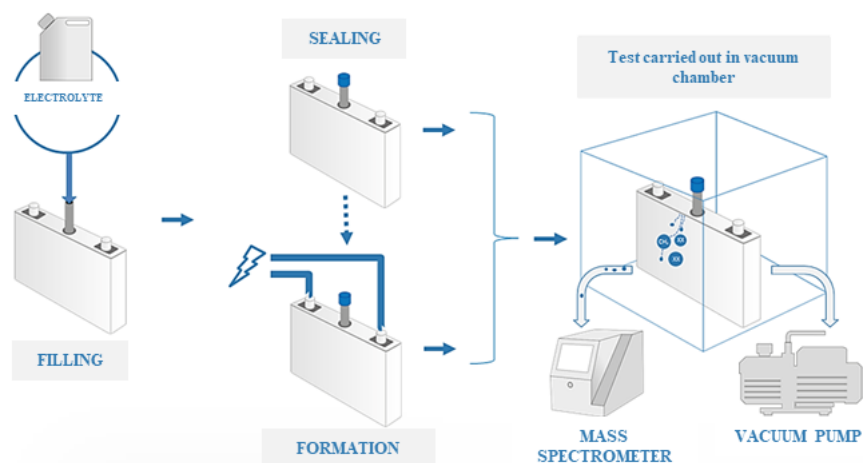


Figure 3.5. Schematic representation of a battery leak test through electrolyte tracing technique. After electrolyte filling, the test can be performed both after cell sealing and/or after formation and aging.

The sealed cell is placed in a vacuum chamber, either soon after the electrolyte filling and sealing process or after the formation cycles (or both), connected to a mass spectrometer. When the test chamber is evacuated, the pressure differential and the capillary force of the liquid through the orifice-like leak govern the behaviour of the liquid through the leakage. The capillary force depends on the surface tension of the liquid (σ) and the contact angle (θ) at which the liquid wets the solid surface of the channel. The surface tension is a measure of the cohesive forces between liquid molecules and strongly depends on intermolecular long-range interactions. Water has indeed a high surface tension, being it $72.7 \times 10^{-3} \text{ N m}^{-1}$ @25 °C [74], compared to dimethyl carbonate that has a surface tension value of $28.55 \times 10^{-3} \text{ N m}^{-1}$ @23 °C [75]. The contact angle describes the angle formed at the interface between the liquid and the solid surface. It is a direct measure of the liquid's wetting behaviour. A small contact angle ($\theta \approx 0^\circ$) indicates excellent wetting, where the liquid spreads out and the adhesive forces at the solid/liquid interface are strong. On the contrary, a large contact angle ($\theta > 90^\circ$) indicates poor wetting and low contact area at the solid/liquid interface (Figure 3.6).



Figure 3.6. Wetting behaviour of different solid/liquid interfaces and associated contact angle values.

The Young-Laplace equation (Equation 13) provides a quantitative relationship between these forces: it describes the pressure difference (ΔP) across a liquid-gas interface, often used to determine the pressure required to drive a liquid out of a capillary.

$$\Delta P = \frac{2\sigma \sin\theta}{r} \quad \text{Eq. 13}$$

where r is the radius of the capillary. In the Young-Laplace equation, ΔP is actually the hydrostatic pressure inside the liquid drop which indicates the force directed towards the solid/liquid interface at the capillary surface. This concept can be adapted to a battery cell placed in vacuum with an orifice-like defect: in this case, ΔP is the direct pressure differential between the internal pressure of the cell and the external pressure of the vacuum chamber. Equation 13 can then be rearranged to find the *critical diameter* at which capillary force equals the external pressure, preventing liquid to spread out of the cell. In case of DMC, an estimation of the blocking diameter can be done based on its surface tension σ and assuming a very low contact angle on the aluminium battery case. The contact angle of DMC is not reported in the literature for the pure solvent in contact with aluminium surface, but rather for electrolyte solutions onto battery separators [75]. However, calculation may be done for a first rough estimation based on the contact angle of water on aluminium surface, reported to be 9° [74]. Given the lower surface tension of DMC compared to water, it is reasonable to hypothesize even a smaller contact angle; therefore, the estimation of the DMC critical diameter for an orifice-like leak on an aluminium foil based on the contact angle of water at room temperature will result in an overestimated value. Nevertheless, based on the assumptions made so far, the equation for calculating the critical diameter becomes:

$$d = \frac{4\sigma \sin\theta}{\Delta P} \quad \text{Eq. 14}$$

For the purpose of this specific example, regarding the value that ΔP assumes, the internal pressure at which generally Li-ion batteries are sealed is roughly 200 mbar_{abs} [76] and the pressure inside the vacuum chamber can be set to 0.01 mbar_{abs}, which is reasonable for applications that make use of hard vacuum. The estimated critical diameter is $d \approx 0.9 \mu\text{m}$. This value represents the threshold below which capillary forces can prevent flow initiation, and thus provides an estimate of the minimum size of an orifice-like defect that can be detected when DMC is used as the tracer compound only in the specific conditions

described above. Any leak larger than this critical diameter would allow solvent evaporation and gas diffusion into the vacuum chamber, driven by the pressure difference between the chamber and the vapour pressure of DMC and other commonly used volatile organic solvents in Li-ion battery electrolytes. Anyway, this value is not universally true, as it strongly depends on the experimental parameters, like case-by-case pressure differential, on the electrolyte composition, which affects its wetting behaviour, and on the materials used for cell sealing.

The setup of electrolyte tracing, showed in Figure 3.5, is composed as follows: the battery is placed in a vacuum chamber, which is evacuated to a pressure lower than 0.01 mbar_{ABS}. A stabilization phase follows, in which the battery is left in static vacuum for several seconds. In this phase, volatile organic solvents accumulate in the vacuum chamber in presence of a leak. The amount of evaporated solvents depends on the leak geometry, as described by the semi-empirical model of Equation 9, and, as a consequence, the pressure inside the vacuum chamber increases. The stabilization phase is followed by the detection step: the vacuum chamber is connected to a mass spectrometer to detect the presence of electrolyte species.

The detection phase is indeed a crucial part of the test. The tracer species of choice must match the requirements of high volatility and relatively high-volume percentage in the electrolyte mixture. This ensures the highest possible signal even in presence of fine-leaks. The intensity of the species-related signals to the mass spectrometer is also a fundamental consideration. Mass spectrometers can differ from the way molecules are ionized and separated according to their m/z ratio (mass-to-charge ratio) by the mass analyser.

Ionization methods can be divided into *hard* and *soft*. Hard ionization methods, such as electron ionization (EI), use high-energy processes that transfer a significant amount of energy to the analyte. This excess energy causes extensive fragmentation, breaking the molecule into smaller, charged pieces. The resulting mass spectrum is rich in fragment ions, which serve as a unique *fingerprint* for the molecule. In contrast, soft ionization methods, such as chemical ionization (CI), transfer a lower residual energy to the analyte. This gentle process preserves the integrity of the molecule, resulting in a mass spectrum dominated by the molecular ion or quasi-molecular ions peaks, such as protonated or positively charged species. EI and CI are the most common ionization methods for molecules in the gas phase. Other ionization methods exist that are more appropriate for surface analyses or

biomolecule in solution, like field desorption and field ionization (FD and FI) or matrix-assisted laser desorption/ionization (MALDI).

The mass analyser is responsible for sorting ions according to their m/z ratio before they are identified by the detector. The most common mass analyser in commercial mass spectrometer is the linear quadrupole. It consists of four parallel rods where a combination of fixed DC and alternating radio-frequency (RF) voltages are applied. This creates an oscillating electric field that allows only ions of a specific m/z ratio to have a stable trajectory and pass through the centre of the rods to the detector. All other ions follow unstable paths and collide with the rods. A mass spectrum is generated by continuously changing the RF and DC voltages to scan for different m/z values. As an alternative, time-of-flight analyser (TOF) is also commonly employed in MS analyses. It separates ions by the time it takes them to travel through a field-free flight tube of a known length. Ions are accelerated by an electric field to give them a uniform kinetic energy. Since all ions have the same energy, lighter ions travel faster than heavier ions. The time of arrival at the detector is measured and correlated to the ion's m/z ratio [77].

Electrolyte tracing can be performed by a variety of combinations of ionization source and mass analyser, coupled with sensitive detectors like secondary electron multiplier (SEM) or less sensitive but cheaper Faraday cup. The configuration of choice in the experimental section of this work involves the use of an electron ionization source, a linear quadrupole mass analyser and a Faraday cup. This configuration was used to either test commercial Li-ion cells with liquid organic electrolyte and to investigate the reactivity of $\text{Li}_6\text{PS}_5\text{Cl}$ towards contaminants like moisture. Further details will be found in the following sections.

It is worth mentioning that electrolyte tracing can be a powerful tool in both battery research and production environment. This work focuses mainly on the setup made for R&D scopes. Nevertheless, an optimized procedure has been adopted for testing on pilot-line and production line, either with semi-automatic or fully automatic machine.

Marposs Leak B-TRACER (Figure 3.7-a) is a semi-automatic machine, adaptable to any cell format and dimension, capable of controlling batches of cells according to the requirements of fast cycle time [78]. It can be further scaled up to the fully automated control system (Figure 3.7-b), which is customized according to the production environment, cell format and size, number of cells in the vacuum chamber and cycle time [79]. Both the solutions have implemented a so-called *gross-leak* station. This prevents

macroscopic defects to poisoning the vacuum chamber and avoid mass spectrometer contamination [80], [81], [82].

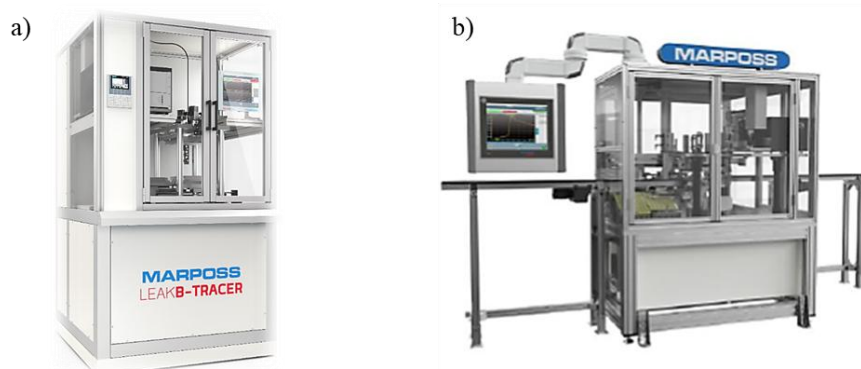


Figure 3.7. a) Leak B-TRACER: semi-automatic electrolyte tracing station for testing on pilot lines; b) example of a fully-automated leak test machine.

This technique can be either used to check for leakage after electrolyte filling process and cell sealing and/or after cell formation and aging, making this method adaptable to any production environment.

3.3. Calibration and rejection limits

Electrolyte tracing aims to be a quantitative reliable technique for detecting battery leakage and therefore requires a method to describe leak dynamics. Modelling a leaking defect on a battery cell presents several complications. The flow rate of volatile solvents composing the electrolyte depends on many parameters, such as leak geometry and environmental conditions. Those characteristics make it difficult to predict whether the leak flow will be in the laminar or molecular flow regime. Moreover, the description of the real system involves delicate equilibrium between liquid and gaseous states, that further complicate the reliability on a single theoretical model.

The reliability of a measuring system is based on the correct calibration method, which must resemble the real case scenario as much as possible. Therefore, calibration is usually performed with the use of standards. In case of helium leak test, the ISO 20486:2018 [83] regulates how to build a standard leak of defined flow rate, how to compare the standard leak to a reference leak as to certify its value and methods to calibrate based on environmental, test conditions and the measuring instrument. On the other hand, for electrolyte tracing instrument, given a leaking battery cell being a system containing a liquid solution from which gas of volatile solvents can escape under certain conditions, a

calibrated leak standard (or *master leak*) is chosen to be a closed system containing the tracer solvent of choice, communicating to the measuring unit via a calibrated orifice or porous medium. The mass flow (expressed in g s^{-1}) of the volatile organic solvent contained in the master can be measured under the conditions of leak test, which means subjecting the master to the same vacuum-stabilization-measure cycles of the battery cell, with the same setup and same environmental conditions (like temperature and pressure differential). Under the assumption of ideal gas flow, the conversion from mass flow to volumetric flow can be done according to Equation 7. The so-obtained volumetric gas flow can be associated to the value of partial pressure read on the mass spectrometer for a given substance at a given m/z ratio to provide valuable quantitative estimation of the real system battery leakage.

The reliability of the measuring system is proved through its accuracy and precision. The accuracy defines how close a given set of measurements are to their reference value. The precision is the degree to which reproducible measurements under unchanged conditions show the same results. These concepts are usually represented as throws on a bullseye, as shown in Figure 3.8.

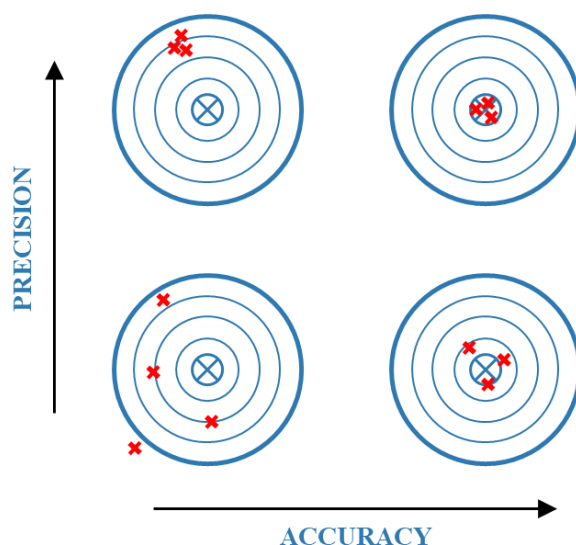


Figure 3.8. Precision and accuracy concepts represented as throws on a bullseye.

A measure of instrument precision is its repeatability, defined as the closeness of the agreement between the results of successive measurements of the same item, when carried out under the same conditions of measurement. The standard deviation (or mean square root σ_N) of a population of N samples quantifies the "scatter" of individual data points (x_i)

around the mean of the data set ($\bar{x}$). It is calculated as in Equation 15 and reported in the same units as the data.

$$\sigma_N = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N}} \quad \text{Eq. 15}$$

While the standard deviation measures the scatter of individual data points, the standard error of the mean (σ_M) measures the accuracy of the sample mean itself.

$$\sigma_M = \frac{\sigma_N}{\sqrt{N}} \quad \text{Eq. 16}$$

Calibration of the leak test measuring system is indeed a process that requires first a leak standard with a known leak rate. This represents a reference value and comparisons of the experimental data with the standard leak value will highlight system accuracy. Once calibration is performed, the system precision is checked through repeatability tests. If the results of the repeatability tests are satisfactory, meaning an acceptable low standard deviation and standard error of the mean, the system can be used to test real samples.

With a calibrated and precise system in place, defining rejection limits becomes essential to identify cells that meet quality standards versus those that must be discarded. The establishment of a rejection limit is not a straightforward process. The water content a cell can sustain without having severe performance drop in its cycle life is not universal for all cell chemistries and it is neither a deep investigated topic in literature. Nevertheless, there are studies reporting the effects of precise amount of water concentration on the cell performance. An investigation on Li-ion cell with LiMn_2O_4 positive electrode and 1M LiPF_6 in ethylene carbonate/diethyl carbonate (EC/DEC 1:1) electrolyte reported that a concentration of water higher than 211.3 ppm was responsible for the sharp increase in battery impedance [84]. Yang et al. studied the effects of different moisture content on anode and cathode half-cells and on the full cell of NMC111/graphite in 1M LiPF_6 in 1:1:1 EC/DMC/EMC in a moisture content range from 200 to 600 ppm [85]. Another investigation on NMC/graphite 18650-type cylindrical cells with 1M LiPF_6 in EC/DMC/EMC electrolyte revealed that trace water in amount lower than 300 ppm is actually beneficial for the SEI growth, while concentration of moisture higher than 300 ppm causes resistance increase and cell capacity fade [86]. However, the proposed studies investigate direct addition of water inside the cell and therefore the short-term effects.

These could not be representative for the long-term effects, meaning the slow, gradual ingress of the same amount of moisture over a long period, for example in a lifespan of 10 years. The rejection limit is therefore evaluated case by case, even by the customer itself, based on the product functionality. For example, the acceptable leak rate for a battery in an electric vehicle with a 10-year warranty must be orders of magnitude lower than for a single-use consumer electronic device, where a minor leak might not compromise functionality before the product is discarded. For helium leak test, a rejection limit commonly defined is 1×10^{-5} mbarLs⁻¹. Translating this value to electrolyte leak rate is not a straightforward process. In general, leak checking with analytes different to helium gives worst performances in terms of sensitivity, since helium is the smallest inert molecule that will penetrate over sub-micrometric defects. A common practice for establishment of a rejection limit is evaluating the electrolyte leak rate on a defect as small as 1 μ m. Therefore, by constructing a master leak with such orifice-like diameter, containing the tracer solvent from the electrolyte mixture and investigating its leak rate in the measuring system, a rejection limit for electrolyte tracing for each case scenario can be evaluated. For DMC, leak rates with respect to orifice diameters are presented in Table 4.

Table 4. Correlation between orifice-like defects and DMC leak rate in mbarLs⁻¹. Reported values were experimentally defined.

ORIFICE DIAMETER (μ m)	SOLVENT LEAK RATE (mbarLs ⁻¹)
1	2×10^{-5}
3	5×10^{-5}
5	1×10^{-4}
10	4.5×10^{-4}

4. Materials and methods

Section 4 provides a detailed description of the materials and methods employed in the experimental activities presented in this work.

First, the theoretical optimization of the key parameters governing the helium bombing test is introduced, followed by the description of the test object used to validate the theoretical assumptions.

Subsequently, the methodology for electrolyte tracing leak testing in fully sealed pouch cells is outlined. This includes the mechanical design of the dedicated test apparatus, the optimization of the operating conditions, and the calibration and repeatability validation of the measurement bench. The finalized procedure is then applied to customer-supplied cells to demonstrate its practical applicability and diagnostic capabilities.

Finally, the section details the approach adopted to assess the chemical reactivity of a next-generation sulphide-based solid electrolyte, selected due to its growing relevance in automotive solid-state battery development. The experimental workflow examines its degradation behaviour under controlled moisture atmospheres, with particular attention to the formation of hydrogen sulphide as a critical safety concern.

Collectively, these methods establish a comprehensive framework for leak assessment and stability evaluation of emerging battery cell technologies under realistic operating conditions.

4.1. Leak test through helium-bombing technique

A laboratory-scale experimental campaign was conducted to validate the theoretical model of the back-pressurising technique. The experimental campaign encompassed two stages. First, the theoretical models described in Section 3.1 will be used to estimate the bombing rejection limit and the optimal parameters for testing sealed objects of different internal volumes. Then, two capillaries constructed to have different flow rates will be mounted on a metal cylinder with a known free volume to experimentally prove the theoretical model.

Section 3.1 describes different theoretical and analytical models of the flux of a gas through a defect according to the leak geometry and the flow regime of the gas. The latter can be estimated from the Knudsen's number by comparing the mean free path of helium gas molecules with respect to the leaking defect diameter. As anticipated in Section 3.3, a typical value of helium leak rate rejection limit is 1×10^{-5} mbarLs⁻¹. Nevertheless, for the purpose of getting the highest possible sensitivity, a value of 1×10^{-6} mbarLs⁻¹ was chosen as rejection limit for this experimental part as to explore the most stringent condition for test parameters. In order to build a master leak with such a flow rate for helium, through the use of Haigen-Poiseuille law, a capillary was designed to have the diameter 5 μ m. In normal ambient conditions, at a pressure of 1 bar, the Knudsen's number results to be lower than one, meaning that the helium flow can be described in the continuum regime. However, when the test object undergoes bombing test, the pressure profile through the leak channel changes. When brought to vacuum, the Knudsen's number of helium through the leak becomes much larger than one, and the flow can be described by the molecular flow regime. Therefore, to find optimal parameters for the bombing test, the Howl and Mann equation for molecular flow regimes has been used. The test parameters to be optimized are the bombing pressure P_B and the bombing time t_B . For a given equivalent standard leak rate L , the volume of the test object strongly influences the apparent leak rate R read by the mass spectrometer. Therefore, different object internal volumes have been analysed on the test parameter estimation phase to understand the impact of this variable on the overall time of test and bombing pressure. The analytical expression relating the apparent leak rate R to the equivalent standard leak rate L (Equation 11) was solved numerically using Python, employing the *root_scalar* function from the *scipy.optimize* library. This tool provides robust algorithms for finding the root of nonlinear equations, enabling the determination of the value of L that satisfies a given R for specified

experimental parameters (bombing pressure, bombing time and internal volume). The experimental parameter used are presented in Table 5 and are chosen according to hypothetical parameters of testing in a final production instrumentation.

Table 5. Parameters and corresponding value ranges used in the optimization simulation.

PARAMETER	CONSTRAINT
R	a) 1×10^{-9} mbarLs ⁻¹ ; b) 1×10^{-6} mbarLs ⁻¹
P₀	1013 mbar
P_B	$(1013 < x < 5000)$ mbar
t_B	$(0 < t < 7200)$ s
t_{dwell}	1 s
L	Calculated

As shown in Table 5, the simulations were performed on different values of the apparent leak rate R . The aim of simulation **a** is to find the equivalent standard leak rate L that falls below the sensitivity of the helium mass spectrometer used and are therefore undistinguishable from the background noise. Simulation **b** sets the flow rate rejection limit as apparent leak rate and will therefore highlight the minimum detectable equivalent standard leak rate. Setting the dwell time t_{dwell} to 1s represents a best-case scenario for estimating the experimental parameters. Optimizing this parameter requires a good understanding of the materials constituting the test object, as their properties influence the rate of helium desorption. Proper adjustment of the dwell time helps minimize measurement errors and avoid false rejections due to residual helium or surface contamination.

As stated, different test object internal volumes were simulated. The volumes were chosen and calculated according to customer technical specifications. These are: 8.500×10^{-4} L, 1.090×10^{-2} L, 4.625×10^{-2} L, 2.180×10^{-1} L and 9.250×10^{-1} L.

The experimental validation of the model was performed designing a test object made of aluminium with an internal volume of 8.500×10^{-4} L, to which a glass capillary was connected as to have two ranges of leak rate, namely 1.28×10^{-6} mbarLs⁻¹ (herein named capillary C1) and 1.25×10^{-5} mbarLs⁻¹ (herein named capillary C2). It is schematically represented in Figure 4.1, where capillaries dimensions for C1 and C2 are also reported.

The test object was validated for its leak tightness as to prevent leakage from the welding parts other than the capillary itself.

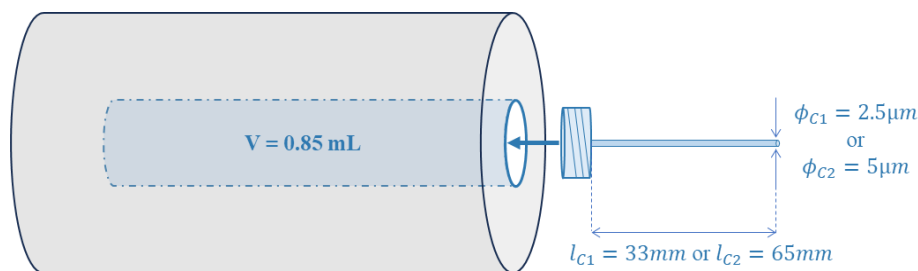


Figure 4.1. Drawings of the test object for validation of the optimized bombing parameters.

The experimental procedure, as described in Section 3.1, comprises three stages: bombing, evacuation and measure. The test object was indeed placed in a bombing chamber first for the bombing phase, then moved to the measuring chamber in certain time t_{dwell} , both tested for their leak tightness. The bombing chamber comprises:

- connection to the helium line, where helium was injected at a pressure of 5 bar.
- connection to an evacuation line.
- a pressure monitoring system.

The measuring chamber is composed by:

- connection to the vacuum pump for the evacuation phase (Pfeiffer HiScroll 18).
- pressure monitoring system (Marposs LeakBox).
- helium mass spectrometer (Inficon LDS3000).

The procedures of the experimental validation are reported below (Table 6):

Table 6. Test parameters used in Experimental Procedure 1 and Procedure 2.

	PROCEDURE 1	PROCEDURE 2
P_B (mbar)	5000	5000
t_B (s)	7200	3600
t_{dwell} (s)	240	240

Experimental procedures 1 and 2 differs from the time of the bombing phase, which is 2 hours for procedure 1 and 1 hour for procedure 2.

4.2. Leak test through electrolyte tracing

A manual bench was designed by MG Marposs to test 40 Ah pouch cells. The theoretical background of the electrolyte tracing technique was explained in Section 3.2. In order to test pouch cells, a test chamber must be designed that fulfils the following requirements:

- It must be leak tight.
- The materials composing the test chamber should be rigid enough to sustain the hard vacuum level reached during the evacuation and stabilization phases, avoiding walls bending that can affect measurement stability.
- The internal volume of the chamber must be provided with insulating materials in contact with the pouch cell tabs to avoid short circuiting of the cell.
- The internal structure must prevent pouch cell swelling during the hard vacuum phases of the test procedure.

Overall, the internal volume of the test chamber should be minimized as much as possible. This parameter affects the test cycle time and leak test resolution.

The test chamber, showed in Figure 4.2, was indeed composed by:

- Aluminium support, which includes slots for two o-ring.
- Connection to an absolute pressure transducer.
- Connection to a vacuum pump (Pfeiffer HiScroll 18).
- Connection to a ventilation valve for test chamber evacuation.
- Aluminium cover.
- Support for a pouch cell to test, made of PEEK.

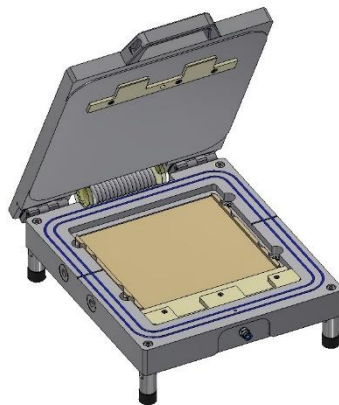


Figure 4.2. Test chamber used to test 40Ah pouch cells with electrolyte tracing technique.

The tightness of the test chamber in vacuum was verified by measuring the rising pressure after reaching a level of vacuum around 0.05 mbar_{ABS}. The test chamber pressure at the end of the vacuum phase hasn't exceed 0.10 mbar_{ABS}. The level of vacuum after entire cycle time has to be below 0.15 mbar_{ABS}. This means the leakage in air has to be below 2.60×10^{-3} mbarLs⁻¹ for the specific conditions of this test. The time required to bring the test chamber to the desired vacuum pressure was 30 s. This sets up one of the parameters for establishing the overall cycle time. Stabilization time and measuring time were set to 2 s and 4 s respectively.

Customer requirements also mentioned the possibility to test pouch cells of different dimensions than the ones provided for this specific test. Therefore, the test chamber has been provided with custom made PEEK test plates and springs to introduce different format cells.

The system is then completed by the measuring system, shown in Figure 4.3-a. It comprises:

- mass spectrometer (Hiden Analytical HPR-20 R&D) equipped with direct vacuum sampling system, electron ionization source (70 eV), single quadrupole mass selector and Farady cup as detector.
- Specific high vacuum valves, which manage the connections between test chamber, mass spectrometer and vacuum pump.
- Stainless-steel connection pipe for vacuum application.
- Vacuum pump (Pfeiffer HiScroll 18).

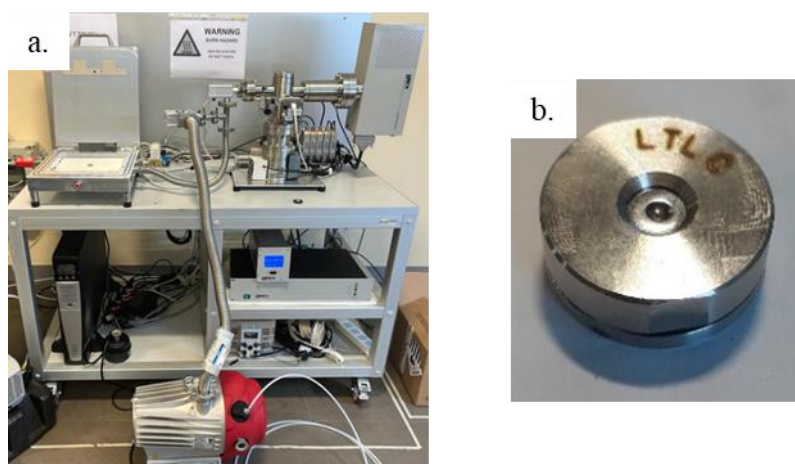


Figure 4.3. (a) Picture of the measuring system setup; (b) Picture of dedicated master leak.

In case a defect is present on the pouch cell under test, the measure will be displayed in unit of solvent flow (mbarLs^{-1}). The sensitivity of the system is $5.00 \times 10^{-6} \text{ mbarLs}^{-1}$; the rejection limit is $1.00 \times 10^{-5} \text{ mbarLs}^{-1}$, which corresponds to a defect generated by an orifice with a diameter of $1 \mu\text{m}$.

Figure 4.3-b shows the master leak (referred to as CL-SOLT) used to calibrate the leak test manual bench. The above shown version of CL-SOLT consists of a tank filled with DMC (Extra dry 99%, Torchiani srl), communicating with the exterior through a $5 \mu\text{m}$ orifice. The master was characterized by its mass flow ($3.70 \times 10^{-7} \text{ g s}^{-1}$), converted to solvent leak rate ($1.00 \times 10^{-4} \text{ mbarLs}^{-1}$) for system calibration. Calibration, indeed, consisted of measuring the mass spectrometer signal at m/z 45 and relating that signal (given in Torr, as nominal partial pressure of DMC with respect to mass spectrometer internal pressure) to the calculated solvent flow rate. After calibration, repeatability test was performed. The master leak underwent 30 measuring cycles, with a result of $(1.10 \times 10^{-4} \pm 6.40 \times 10^{-7}) \text{ mbarLs}^{-1}$. Given a coefficient of variation lower than 1%, the repeatability test can be considered successful and the overall system performance validated.

The experimental setup involved the following steps:

- Measure of the test chamber background level.
- Measure of the pouch cell under test.
- Measure of the $5 \mu\text{m}$ master leak.

The above-described procedure ensures system stability and reliability through the entire experimental campaign.

4.3. Experimental setup for H_2S monitoring in sulphide solid-electrolytes

As anticipated in Section 1.4.2, sulphide-based solid-state electrolytes are known to react with water in a moisture containing environment to produce harmful H_2S through a cascade of reactions that not only affect safety but also battery performances.

In this work, a study was conducted on investigating how $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) behaves in environments at different moisture concentration. The material of solid-electrolyte used was provided by Fraunhofer ISE. The solid-electrolyte layer (SE) preparation method was explained in [42] and [54].

The instrumentation used to carry out the experimental part was designed and provided by MG Marposs. The aluminium test chamber has a halar-coated internal volume (0.5 L) and dimension such to be capable to host up to a 5 Ah pouch cell. It is equipped with temperature sensor (TD2501, IFM Gmbh) and pressure sensors (PT0505, IFM Gmbh and Pirani sensor, Pfeiffer Gmbh). The test chamber holds several connections through leak tight valve to the vacuum pump for chamber evacuation, to the air treatment group and to the mass spectrometer (Figure 4.4-a).

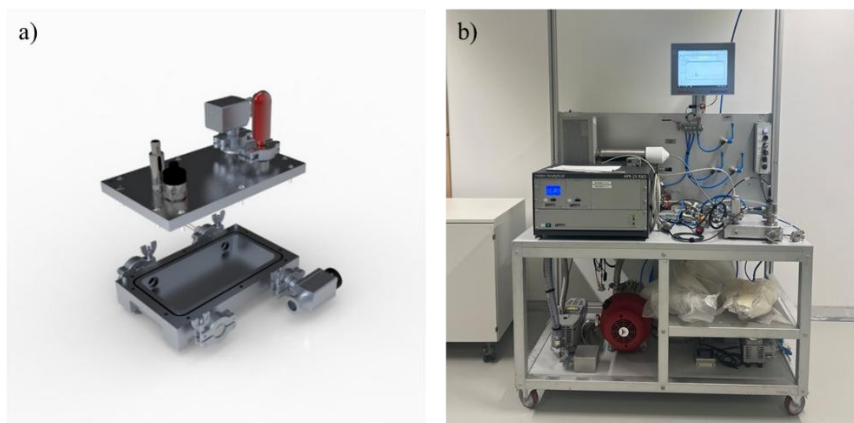


Figure 4.4. (a) Rendering of the test chamber equipped with sensors and connections to the air treatment group and mass spectrometer; (b) instrumental bench: description can be found in the text.

The test chamber can be also equipped with leak tight electrical connections. It allows to perform electrochemical characterization of a full cell under different environmental condition and monitor its performance degradation rate in presence of a leak. For example, an orifice-like defect can be introduced on a coin cell case via laser drilling and used to simulate a leaking battery. In this way, it is possible to assess the real effects of a leak on a specific battery chemistry, both monitoring the eventual releasing of gas and measuring the performance drop in real electrochemical tests. Further studies will be conduct to validate this additional feature.

The full instrumental bench is showed in Figure 4.4-b and is composed as follows:

- Mass spectrometer HPR-20 R&D (Hiden analytical) equipped with heated capillary sampling system, electron ionization source (70 eV, 1000 μ A), single quadrupole mass selector and Faraday cup as detector.
- Air treatment group composed by:
 - Mist and micro mist separator (SMC)
 - Membrane air dryer (IDG50A, SMC)

- Relative humidity sensor (RH range: 0-100%, SMC).
- Vacuum pump Pfeiffer Hi-Scroll 18.

It is possible to choose the relative humidity of air introduced in the test chamber by switching on/off the connection of the chamber with the air dryer unit. The minimum value of relative humidity at 25 °C that can be reached by the equipment depends on air pressure at the air dryer inlet. In the specific case of these tests, the minimum value reached 0.5% RH, which corresponds to a value of 53 ppm of water in the introduced air.

The instrumentation used for analysis of the LPSCI samples was initially tested with solutions of isopropanol 99.5% (Sigma-Aldrich) in acetonitrile (Sigma-Aldrich). Isopropanol/acetonitrile ratio was calculated to have, after complete evaporation of the drop, 5 and/or 50 ppm of gaseous isopropanol in the test chamber. Isopropanol, as well as acetonitrile, were selected due to their high vapour pressure, ensuring complete vaporization. Acetonitrile is also a good solvent for the purpose of this analysis, since the peak of its MS fingerprint is not overlapping with the most intense peak of isopropanol. Complete evaporation of the drop was followed by monitoring the internal pressure of the chamber.

The analysis of the mass spectrometer data was performed based on the mass spectra of isopropanol and hydrogen sulphide (H₂S) obtained with an electron ionization source, as reported by the National Institute of Standards and Technologies (NIST webbook) [87], [88]. Initially, full mass spectra of the internal chamber atmosphere were acquired. These background spectra were analysed to characterize the fragmentation patterns and relative intensities of air molecules [89]. A representative mass spectrum of air is presented in Figure 4.5-a. Signal overlap between target analytes and air molecules must be taken into account. Specifically, an analyte's signal might be masked by fluctuations in the background noise when its concentration is several ppm lower than the concentration of the overlapping air molecule. Therefore, it is necessary to identify appropriate m/z ranges within the spectrum for distinguishing analyte signals from those originating from air molecules. Figure 4.5-b shows the fingerprints of isopropanol and hydrogen sulphides. In both cases, the most intense m/z signal does not overlap with the air pattern.

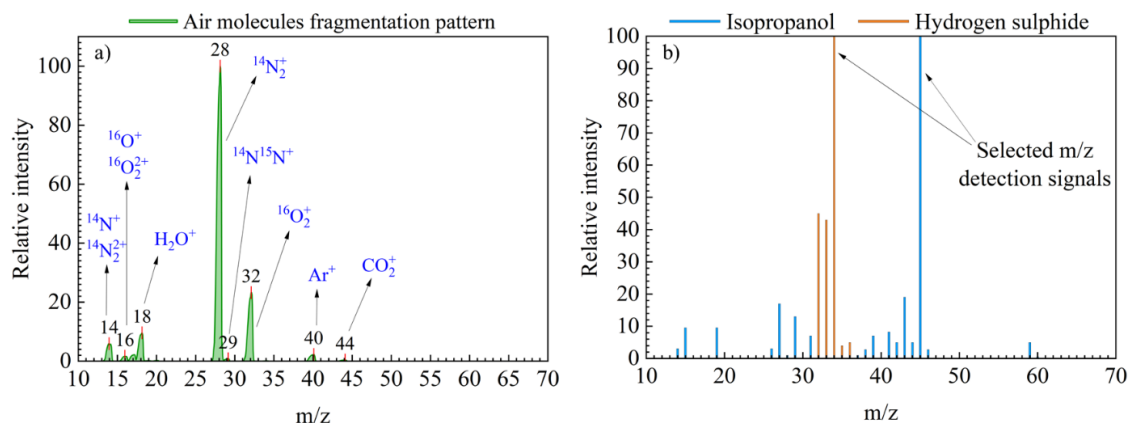


Figure 4.5. (a) Air molecules fragmentation pattern.[89] (b) Isopropanol and hydrogen sulphide fingerprint. Reproduced from [87], [88]

The procedure for the tests with isopropanol was the following:

- Isopropanol drop in a controlled amount was inserted into the test chamber through one of the available inserts, as shown in the rendering of the test chamber in Figure 4.4-a.
- Test chamber internal pressure was monitored to track the isopropanol drop evaporation since the chamber internal pressure resulted to be atmospheric pressure plus the isopropanol partial pressure, as calculated from ideal gas law.
- Once evaporation was completed, the test chamber was connected to the mass spectrometer for isopropanol detection.

The repeatability of the measuring system was assessed and the standard deviation of the repeated measures was calculated and are presented in Section 5.3.

Solid-electrolyte samples were prepared according to the procedure described in [42] and [54], that resulted in a flexible thin layer of infiltrated LPSCl (total thickness $\approx 30\text{ }\mu\text{m}$, average areal density including scaffold 5.37 mg cm^{-2}). This thin film was punched in 8 mm disk samples that were tested according to the following. The test method used implies isolating the SE layer in a leak tight test chamber under argon atmosphere. Subsequently, the argon atmosphere is evacuated by means of a vacuum pump connected to the laboratory air evacuation system. Once an internal pressure of few mbar is reached, the chamber is filled with air containing a controlled amount of moisture until reaching an internal pressure of roughly $1\text{ bar}_{\text{ABS}}$. The moisture level was regulated by the air treatment group and controlled through the relative humidity sensor at specified temperature.

Electrolyte samples were tested under air atmospheres drawn from the facility's compressed air line and passed through the air treatment group, containing 53 and 470 ppm of water (calculated from the relative humidity measured by the sensor, corresponding to water vapor content). According to the theory described in [90], these values correspond to dew points of -50 °C and -27.8 °C in a dry room environment, respectively. A third test was performed using air drawn from the Fraunhofer ISE dry room with a dew point of -30 °C, corresponding to 380 ppm of water according to the dry room specifications. Finally, a test was conducted under ambient air conditions with a relative humidity of approximately 40%; this sample is referred to as “ambient”. The samples were left in the specified atmosphere for a certain time, ranging from 2 h to 24 h, during which mass spectra were acquired. The resulting mass spectra were analysed to monitor H₂S formation. Subsequently, the tested electrolyte samples were used to assemble cells with silicon anodes (average areal density 4.43 mg cm⁻², AAM ratio 48.5%) and NMC-83 (LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂, average areal density 23.82 mg cm⁻², CAM ratio 79.2%) cathodes provided by Fraunhofer ISE.

All the cells were assembled following ref [42] and [54] in a glovebox (GS GLOVEBOX) and tested in an ASC-A(+) cell (Sphere Energy), tightened using a torque of 5.8 Nm, and cycled at 50 °C. The cycling protocol included an initial formation cycle performed in constant-current/constant-voltage (CC–CV) mode with charging and discharging currents of 31 mA g_{NMC}⁻¹ and CV cutoff of 11 mA g_{NMC}⁻¹. The specific discharge capacity obtained during the formation cycle was used to define the C-rates. Subsequently, 20 charge/discharge cycles were carried out in CC–CV mode at 2C (with a current cutoff of 0.2C for the CV phase). Before and after this cycling protocol a check-up cycle performed in CC–CV mode with a charge C-rate of 2C (CV cutoff at 0.2C) and discharge rate at 0.2C (CV cutoff at 0.1C). Rate capability tests were performed in CC–CV mode at C-rates of 0.5C, 1C, 2C, 4C, 8C, and again 0.5C (with a CV cutoff of 0.2C), with five cycles executed at each rate. Finally, a long term stability test was conducted by applying 100 CC–CV cycles at 2C (with a 0.2C cutoff in the CV phase). This 100-cycle block was repeated five times to evaluate long-term degradation under accelerated conditions. Energy testing cycles were also performed in CC–CV mode with a charge and discharge C-rate of 0.14C (CV cutoff 0.05C). These tests were carried out after the formation cycle and before the start of regular cycling, after the 20 cycles at 2C, and then every 100 cycles during the rapid aging test. Energy testing cycles are designed to evaluate the cell's energy retention and efficiency

under controlled conditions, providing a more accurate assessment of its state of health and degradation behaviour over time.

Table 7. Cycling protocol

Test type	Mode	C-rate (charge/discharge)	CV cutoff	Number of cycles	Notes
Formation cycle	CC–CV	31 mA g _{NMC} ⁻¹	11 mA g _{NMC} ⁻¹	1	Defines specific capacity and baseline for C-rate calculation.
Regular cycling	CC–CV	2C / 2C	0.2C	20	Evaluation of cell performance under standard cycling conditions.
Check-up cycle	CC–CV	2C (charge) / 0.2C (discharge)	0.2C (charge) / 0.1C(discharge)	Before and after cycling	Evaluate cell health
Rate capability test	CC–CV	0.5C → 1C → 2C → 4C → 8C → 0.5C	0.2C	5 cycles per C-rate	Determines capacity retention and power capability at various C-rates.
Long term stability test	CC–CV	2C / 2C	0.2C	100 cycles × 5 repetitions	Accelerated test to assess long-term cycling stability and degradation trends.
Energy testing cycle	CC–CV	0.14C	0.05C	After each 100-cycle block	Evaluates energy retention, efficiency, and cell health evolution.

5. Results and discussion

This chapter presents the results of experimental campaigns in helium bombing test, electrolyte tracing leak test and monitoring of the reactivity of $\text{Li}_6\text{PS}_5\text{Cl}$ solid-state electrolyte. The results are critically discussed.

5.1. Helium bombing leak test: theoretical study and experimental validation

As explained in Section 3.1, given a defined volume V of the test object, fundamental parameters to optimize for the implementation of helium bombing leak test in a production environment are bombing time and pressure (P_B and t_B , respectively) as well as dwell time (t_{dwell}) between the bombing and the measuring phases. Their influence on the apparent leak rate R is described by the Howl and Mann theory for laminar (Equation 10) and molecular (Equation 11) flow regimes. Under defined experimental conditions, the theory also predict the equivalent standard leak rate L .

In this work, under the assumptions made in Section 4.1, the analytical expression that accounts for the molecular flow regime was numerically solved for different internal volumes of the test object. Each solution shows the dependence of the technique sensitivity on bombing pressure and bombing time. First, the equivalent standard leak rates are calculated by setting the apparent leak rate equal to the mass spectrometer sensitivity, which identifies the minimum detectable leaking defect whose signal distinguishes from the background noise. Then, the equivalent standard leak rate was calculated for value of $R=1.00\times 10^{-6}$ mbarLs⁻¹, namely the rejection limit above which the sample under test is considered scrap. The results are shown in Figure 5.1. The grey areas identify all the standard leak rates that fall below the background noise of the mass spectrometer under the specified conditions of bombing time and pressure. The green areas identify all the standard leak rates that falls between the rejection limit and the background noise, thus the region that contains all the “good samples” under specified conditions of bombing time and pressure. The bottom-right corner of each graph gives the best test performances for a given test object’s volume, as the R values for background noise and rejection limit relates to smaller real leak rates L .

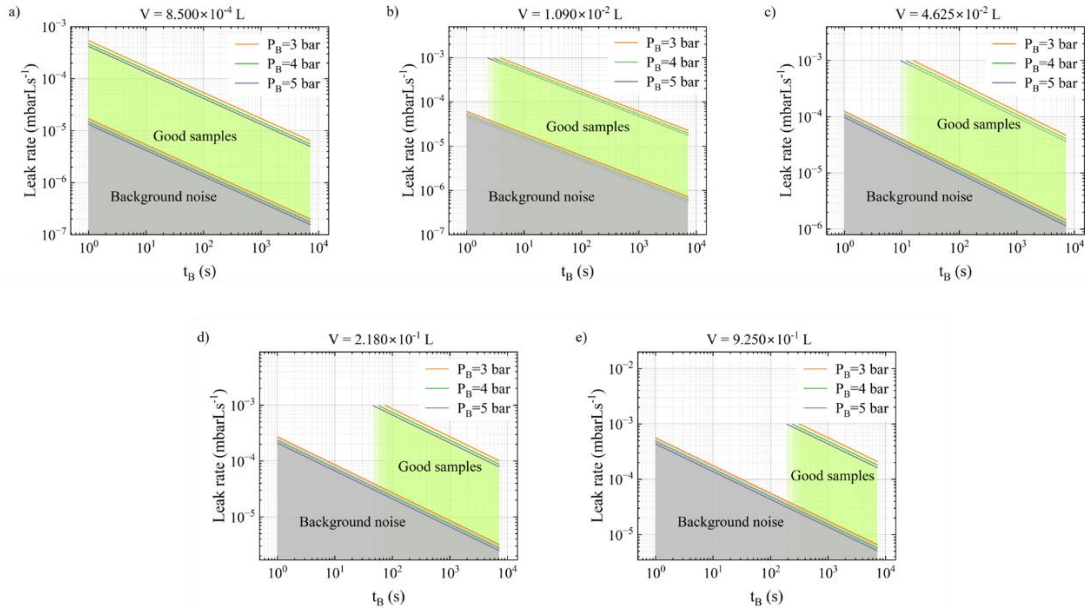


Figure 5.1. Numerically solved Howl and Mann equation to calculate the equivalent standard leak rate given a certain value of apparent leak rate and volume of the test object, assuming a molecular flow regime.

From the comparison among the results in Figure 5.1(a-e), it is evident that the internal volume strongly affects the test sensitivity. For smaller volumes (Figure 5.1 a–b), equilibrium between the helium partial pressure inside the sample and the bombing atmosphere is reached more rapidly, allowing detectable signals even for relatively short bombing times. As the internal volume increases (Figure 5.1 c–e), the same helium uptake requires significantly longer exposure times, shifting the boundary between the “Good samples” and “Background noise” regions toward higher t_B values. This dependence on the internal volume can also lead to opposite classification outcomes for the same nominal leak rate under same testing conditions. For example, considering a leak rate of 10^{-4} mbarL s $^{-1}$ tested with a bombing time of 10^3 s and a bombing pressure of 5bar, the corresponding interpolated point lies above the green region in Figure 5.1-a and -b. Under those conditions, the helium signal would be too high and such samples would be classified as defective. However, in the case of larger internal volumes, such as in Figure 5.1-e, the same point falls within the “Good samples” region, meaning that the same equivalent standard leak rate would be detectable below the rejection limit, and the samples would therefore be considered acceptable. In conclusion, the same physical leak rate can produce different test outcomes depending on the internal volume of the sample, pointing out the need to account for the interplay between volume, bombing pressure, and bombing time when defining acceptance criteria.

The theoretical model obtained from the numerical resolution of the Howl and Mann equation was experimentally validated through a dedicated test campaign.

For this purpose, two artificial leaks were designed and manufactured, consisting of appropriately sized capillaries such to have a defined leak rate under 1 bar of pressure differential. This nominal equivalent standard leak rates were 1.28×10^{-6} mbarLs⁻¹ (referred to as C1) and 1.28×10^{-5} mbarLs⁻¹ (referred to as C2). Both leaks were mounted on a reference test object with a known internal volume of 0.085 mL, as shown in Figure 4.1.

The test parameters were selected to ensure the best achievable sensitivity for this specific volume configuration, meaning operating in the lower right region of the sensitivity map previously discussed (Figure 5.1-a), where the detection capability is maximized.

Based on this criterion, the test object was bombed with helium at a pressure of 5 bar for a bombing time of 2 hours, as previously shown in Table 6 of Section 4.1 referred to as *Procedure 1*. After the bombing phase, the test chamber was evacuated and the sample was left connected to the mass spectrometer for approximately 15 hours, during which the apparent leak rate R was measured as function of the measuring time t_m . The use of such long measurement times was motivated by the need to observe not only the steady-state flow of helium through the calibrated leak, but also any transient phenomena influencing the overall signal. In particular, extended observation allows the identification of:

- Helium desorption from the internal surfaces of the test object or the chamber walls.
- Outgassing or delayed release from small trapped volumes or poorly evacuated regions (dead volumes).
- The gradual emptying of helium-filled cavities characterized by low conductance, which can cause a delayed pressure equilibration.

These effects are typically manifested as a transient decay of R over time before reaching a stable plateau.

For the experimental validation of the model, both the molecular and laminar flow regimes were considered. As previously discussed, the description of a gas flow through a capillary is not always univocal, since it depends on several parameters such as the pressure gradient, the capillary geometry, and the gas mean free path, all of which can vary during a bombing test. In practical conditions, especially at intermediate pressures and relatively small leak dimensions, the flow may exhibit transitional behaviour between the molecular and viscous

(laminar) regimes, or even a gradient of regimes along the leak path. For this reason, in addition to the theoretical curve for molecular flow, the laminar flow model derived from the Howl and Mann theory was also plotted. This allowed proving if the assumption of molecular flow, used in the theoretical interpretation of the equivalent standard leak rate L , remains valid under the test conditions adopted in this work. The results are shown in Figure 5.2-a and -b.

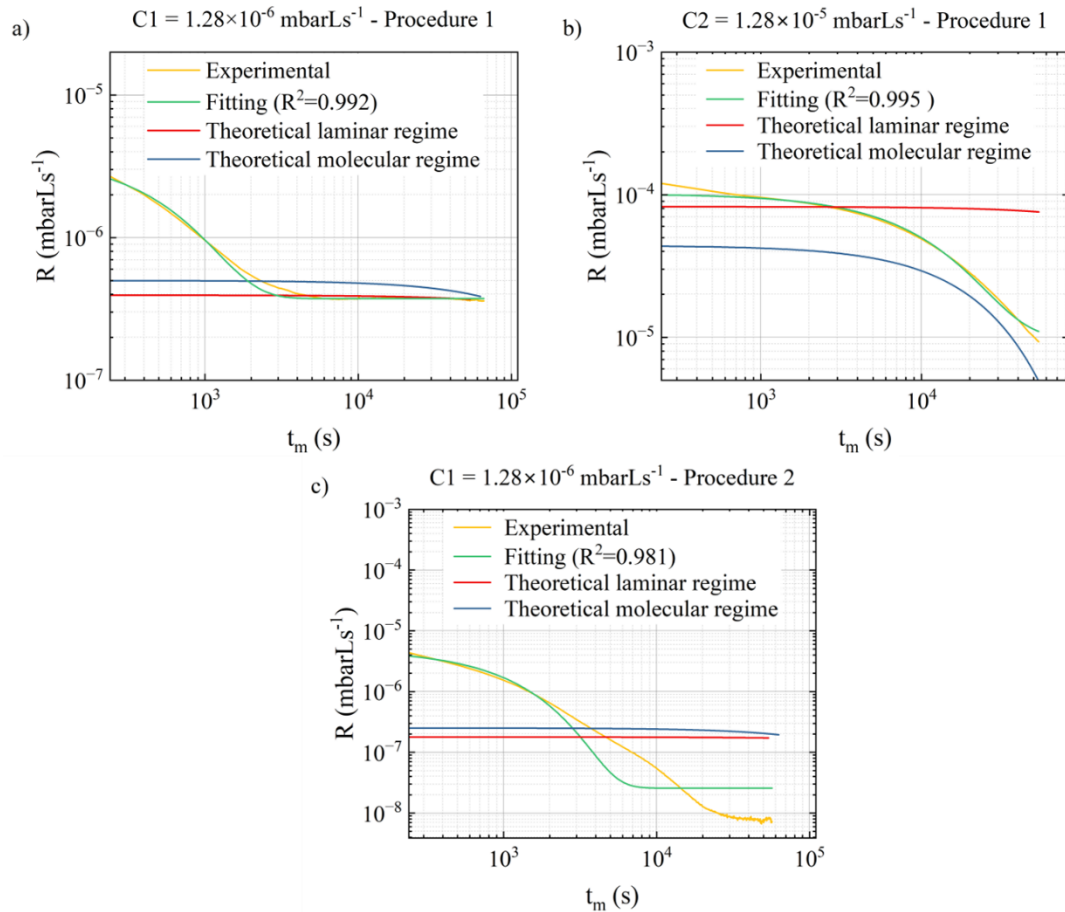


Figure 5.2. Experimental results of a) capillary C1 under condition of Procedure 1; b) capillary C2 under conditions of Procedure 1; c) capillary C1 under conditions of Procedure 2. Blue and red lines shows the theoretical trend for laminar and molecular flow regimes, respectively, under the specified conditions.

The experimental curve for capillary C1 tested in conditions of *Procedure 1* (yellow curve of Figure 5.2-a) shows an initial transient characterized by a sharp exponential decay in the detected leak rate R . This transient can be attributed to helium desorption from the internal surfaces and the emptying of small dead volumes inside the fixture and the test chamber. The decay is well described by an exponential fit ($R^2 = 0.992$), with a time constant of about 575 s. After this phase, R approaches a steady value which lies between the theoretical molecular and laminar flow predictions, although slightly closer to the laminar regime (red line). This indicates that the flow through capillary C1 does not occur under purely

molecular conditions. The relatively small leak conductance, combined with the low internal pressure achieved after bombing (≈ 1.2 bar), makes the mean free path of helium comparable to the characteristic dimension of the capillary, placing the flow in an intermediate or transition regime between molecular and viscous behaviour. The steady-state value of R remains consistent with the nominal equivalent standard leak rate of 1.28×10^{-6} mbarLs $^{-1}$; the small deviation between experiment and theory is therefore attributed to the finite helium loading during bombing and to the partial equilibration between the helium-filled volume and the external environment.

Figure 5.2-b shows the experimental and theoretical curves for the leak with capillary C2 under conditions of *Procedure 1*. The experimental leak rate R is approximately one order of magnitude higher, as expected from the nominal leak rate. The overall trend is again characterized by a monotonic decay of R with time, well described by an exponential fit ($R^2 = 0.995$). However, unlike C1, this exponential decrease is not dominated by desorption or dead-volume effects, but rather represents the intrinsic pressure equilibration process predicted by the Howl and Mann model itself. In the molecular flow formulation, when the internal test volume V is finite, the model naturally yields an exponential decay term, as shown in Equation 17:

$$e^{-\frac{Lt_{dwell}}{P_0 V} \sqrt{\frac{MW_{air}}{MW_{He}}}} \quad \text{Eq. 17}$$

which describes the gradual emptying of helium from the test object as the internal pressure decreases toward ambient. This theoretical feature explains why the molecular flow curve (blue line) exhibits a decaying trend rather than a constant plateau. The agreement between the experimental data and the molecular flow prediction confirms that gas transport through C2 occurs predominantly under molecular flow conditions. The laminar flow prediction, conversely, significantly overestimates R , lying about one order of magnitude above the measured data.

The conditions of *Procedure 1* may not always be ideal in industrial environments, especially for the high bombing time of 2 h. In the production workflow, the throughput, defined as the number of inspected parts per unit time, is a critical parameter and shorter testing cycles enable faster leak control, directly contributing to maintaining a high production rate. For this reason, it is important to assess whether the bombing test can still provide sufficient sensitivity when the exposure time to helium is reduced. However, it is

worth mentioning that when longer bombing times are unavoidable, throughput can still be optimized by testing multiple samples in parallel. Based on these practical considerations, a second procedure (*Procedure 2*) was carried out using the smaller calibrated leak C1, which represents the most challenging case for detection sensitivity. This test allows evaluating how reducing the bombing phase from 2h to 1h affects the measured apparent leak rate. Figure 5.2-c shows the results obtained under this condition.

The experimental data exhibit a rapid initial decrease followed by a gradual decay over time. This highlights that a shorter exposure leads to incomplete helium saturation within the test object, resulting in a weaker measurable signal during the subsequent dwell period. The decay can still be described by a single exponential function ($R^2 = 0.981$) with a time constant of approximately 911 s, which is shorter than that obtained in the previous test (575 s for the same capillary C1 in *Procedure 1*). This suggests that the desorption and equilibration processes occur more rapidly when the total helium content is smaller, since the diffusion and release from internal surfaces complete in a shorter time. Unlike Procedure 1, the experimental curve does not match either the molecular nor laminar theoretical predictions throughout the entire measurement window. This indicates that the signal is dominated by transient outgassing phenomena rather than by steady molecular flow through the capillary. In this condition, the reduced helium loading prevents the establishment of a true equilibrium state, making the theoretical steady-state regime unattainable within the measurement time. Consequently, these results highlight the critical role of the bombing time in ensuring accurate and reproducible measurements. While shorter testing cycles are advantageous for industrial integration and high-throughput leak control, excessive reduction of the bombing duration can compromise sensitivity, especially for smaller leaks such as C1, by preventing complete helium penetration and equilibration.

Overall, the comparison between experimental and theoretical data demonstrates that the Howl and Mann formulation provides an accurate description of helium leak behaviour across different leak magnitudes. The experiments demonstrate that:

- For C1, the flow is transitional, and the decay primarily reflects desorption and partial equilibration effects.
- For C2, the flow is molecular, and the exponential decay is an intrinsic feature of the pressure equilibration process.

- Shorter bombing times significantly reduce helium loading, leading to signals dominated by transient outgassing rather than true steady leak flow.

The choice of bombing parameters should represent a compromise between test sensitivity and industrial throughput, which must be optimized depending on the application.

However, the experimental evidence obtained in this work also highlights the limitations and critical aspects of applying this type of test to complex systems such as lithium-ion batteries.

In such systems, the internal free volume is often not precisely known, and additional factors, such as the porosity and tortuosity of the separator, the presence of liquid electrolyte, and possible gas–solid interactions within the cell, can significantly affect the apparent leak rate. These effects may combine with the exponential decay phenomena observed in the early stages of the tests with capillaries C1 and C2, leading to strong deviations from the ideal theoretical behaviour even under the best experimental conditions.

Therefore, while the bombing method provides valuable insight into leak mechanisms and sensitivity limits, its direct application to electrochemical cells should be approached with caution and supported by a thorough understanding of the system's internal structure and gas transport properties.

5.2. Electrolyte tracing technique: a leak test suitable to battery cell

The electrolyte tracing technique is a diagnostic method that enables the detection of sealing defects in lithium-ion batteries through the direct identification of solvent leakage. This technique is of fundamental importance since, as discussed in Section 0, even minor sealing defects can lead to severe consequences not only for the electrochemical performance of the cell but, more critically, for consumer safety. This method allows testing of battery cells that have already been sealed and filled with electrolyte, i.e., after the filling and sealing steps and/or following the formation and aging processes prior to commercialization.

Electrolyte tracing typically relies on the use of a mass spectrometer to detect the presence of volatile organic solvents, which are the main components of the electrolyte in lithium-

ion batteries. While it is possible to acquire full mass spectra to identify the solvent fingerprint, in practice a preliminary spectral study is often performed to select a single m/z peak, as discussed in Section 4.2 and 4.3. This peak is chosen for its relatively high intensity and its minimal overlap with ambient air peaks of comparable magnitude, in order to improve measurement accuracy.

In this work, the electrolyte tracing technique was applied to the testing of 40 Ah lithium-ion pouch cells at 10% SOC (state of charge), all nominally sealed according to the manufacturer's specifications. To perform these tests, a dedicated test chamber was designed to accommodate the cell dimensions provided by the customer. The chamber's tightness was validated experimentally, and the timing parameters for the different test phases were defined based on this validation.

The electrolyte tracing technique typically consists of three main stages, here summarized:

- a dynamic vacuum phase, in which the chamber pressure is reduced to a few mbar_{ABS} (0.05 mbar_{ABS} in this case).
- a stabilization phase, during which the chamber is kept under static vacuum for a few seconds to allow accumulation of any solvent vapours released through potential leaks. The internal pressure of the chamber in this phase is allowed to vary up to 0.10 mbar_{ABS}.
- a measurement phase, in which the chamber is connected to the mass spectrometer for signal acquisition.

After the optimization of the chamber parameters, the system was calibrated using a certified master leak of known flow rate. The master leak was also employed to verify the repeatability and stability of the measurement system. Finally, a batch of nine 40 Ah pouch cells was tested, and the results of these measurements are presented and discussed in the following.

Calibrating the measurement system involves correlating the partial pressure signal detected by the mass spectrometer with a quantitative unit of solvent leakage rate, expressed in mbarLs⁻¹. To achieve this, a calibration master with well-defined geometric characteristics was designed and fabricated. The master consisted of a chamber of known internal volume and a precision-calibrated orifice with a diameter of 5µm. The master was first weighed to determine its tare mass. It was then filled with DMC and subjected to the same vacuum cycles defined for the electrolyte tracing measurements. The mass of the

master was recorded before and after each test cycle in order to determine the DMC mass loss. From these measurements, the relationship between mass flow rate (g s^{-1}) and volumetric leak rate (mbar L s^{-1}) was calculated for the master (Equation 7 of Section 3.1). The mass flow rate resulted to be $3.71 \times 10^{-7} \text{ g s}^{-1}$ which, converted to volumetric leak rate is $1.00 \times 10^{-4} \text{ mbar L s}^{-1}$.

Subsequently, the calibrated master was connected to the measurement system to correlate the spectrometer's partial pressure reading to the absolute solvent leak rate. A repeatability test was indeed carried out to verify the stability and reproducibility of the measurement system. A series of 30 consecutive measurements was performed using the certified master leak. The results are summarized in Figure 5.3.

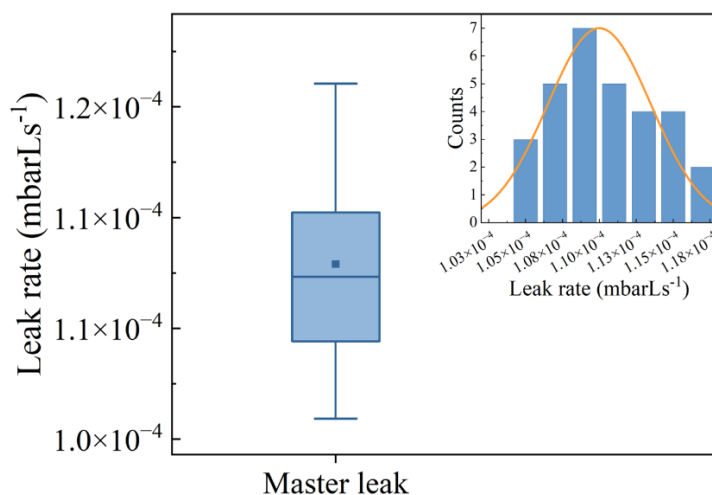


Figure 5.3. Repeatability of the electrolyte tracing measuring system performed with the master leak. The box plot summarises the distribution of 30 repeated measurements of the leak rate, whereas the inset displays the frequency distribution of the measured values. The normal distribution curve (orange line) highlights a good agreement with a Gaussian behaviour centred on the mean value.

The mean leak rate is $1.10 \times 10^{-4} \text{ mbar L s}^{-1}$, with a standard deviation of $3.5 \times 10^{-6} \text{ mbar L s}^{-1}$, corresponding to a relative standard deviation of approximately 3.2%. The minimum and maximum measured values were $1.04 \times 10^{-4} \text{ mbar L s}^{-1}$ and $1.17 \times 10^{-4} \text{ mbar L s}^{-1}$, respectively, with the interquartile range (Q1-Q3) extended from $1.07 \times 10^{-4} \text{ mbar L s}^{-1}$ and $1.12 \times 10^{-4} \text{ mbar L s}^{-1}$. As shown in the box plot, the measurements are tightly grouped around the mean, with no significant outliers, indicating excellent repeatability of the system. The inset displays the corresponding frequency distribution centred at the same mean value. The narrow dispersion and Gaussian-like behaviour of the data confirm that the fluctuations observed during repeated tests are random in nature and not related to instrumental drift.

The electrolyte tracing tests were carried out on a batch of 40 Ah lithium-ion pouch cells using the setup described in the previous section. Each measurement consisted of three sequential phases: a 30 s dynamic vacuum step to reach the desired vacuum pressure inside the chamber, followed by a 2 s stabilization phase and finally a 4 s measurement phase. During the stabilization phase, the system continuously monitored the chamber pressure. If the absolute pressure exceeded 0.15 mbar_{ABS}, the test sequence was automatically interrupted, and a *vacuum reject* alarm was triggered. This safety interlock serves as a gross leak control, preventing excessive solvent vapor from entering the mass spectrometer and contaminating the quadrupole. Prior to each test, the system background signal was recorded, and after each measurement, the master leak was read to verify system stability and validate the result. The rejection limit for this configuration was set at 1×10^{-5} mbarLs⁻¹, which corresponds approximately to the leak rate of a 1 µm calibrated orifice under this specific test conditions. The results are summarised in Figure 5.4.

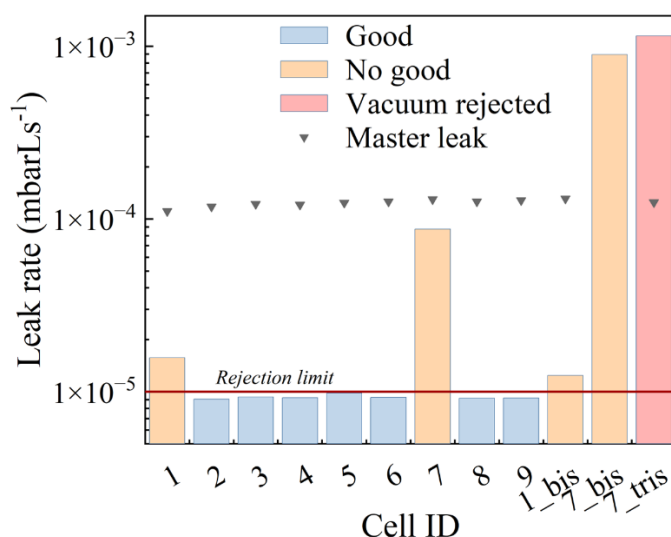


Figure 5.4. Leak rate results for the tested 40 Ah pouch cells obtained using the electrolyte tracing setup. Blue, orange, and red bars represent good, no good, and vacuum rejected cells, respectively, while grey triangles correspond to master leak readings acquired after each test. The red line indicates the rejection limit (1×10^{-5} mbarLs⁻¹).

Blue, orange, and red bars represent good, no good, and vacuum rejected cells, respectively. The grey triangles correspond to the master leak values measured after each test, confirming the consistency of the calibration reference throughout the test campaign.

Most of the tested cells exhibited leak rates around 9×10^{-6} mbarLs⁻¹, below the rejection limit and thus classified as *good*. Two cells, classified with ID 1 and ID 7, initially showed leak rates slightly above the threshold and were therefore classified as *no good*. To confirm the reliability of these results, both cells were retested with ID 1_bis and ID 7_bis,

respectively. In the case of ID 1, the second measurement confirmed the previous result, supporting the validity of the initial finding. Conversely, the repeated test on ID 7 produced similar values. Nevertheless, the high value of recorded flow rate suggested performing a third test (ID 7_tris) to further verify consistency. During this last test, the chamber pressure exceeded 0.15 mbar_{ABS} during the stabilization phase, triggering a vacuum reject event and indicating the presence of a gross leak.

Overall, the results demonstrate the ability of the electrolyte tracing method to detect and classify leaks in sealed pouch cells with high sensitivity and reproducibility. The consistency of the master leak readings throughout the measurement sequence further confirms the reliability and stability of the testing system.

These tests were performed using a laboratory-scale setup, designed for the analysis of a single cell at a time, where sample insertion and removal are carried out manually. Despite this limitation, the results clearly highlight the importance of leak testing in battery manufacturing and validation. In a laboratory environment, such measurements are particularly valuable as they provide essential feedback on the quality of the cell sealing process during its optimization phase. On production lines, similar tests can be implemented through semi- or fully automated systems capable of testing multiple cells simultaneously, thereby increasing throughput and ensuring consistent quality control.

Furthermore, the case of the cell with ID 7 underlines the relevance of the solution adopted by Marposs, which integrates a gross-leak detection station within automated leak test equipment, as anticipated in Section 3.2. In this configuration, a photoionization detector (PID) sensor allows for the early identification of cells exhibiting large leaks, enabling their removal from the measurement sequence before entering the vacuum phase [80], [81], [82]. This preventive step effectively safeguards the integrity of the spectrometer and improves process efficiency by minimizing contamination events.

5.3. H₂S evolution monitoring in sulphide solid-state electrolyte

As anticipated in Section 1.4.2, the development of solid-state batteries is driven by the need for safer and higher-energy storage systems. The use of a solid-electrolyte opens the possibility to develop high-energy density devices that make use, for example, of lithium

metal anodes and high-voltage cathode materials. Overall, solid-state batteries offer great potential for applications requiring both high safety standards and enhanced energy density, particularly in the automotive sector. Among them, $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) is one of the best candidates for its relatively high ionic conductivity at room temperature and ease of processability. However, one of the main challenges associated with these materials is their strong reactivity with moisture, leading to the formation of toxic H_2S and requiring strict environmental control during production. Therefore, in order to investigate this phenomenon, a dedicated experimental setup was designed and assembled, consisting of a sealed test chamber connected to a mass spectrometer and equipped with an air treatment module allowing the controlled variation of relative humidity inside the chamber. The detailed description of the equipment and measurement methodology is provided in Section 4.3. The experimental activities described in this chapter were carried out during a research stay at the Fraunhofer Institute for Solar Energy Systems (Fraunhofer ISE, Freiburg, Germany), within the laboratories of the Battery Cell Production and Technology Assessment research group.

A preliminary study was carried out to characterize the background noise of the mass spectrometer and to establish a reliable detection threshold. This step was necessary to ensure that the variations observed in the subsequent measurements could be confidently attributed to changes in analyte concentration rather than to intrinsic background fluctuations. All spectra were acquired as partial pressure signals, where the intensity of each m/z corresponds to the partial pressure of the respective analyte relative to the total pressure inside the spectrometer mass analyser. All measurements are reported in units of *mbar*. Blank spectra acquired in the absence of analyte were first processed to remove baseline drift using the asymmetric least-squares (ALS) algorithm, and the residual noise distribution was analysed to determine its mean value and standard deviation. Based on these parameters, a statistical threshold ($\text{LOD} = \text{limit of detection}$) was defined as the background mean plus three times the standard deviation, corresponding to a 99.7% confidence level that the observed signal exceeds random noise. The so-defined LOD was 5.6×10^{-10} mbar calculated on a total of 100 blank spectra acquired.

To validate this criterion, the experimental campaign consisted of testing drops of solutions containing 5 ppm and 50 ppm of isopropanol under defined test conditions. Although isopropanol was not used for quantitative calibration, since its response differs from that of H_2S , the comparison between signal and background levels allowed assessing the system's

qualitative sensitivity. The difference between the signal peak and the background was calculated for both concentrations, and a short repeatability test (up to ten replicates) was performed to evaluate the stability of this difference over multiple measurements. In order to ensure that environmental conditions would not affect the results, ambient air and pressure were monitored for 18 h. Temperature variations were lower than 0.14 °C, while pressure variations were around 0.33 mbar h⁻¹, thus confirming stability. Figure 5.5 shows the distribution of the measured partial pressure differences (signal–background) for isopropanol concentrations of 5 ppm and 50 ppm.

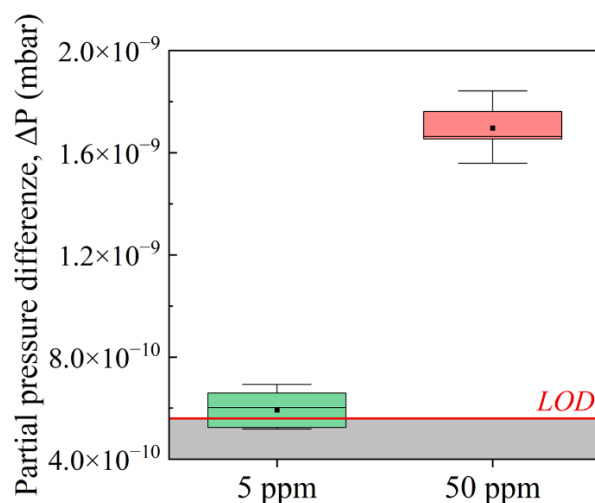


Figure 5.5. Box plot of partial pressure differences (ΔP) measured for 5 ppm and 50 ppm isopropanol. The red line indicates the detection limit ($LOD = 5.6 \times 10^{-10}$ mbar).

The red line indicates the limit of detection (LOD), previously estimated at 5.6×10^{-10} mbar from background noise analysis. The results clearly show that the mean response at 5 ppm lies close to the LOD, with a relatively narrow spread confirming good repeatability but limited distinguishability from background fluctuations. In contrast, the 50 ppm signal is approximately one order of magnitude higher, well above the detection threshold.

The same analytical setup was employed to investigate the interaction between the sulphide-based solid electrolyte Li_6PS_5Cl and air under controlled humidity conditions. The aim is to qualitatively assess the formation of H_2S resulting from the electrolyte's exposure to moisture, in order to evaluate its environmental stability and the potential safety risks associated with its handling in non-inert atmospheres. The tests were performed using the procedure previously described in the Section 4.3. In brief, solid-electrolyte samples were prepared in a glovebox under argon atmosphere and placed in the test chamber, then exposed to air atmospheres with controlled moisture contents. The moisture level was

adjusted through an air treatment unit and monitored via a calibrated humidity sensor. Four different air conditions were tested: two controlled atmospheres containing approximately 53 ppm and 470 ppm of water, corresponding to dew points of $-50\text{ }^{\circ}\text{C}$ and $-27.8\text{ }^{\circ}\text{C}$, respectively; one atmosphere directly drawn from the Fraunhofer ISE dry room (dew point = $-30\text{ }^{\circ}\text{C}$, $\approx 380\text{ ppm H}_2\text{O}$); an ambient air condition with relative humidity around 40%. Samples were kept under these conditions for periods ranging from 2 h to 24 h, during which mass spectra were continuously acquired to monitor H_2S evolution. The spectra were analysed as to identify the fingerprint of H_2S ; then, the most intense peak at $m/z = 34$ was chosen to compare the reactivities under different environmental conditions. The results are reported as partial pressure difference between a background signal acquired before measurement start and the signal acquired after 2 or 24h at the same m/z ; these are shown in Figure 5.6.

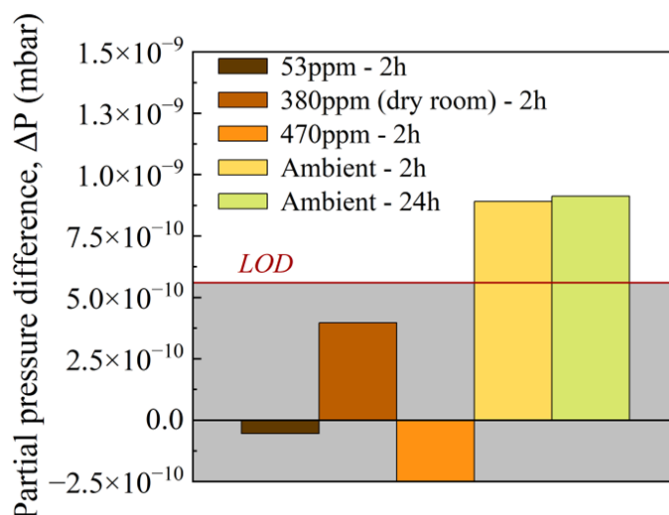


Figure 5.6. Partial pressure differences (ΔP) at the H_2S -related m/z signal measured after exposing $\text{Li}_6\text{PS}_5\text{Cl}$ to different humidity conditions for 2h and 24h. The red line indicates the detection limit ($\text{LOD} = 5.6 \times 10^{-10}$ mbar).

Figure 5.6 reports the partial pressure differences (ΔP) at the m/z corresponding to H_2S formation ($m/z = 34$), obtained after 2 h and 24 h of exposure to different humidity levels. The grey area represents the region below the previously defined detection limit ($\text{LOD} = 5.6 \times 10^{-10}$ mbar), indicated by the red horizontal line. When the solid electrolyte was exposed to controlled atmospheres with 53 ppm and 380 ppm of water, the measured signals remained below the LOD, indicating no detectable H_2S formation within the applied exposure time. Similarly, exposure to 470 ppm for 2 h produced a response still below the threshold, suggesting that the interaction kinetics are too slow at this humidity level under these conditions and the resulting variations are indistinguishable from noise. A slightly

negative ΔP was observed, which is consistent with expected baseline fluctuations and falls within the natural variability of the background noise of the system. In contrast, exposure to ambient air ($\approx 40\%$ RH at 24°C) resulted in ΔP values clearly exceeding the LOD already after 2h. Only a marginal increase was observed after 24h, suggesting that under high-humidity conditions most of the hydrolysis reaction leading to H_2S formation takes place within the first hours of exposure.

In agreement with literature, the extent of degradation of $\text{Li}_6\text{PS}_5\text{Cl}$ depends strongly on the moisture level. Tsukasaki et al. investigated the deterioration mechanism by TEM and reported that, after exposure to controlled humidity corresponding to a dew point of -50°C , the crystalline structure of argyrodite powders remained unchanged, with electron diffraction patterns still indicating single-domain crystallinity. Exposure at -20°C dew point only leads to micrometre-sized crystals transformed into nanocrystalline domains, revealing a loss of crystallinity and the formation of LiCl , Li_2SO_4 , Li_2CO_3 and Li_3PO_4 on the particle surface [91]. On the other hand, Sano et al. showed that no H_2S could be detected when the electrolyte powder was exposed to dry air at -50°C dew point for 1 h, while measurable H_2S evolution occurred already after 1h at -20°C dew point. The electrochemical impedance spectra indicated that the decrease in ionic conductivity was mainly related to surface and grain boundary degradation, with the conductivity retention dropping from 100% in the pristine state to 36% after exposure at -20°C dew point, whereas only minor changes were observed at -50°C dew point. However, these findings relate to a powder LPSCl sample [92]. In this work, as previously discussed, a layer of $\text{Li}_6\text{PS}_5\text{Cl}$ infiltrated into a non-woven scaffold was investigated. The different exposed surface area of the electrolyte in this configuration likely slows down the gas–solid reaction kinetics, which may explain the lower reactivity observed in our tests compared to the powder-based experiments reported by Sano et al.

After each exposure test, the electrolyte samples were collected and stored inside an argon-filled glove box before cell assembly and electrochemical testing. All samples showed a pristine appearance after air exposure at controlled humidity levels (53 ppm, 380 ppm, and 470 ppm). In contrast, the sample exposed to ambient air ($\approx 40\%$ RH) exhibited visible degradation, becoming yellowish and mechanically fragile, with a warped morphology. This deterioration avoided the use of the ambient-exposed electrolyte in cell fabrication, confirming the strong and rapid reactivity of $\text{Li}_6\text{PS}_5\text{Cl}$ in uncontrolled environmental conditions.

The electrolyte samples exposed to different humidity levels were then used to assemble electrochemical cells in order to assess the impact of environmental exposure on their performance. The cell configuration adopted in this work was NMC-83 cathode / surface-treated $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte / Si-based anode, as described in detail in Section 4.3. Each cell is labelled according to the humidity condition experienced by the corresponding electrolyte sample prior to assembly. Accordingly, the cells are identified as 53 ppm, 380 ppm, and 470 ppm, referring to 2h exposures at these water vapor concentrations. As mentioned earlier, the ambient-air sample was not suitable for cell assembly due to the severe degradation observed after exposure. The cycling protocol was already discussed and can be found summarised in Table 7. The results are shown in Figure 5.7.

The formation cycles of the three cells are shown in Figure 5.7-a, where cell voltage U (NMC-83 vs Li_xSi) is shown versus cell specific capacity ($\text{mAh}_{\text{NMC-83}}^{-1}$). During the formation of the cell assembled with the electrolyte treated at 380 ppm, the cycling protocol was temporarily interrupted due to a device malfunction, as highlighted by the arrow in the figure. The test was then resumed and the cycle was successfully completed, with no appreciable impact on the resulting electrochemical performance. In the case of the 53 ppm sample, the applied charge current was slightly higher than the programmed formation current, due to an adjustment in the current setting. This deviation did not affect the performance metrics of the cell, as will be further demonstrated in the subsequent cycling analysis. Nevertheless, the collected data are sufficient to qualitatively assess the influence of the different moisture exposures on the formation behaviour of the solid-state cells. Comparing the three electrochemical responses, the cell fabricated with the electrolyte exposed to 470 ppm of water shows a slightly higher discharge capacity after formation, but also a reduced coulombic efficiency (77.4%) compared to the 53 ppm (78.6%) and 380 ppm (78.2%) cells.

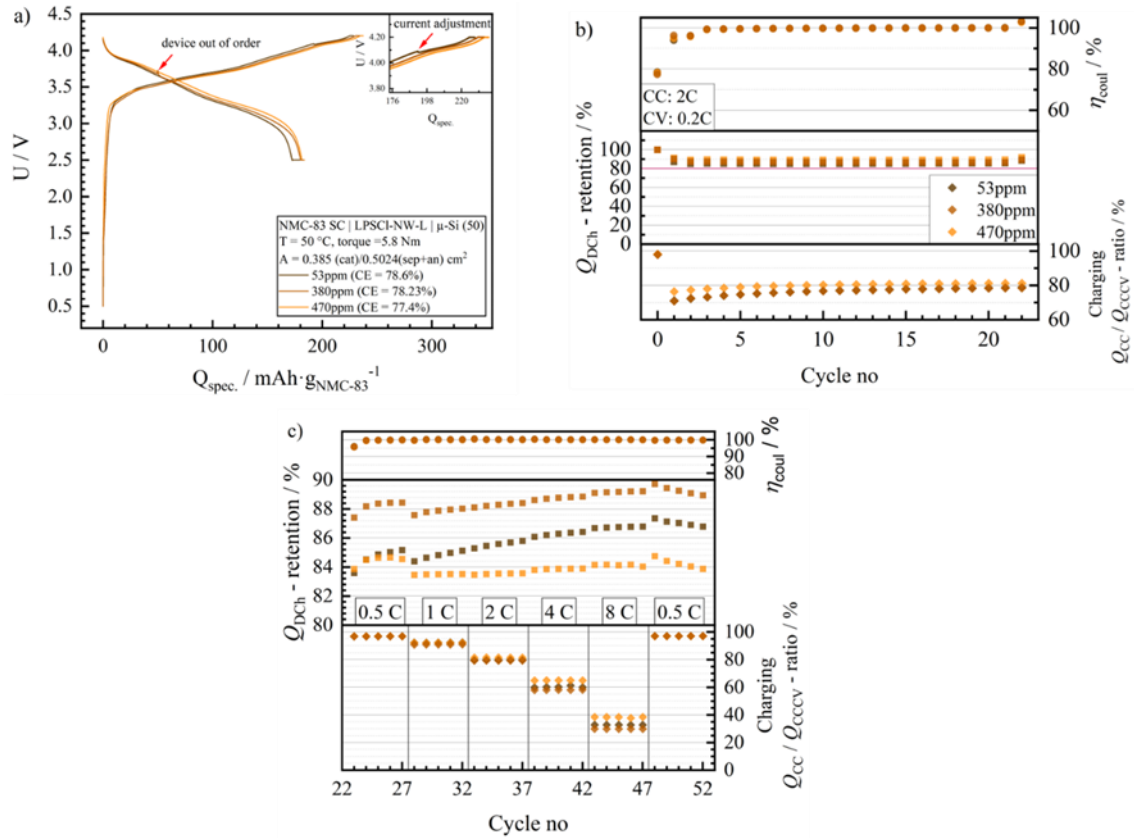


Figure 5.7. Electrochemical performance of all-solid-state cells assembled with $\text{Li}_6\text{PS}_5\text{Cl}$ electrolytes previously exposed to different humidity levels (53 ppm, 380 ppm and 470 ppm). (a) Formation voltage profiles (1st cycle). Minor deviations occurred during testing: a temporary device interruption in the 380ppm cell and a slight current adjustment in the 53ppm cell, neither of which affected performance; (b) Galvanostatic cycling at 2C – 0.2C (CC–CV charging). All cells exhibit similar capacity retention and coulombic efficiencies throughout cycling; (c) Rate capability test from 0.5C to 8C and back to 0.5C.

Figure 5.7-b shows the discharge capacity retention, coulombic efficiency and the $Q_{\text{cc}}/Q_{\text{cccv}}$ -ratio over cycling. Overall, no substantial performance differences can be observed between the three cells during the initial cycling, indicating that exposure of the solid electrolyte to moisture levels up to 470 ppm does not hinder the formation of a stable electrolyte/electrode interface during repeated cycling. All cells exhibit a discharge capacity retention higher than 90% after the initial cycles, with values quickly converging to a plateau and remaining nearly constant during the test. The coulombic efficiency stabilizes above 90% for the three cells after a short activation period. The $Q_{\text{cc}}/Q_{\text{cccv}}$ -ratio remains consistently above 80% for all cells, indicating fast charge-transfer kinetics and no transport limitations at the electrolyte interfaces.

Figure 5.7-c presents the rate capability behaviour of the three cells when the cycling current was sequentially increased from 0.5C to 8C and then returned to 0.5C. For all electrolyte treatments, the discharge capacity progressively decreases with increasing C-

rates, as expected due to the increased polarization and transport limitations characteristic of solid-state interfaces. Throughout the test, the coulombic efficiency remains high (>95%) for all samples at any applied current, indicating that charge-transfer processes remain largely reversible despite the more demanding cycling conditions. The trends observed for the Q_{CC}/Q_{CCCV} -ratio confirm this behaviour: while the constant-current contribution decreases at higher currents, reflecting the reduction in accessible capacity at fast rates, values remain comparable across the three cells, suggesting that charge-transfer kinetics are not significantly altered by the humidity exposure carried out in this work. When the current is decreased again to 0.5C at the end of the test, the discharge capacity retention rapidly recovers to levels close to those observed before the rate steps, demonstrating the absence of irreversible degradation effects during the test sequence. No substantial differences are detected between samples initially exposed to 53, 380, and 470 ppm of water, indicating that such moderate humidity exposure does not noticeably impact the rate capability or interfacial transport behaviour over the investigated current range.

The cells were subjected to long-term electrochemical stability to further investigate how the moisture exposure carried out prior to assembly could affect cycle life. Therefore, cycling was continued up to 500 cycles under constant-current (2C) charge/discharge at 50 °C. The results are presented in Figure 5.8.

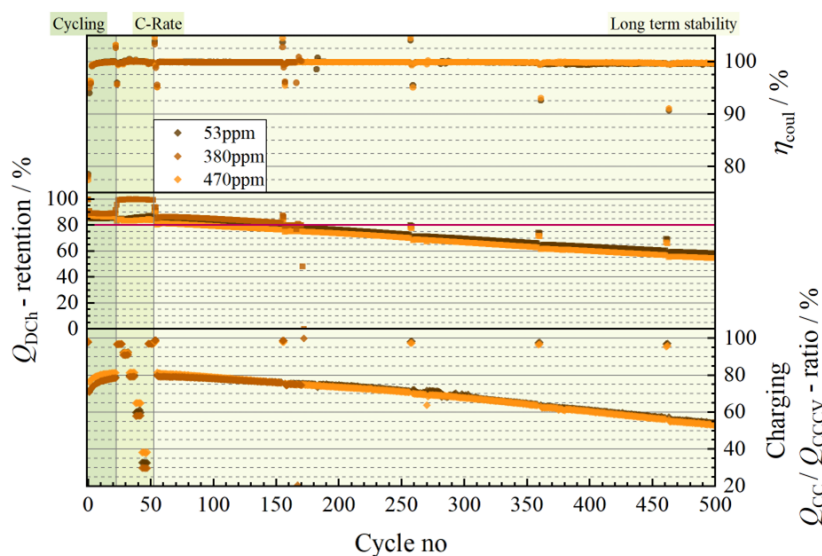


Figure 5.8. Long term stability test up to 500 cycles at 2C and 50 °C for cells assembled with electrolytes exposed to 53 ppm, 380 ppm and 470 ppm of water before assembly. 53 and 470 ppm cells show a progressive reduction in discharge capacity and charge-transfer performance, with similar degradation trends regardless of the initial moisture exposure. The cell for the 380 ppm treated electrolyte shows a premature failing, which was not directly attributed to moisture effects, but rather to occasional issues such as local defects or interfacial contact loss.

In general, all cells show a progressive capacity decay with increasing cycle number, as expected. The trends observed for the different humidity treatments are similar, indicating that a prior exposure of the electrolyte to moderate moisture levels (≤ 470 ppm H_2O) does not induce major differences in degradation kinetics during extended cycling. The coulombic efficiency remains above 90% for most of the test, confirming good charge/discharge processes reversibility. The steady reduction of the $Q_{\text{CC}}/Q_{\text{CCCV}}$ -ratio suggests an increasing charge-transfer resistance at the solid-solid interfaces; however, the similarity in degradation rate among the cells assembled with samples treated at 53 and 470 ppm demonstrates that the limited deterioration induced by humidity exposure does not critically compromise long-term electrochemical performance. It has to be noted that the cell assembled with the electrolyte exposed to 380 ppm experienced a premature failure. This failure is not considered directly correlated to the moisture exposure, but rather attributed to occasional experimental factors such as non-uniform infiltration, localized assembly defects, or interfacial delamination, which may occur in manually assembled laboratory solid-state cells. For this reason, no specific mechanistic interpretation is drawn from this event, and the global trends observed across the samples are considered more representative.

In conclusion, the effectiveness of partial-pressure mass spectrometry as a tool to assess the environmental reactivity of sulphide-based solid electrolytes was demonstrated. The experimental setup was first validated through measurements on isopropanol samples at controlled concentrations. By statistically characterizing the instrumental background noise, a reliable limit of detection (LOD) was established, enabling confident distinction between true analyte signals and random fluctuations. Repeatability measurements conducted at 5 ppm and 50 ppm confirmed the ability of the system to detect signals near the LOD and to clearly resolve higher concentrations.

The methodology was then applied to investigate H_2S evolution from $\text{Li}_6\text{PS}_5\text{Cl}$ electrolyte films infiltrated into a non-woven scaffold when exposed to humid air. Under dry-room-relevant atmospheres (53–470 ppm H_2O), the H_2S signal remained within the background noise range, indicating limited degradation below the instrumental detection threshold. Conversely, exposure to ambient air ($\approx 40\%$ RH) resulted in a rapid and detectable formation of H_2S within 2 hours, accompanied by severe physical deterioration of the electrolyte (yellowing and mechanical damage), which ultimately prevented its use in cell assembly.

Electrochemical cells (NMC-83/LPSCI/Si) assembled with electrolyte samples exposed to controlled humidity were tested to assess the impact of such mild degradation on performance. Formation, initial cycling, and rate capability results showed comparable behaviour across all humidity conditions, demonstrating that moderate moisture exposure does not hinder the formation of a stable solid–solid interface nor affect charge-transfer kinetics in the early stages of cycling. Long term stability measurement up to 500 cycles revealed similar degradation trends for all cells, suggesting that moisture concentrations ≤ 470 ppm does not critically affect the long-term electrochemical performance.

The experimental setup proved to be a robust, laboratory-grade bench for assessing gas evolution from sulphide solid electrolytes and for preparing cells for electrochemical evaluation. In this campaign, samples were exposed to selected atmospheres and subsequently transferred into an argon-filled glovebox for cell assembly. Beyond this “ex-situ exposure to glovebox assembly” workflow, the test chamber also enables an alternative “in-chamber” approach: a pouch or coin-type cell can be mounted directly inside the sealed chamber and characterized electrochemically while being exposed to controlled environments (humidity/air compositions). If a controlled defect is introduced (in analogy to the calibrated “master leak” used in other applications), leak severity, atmosphere, and electrochemical response can be correlated in a single, well-controlled experiment. This capability allows operando studies of moisture-induced degradation, providing a link between gas evolution, interface stability, and performance.

6. Marposs Electrode Expansion Test bench: developments and performance assessment

This section presents the state-of-the-art of a Marposs dilatometric bench designed for the characterization of Li-ion battery materials and discusses the ongoing developments aimed at extending its applicability to next-generation chemistries. The current configuration of the bench is described in terms of measurement principle, operational capabilities, and performance limits.

Overall, this section provides a comprehensive framework for understanding both the present maturity of the dilatometric testing platform and the roadmap for its evolution toward materials that are expected to play a key role in future automotive battery systems.

Most secondary (rechargeable) batteries operate through the intercalation and de-intercalation of alkali ions, a process that inherently induces expansion and contraction of the active materials during lithium insertion and removal. As a consequence, measurable dimensional changes occur at the cell and electrode level during operation. A well-known example is LiFePO_4 : upon delithiation during charge, triphylite undergoes a phase transition to heterosite (FePO_4), resulting in a lattice volume contraction of approximately 6.8%, as already reported in early studies on olivine cathodes [93]. The same material, with metal ion substitution from lithium to sodium, can be used as cathode for Na-ion batteries. In this instance, for example, the larger ionic radius of Na^+ (2.27 Å vs 1.82 Å for Li^+ [94]) results in more pronounced mechanical strain in the host lattice during cycling. Recent studies have shown rate-dependent irreversible strain associated with irreversible capacity loss, suggesting that kinetic contributions (e.g., CEI formation) may influence volumetric evolution beyond the expected crystallographic changes [95]. Therefore, dedicated experimental tools for in-situ or operando dimensional monitoring, such as dilatometry, have become increasingly valuable for characterizing and mitigating volume-change-induced failure mechanisms.

In this context, the M-EET (Mechanical Electrochemical Expansion Tester) represents a dedicated measurement system for dilatometric analysis of lithium-ion battery materials. One of the main advantages of this instrument is its ability to operate in both two-electrode and three-electrode configurations, thanks to specifically designed sample holders. In the three-electrode setup, a patented solution [96] ensures a mechanically and electrochemically stable placement of the reference electrode inside the sample holder, enabling artifact-free half-cell potential measurements while simultaneously maintaining accurate dilatometric monitoring. In the two-electrode configuration, the entire cell contributes to the measured thickness variation; thus, the resulting signal represents the combined expansion/shrinkage of the anode, separator, and cathode during cycling. Conversely, the three-electrode configuration allows isolating the mechanical behaviour of the working electrode. This is achieved by employing a rigid separator with suitable dimensions and mechanical confinement: the counter electrode is allowed to expand in the opposite direction from the displacement sensor, ensuring that only the thickness change of the working electrode is transduced into the measured signal. A schematic representation of both configurations is shown in Figure 6.1-b and -c.

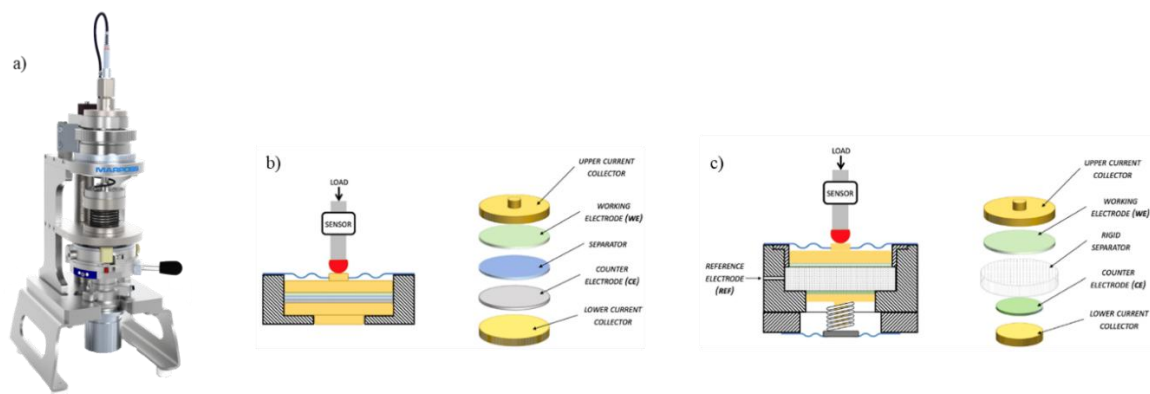


Figure 6.1. (a) Mechanical frame of the M-EET dilatometry setup, showing one of the interchangeable sample holders mounted. (b) Schematic representation of the two-electrode configuration, where the overall cell thickness variation (anode + separator + cathode) is monitored. (c) Schematic of the three-electrode configuration, featuring a rigidly confined separator and a dedicated reference electrode setup to enable selective monitoring of the working electrode expansion together with stable half-cell potential measurement.

The measurement assembly consists of a mechanical frame and two sample holders, as displayed in Figure 6.1. The frame (Figure 6.1-a) hosts a contact displacement sensor, an ambient temperature probe, a force-regulation system, and a load cell for real-time monitoring of the applied mechanical pressure. The sample holders are composed of interchangeable inserts, allowing the tester to be adapted to the material compatibility requirements of different cell chemistries. In particular, the current collectors may be selected among stainless steel (AISI 316L), copper, titanium, or glassy carbon, depending on the electrochemical conditions being studied.

Based on this configuration, which is suitable for dilatometric measurements on liquid-electrolyte cell chemistries, a design study was carried out to integrate operando gas generation testing capabilities. Driven by industrial requests aimed at monitoring SEI formation and lithium metal degradation during extended cycling, the integration of an analytical interface for gas detection was considered a valuable functional enhancement of the instrument. To this end, the sample holders were redesigned to include two dedicated gas ports, enabling connection to analytical tools such as a mass spectrometer and/or gas-phase IR spectrometer. These connections allow direct monitoring of the gas species evolving during electrolyte decomposition and parasitic reactions. Such information, which is generally inaccessible in closed-cell systems and often limited to post-mortem analysis, would provide unique insights into reaction pathways occurring at the electrode–electrolyte interface. In particular, coupling gas detection with simultaneous dilatometry would enable a deeper interpretation of SEI formation mechanisms, as well as the identification of performance-detrimental parasitic reactions, whose origin is frequently unknown.

An example of the current implementation is shown in Figure 6.2.

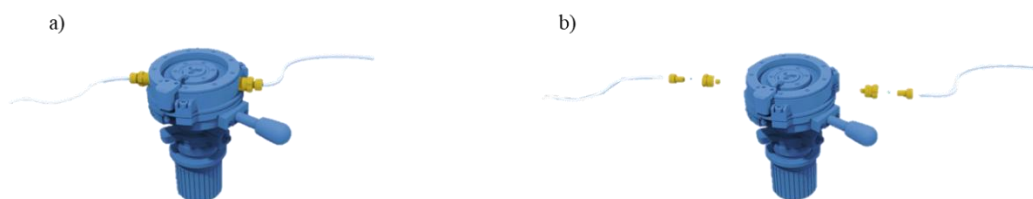


Figure 6.2. (a) Modified sample holder featuring integrated gas ports for operando gas-generation analysis. (b) Exploded view of the gas-line connection components enabling interface with external analytical instruments (e.g., mass spectrometry or gas-phase IR spectroscopy)

Figure 6.2-a shows the integrated gas ports. In conventional gas-analysis setups, an inert carrier gas flow is typically employed to continuously transport evolved species toward the analytical instruments while maintaining an approximately constant pressure inside the measurement chamber. For this reason, the upgraded sample holder was designed with two gas ports: one serving as the carrier-gas inlet and the other as the exhaust line directed to the external detector. This configuration ensures a stable flow regime and prevents unwanted pressure build-up inside the sample space, thereby minimizing perturbations to the dilatometric measurement while enabling reliable gas sampling. Figure 6.2-b shows the exploded view of the gas ports, highlighting its mounting operations.

Future work will be dedicated to validating this solution and establishing its analytical performance in operando environments.

The same instrument mechanical configuration presented so far is being considered for characterization of next-generation cell chemistries, such as polymer-based solid electrolytes. As discussed in Section 1.4.1, these systems typically require lower mechanical loads than inorganic sulphide or oxide electrolytes, a condition that is fully compatible with the current instrument capability, which can apply forces in the 0–100 N range.

However, polymer electrolytes generally do not operate efficiently at room temperature and must often be tested near or above their glass transition temperature (T_g) to enable sufficient ionic mobility. For this reason, a development study has been initiated with the aim of exceeding the present temperature operating limits of the instrument (0–50 °C). The new solution consists of integrating a localized heating module directly around the sample region, enabling precise thermal control without the need to place the entire instrument

inside a climate chamber or oven. This approach allows the dilatometer to remain on a standard laboratory bench while still providing the temperature conditions required for realistic operando measurements on polymer electrolyte systems. This upgraded configuration is currently at the end of its design phase; however, the localized heating module has not yet been physically implemented in the two sample holders and therefore remains to be validated through experimental testing.

Nevertheless, in parallel with the ongoing upgrade activities, quasi-solid-state cells with solid-state polymer electrolyte were tested in collaboration with a research centre interested in the use of the instrument. Although the bench was not yet capable of operating above 50 °C, this did not limit the planned activities since the partner explicitly required tests only at room temperature and within the currently available force range. Despite these conditions being fully aligned with the instrument's present specifications, the results obtained during these preliminary operando measurements were not consistent with the customer's expectations.

Further investigation revealed that the air-tightness level of the sample holder was insufficient to guarantee the expected electrochemical cell performance. For this reason, helium leak tests were carried out using the same methodology described in Section 3.1 applied to the so-called sniffing technique. In this technique, the object under test is filled with helium and sealed. A probe connected to the mass spectrometer is then used to scan the sample to localize potentially critical sealing regions. The leak rate was found to be higher than 10^{-2} mbarLs⁻¹. This approach allowed the identification of specific components requiring design modifications.

The sample holder parts identified as leakage sources were subsequently redesigned and replaced, after which the helium leak tests were repeated. The improved configuration achieved a new leakage rate of 2.4×10^{-4} mbarLs⁻¹, confirming enhanced sealing performance. To assess whether this solution could support reliable electrochemical testing, a dedicated characterization protocol was then defined.

A validation procedure has been defined for the current instrument configuration. This procedure consists of testing widely accepted benchmark lithium-ion materials, in order to compare the measured dilatometric response with well-established trends reported in the literature. The test cell was assembled using a commercial graphite electrode as the working electrode (MSE Supplier), LP30 as the liquid electrolyte (Solvionic), a Whatman GF/A

separator (Cytiva, Sigma-Aldrich), and lithium metal (Cambridge Energy solutions) as the counter electrode.

The electrochemical protocol includes an initial 12 h resting phase, followed by three formation cycles at 0.1C and five cycles at C/3. The applied C-rates were calculated based on the theoretical specific capacity of the graphite electrode as reported in its technical datasheet. The same protocol was performed using two configurations: the cell assembled inside the M-EET sample holder 2-electrode configuration and a reference cell assembled in a commercial EL-Cell setup (ECC-Ref, EL-Cell), in order to compare both electrochemical response and dilatometric behaviour. All the cells experienced an applied load of 13 N. The tests were repeated twice and the results are shown in Figure 6.3. Spectra acquired immediately after assembly are compared in Figure 6.3-a, while spectra acquired after 12 h resting period are compared in Figure 6.3-b.

The initial spectra (Figure 6.3-a) already show noticeable variability: while EL-Cell #1 and #2 display similar impedance values, the M-EET #2 cell exhibits a significantly higher cell resistance, at least three times larger than the EL-Cell references and M-EET #1. After the 12h resting period (Figure 6.3-b), the impedance evolution reveals further differences between the two setups.

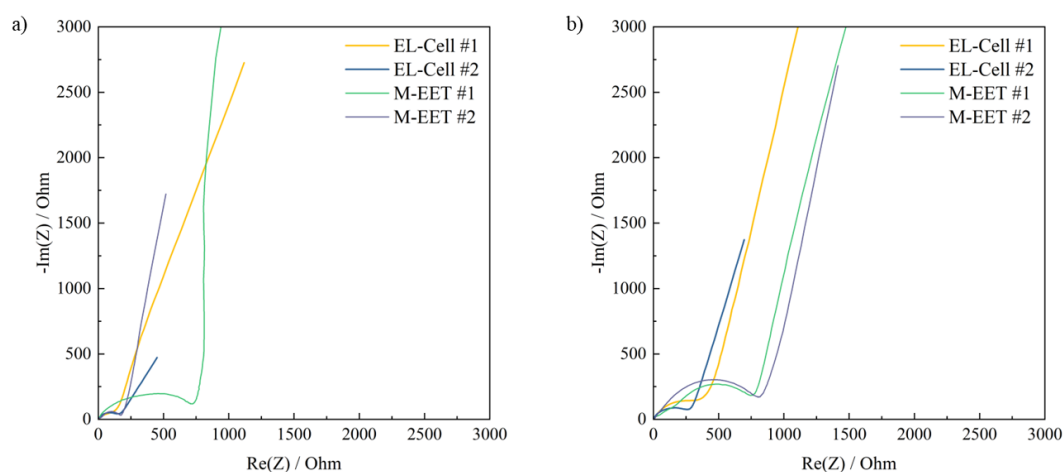


Figure 6.3. Electrochemical Impedance Spectroscopy (EIS) Nyquist plots for graphite/Li benchmark cells assembled in EL-Cell and M-EET configurations. (a) Spectra recorded immediately after assembly, showing the initial interfacial resistance. (b) Spectra acquired after 12 h of resting. The comparison highlights the effect of the sample-holder configuration on cell impedance evolution.

All cells exhibit a slight increase in resistance, which can be attributed to the early stabilization of interfacial species at the electrode–electrolyte interfaces. However, while

the EL-Cell samples show only a modest rise, both M-EET cells experience a more significant increase in total impedance. In particular, the M-EET #1 cell, initially displaying values close to the EL-Cell references, rises to nearly double the resistance of the EL-Cell samples, suggesting that the mechanical configuration inside the M-EET holder may promote differences in cell stabilization.

The cells were then cycled according to the validation protocol described above, and the results are reported in Figure 6.4-a. As anticipated from the impedance analysis, the cells assembled in the M-EET configuration exhibited significantly different performance compared to the EL-Cell benchmarks. Cell M-EET #1 showed a rapid fading of discharge capacity, becoming essentially inactive after the first few cycles. M-EET #2 initially delivered a measurable discharge capacity, although much lower than that of the EL-Cell references, and experienced a continuous capacity decline during cycling.

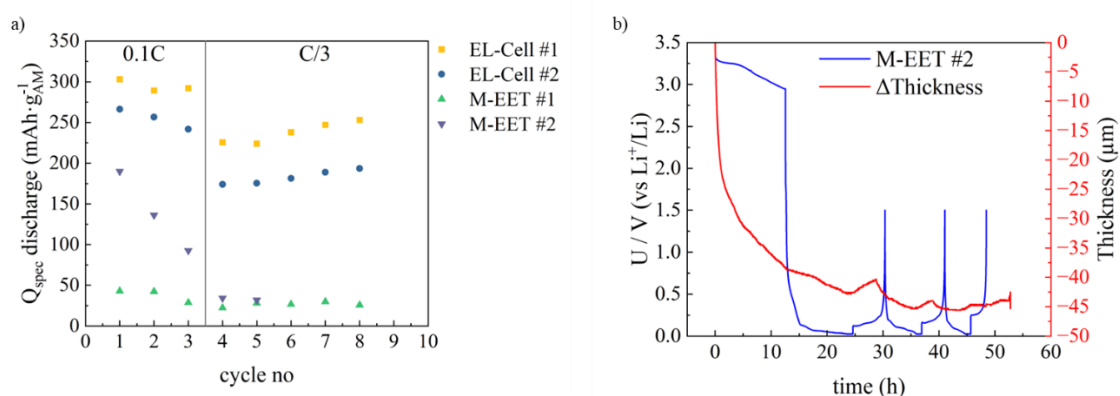


Figure 6.4. Electrochemical performance of benchmark graphite/Li cells assembled in EL-Cell and M-EET configurations. (a) Specific discharge capacity vs. cycle number during formation (C/10) and early cycling (C/3); (b) Operando dilatometry signal (right axis) recorded for cell M-EET #2 during the first cycles, alongside the corresponding voltage profile (left axis).

For M-EET #2, the operando dilatometry signal recorded during the first cycles is also shown in Figure 6.4-b. A reasonable correlation can be observed between the thickness evolution and the electrochemical profile in the initial cycle, before severe performance degradation takes place. This confirms that the dilatometry sensing chain operates correctly as long as the cell maintains a stable electrochemical response.

It is worth noting that the dilatometric behaviour observed during the initial resting period (~ 12 h) is consistent with previous experiments performed using earlier versions of the M-EET. The gradual thickness decrease reflects a normal mechanical relaxation of the stacked components under the applied load, rather than a chemically driven transformation. Despite this phase being electrochemically inactive, operando monitoring of mechanical relaxation

may provide valuable information in future studies, especially when the goal is to investigate aging-driven structural changes and translate such insights into industrial scale-up conditions.

Overall, the electrochemical performance obtained with the current configuration of the M-EET was not sufficient to consider the bench fully validated. The strong degradation and low reproducibility observed during the tests were attributed to an insufficient sealing level of the sample holders. The ingress of ambient air, and therefore moisture, is considered the primary cause of the poor performance.

Post-mortem visual inspection of the M-EET #2 sample revealed gas bubbles and regions of inactive “dead lithium” (Figure 6.5), phenomena consistent with parasitic reactions triggered by atmospheric humidity exposure. These findings support the conclusion that the sealing of the sample holder was inadequate to preserve stable electrochemical conditions during cycling.

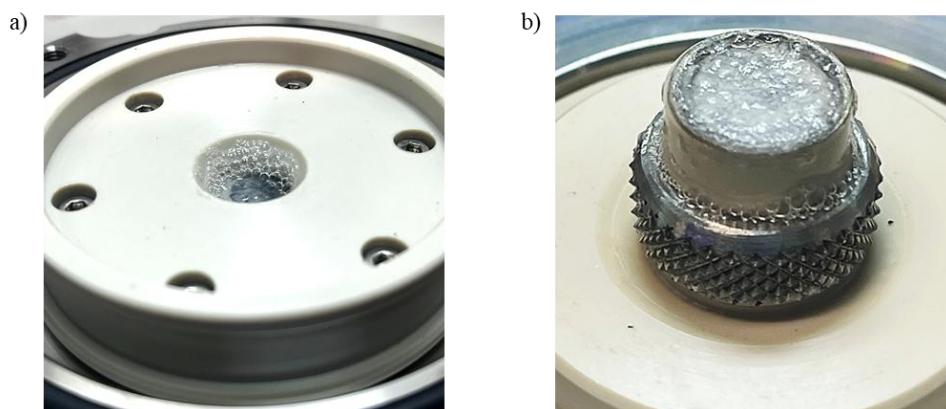


Figure 6.5. Post-mortem visual inspection of the M-EET #2 cell. (a) Bubbles formed within the separator region and (b) areas of inactive “dead lithium” accumulated on the metallic surface, indicating parasitic reactions triggered by atmospheric moisture ingress due to insufficient sealing of the sample holder.

Dedicated improvement efforts are currently ongoing to enhance the leak-tightness of both sample holders and therefore enable more reliable and representative electrochemical and dilatometric measurements in future validation campaigns.

This instrument and its capabilities represent a strong opportunity to position the technology within a highly active and rapidly evolving market focused on the development of next-generation battery materials. The push for high-performance and high-energy-density solutions for the growing electric-vehicle industry continuously drives the need for advanced characterization tools capable of providing deeper insight into electrochemical and mechanical degradation mechanisms.

The experimental campaign conducted so far constitutes an essential first step toward identifying the remaining engineering challenges and guiding the refinement of the system. Once these aspects are addressed, the instrument will be able to reach the level of performance expected in research laboratories and offer the versatility required to characterize a broad range of chemistries using a single platform.

7. Conclusions

The research activities carried out in this doctoral work fit into the strategic context of the European energy transition, where the electrification of the transport sector is accelerating the need for high-performance batteries. As the European automotive industry progressively abandons internal combustion technologies, achieving independence from external battery suppliers becomes a key industrial objective. To support this transformation, Europe is strongly investing in next-generation solid-state batteries. As shown by the market and patent analysis discussed in Section 2, the global innovation effort in solid-state battery technologies is being strongly driven by the automotive sector, which aims to unlock higher energy density and enhanced safety compared to conventional lithium-ion systems. Worldwide, patents and scientific publications indicate a predominant focus on the most technically challenging electrolyte families, particularly sulphides and oxides, due to their superior ionic conductivity and compatibility with lithium metal.

In Europe, although academic research in these areas is highly active, the industrial ownership of solid-state battery patents remains comparatively limited. Among European countries, Germany stands out thanks to its established automotive ecosystem and significant investments across the mainstream solid-electrolyte families, sulphides, oxides, and polymers, ensuring a relatively balanced innovation landscape.

However, as reviewed in Section 1.4.1, polymer electrolytes present intrinsic performance limitations that make them a less suitable candidate for EV propulsion systems. The industrial strategies of several major market players therefore converge toward sulphide- and oxide-based chemistries, which offer the best prospects for meeting the stringent performance targets required by the electromobility sector.

These considerations highlight the strategic importance of developing not only novel materials but also manufacturing-compatible diagnostic technologies capable of supporting the industrial transition from liquid-electrolyte lithium-ion cells to solid-state cells.

Within this framework, this thesis has focused on the development of innovative metrology solutions specifically designed around the requirements expressed by industrial stakeholders. The work has been performed at Marposs SpA (Bentivoglio, BO), MG SpA (Marposs group, Travagliato, BS) and other companies of the same industrial group,

ensuring constant alignment with real manufacturing needs. Furthermore, a research period hosted by Fraunhofer ISE (Freiburg im Breisgau, Germany) enabled direct exposure to cutting-edge research on solid electrolyte processing and testing.

The aim of this thesis is the design and implementation of diagnostic methods that are not merely laboratory concepts, but can evolve into ready-to-market solutions for inline quality control. Three complementary approaches were developed and validated at different maturity levels.

A methodology was established to correctly set helium bombing parameters according to the internal free volume of the cell, demonstrating that ignoring this contribution may lead to false-good classifications. This work highlighted that the equilibration between the helium partial pressure inside the cell and the external bombing atmosphere is strongly influenced by the amount of free internal gas volume: cells with smaller void space saturate more rapidly, allowing for efficient testing even with short bombing times, whereas larger void volumes require significantly longer exposure to reach the same level of detectability. The systematic investigation of this relationship revealed that the same physical leak rate may produce opposite test outcomes depending on the volume assumptions made during test design. In practical terms, if the effective internal volume is underestimated, insufficient helium may enter the cell, leading to the incorrect classification of a defective cell as acceptable (false-good). Conversely, an overestimated volume may result in excessive helium filling and false-reject decisions.

Experimental validation performed using calibrated capillary leaks confirmed the predictive accuracy of the theoretical model (Howl and Mann formulation), while also exposing critical limitations when the method is applied to real electrochemical cells. Complex internal architectures (such as separator porosity, tortuosity of diffusion paths, the presence of liquid electrolyte, and possible gas–solid interactions) can introduce deviations from ideal behaviour, especially in the early transient stage of the decay curve.

Together, these findings provide both a theoretical and practical guideline for configuring bombing test parameters in industrial environments. They emphasize that case-specific tuning is required when adopting helium leak testing in cell manufacturing, ensuring that proper sensitivity is achieved without compromising throughput, a key requirement for high-volume battery production.

Electrolyte tracing is a powerful technique to assess battery sealing from laboratory to production environment. A custom device, mechanically and analytically engineered for pouch-cell characterization, was designed, prototyped, and calibrated using a certified master leak. The test chamber and interface components were tailored to the specific dimensional and operational requirements provided by the industrial partner, ensuring compatibility with the exact cell format and with the sensitivity thresholds required for the application. Particular attention was given to tightness, gas-flow control and volume minimization in the chamber design, as all of these features directly affect test resolution and response time. The system demonstrated high repeatability and excellent sensitivity, as validated through a series of 30 consecutive measurements on the master leak, thereby enabling reliable and quantitative detection of sealing defects in commercial 40 Ah pouch cells. The test procedure was optimized to include automatic gross-leak rejection based on pressure-rise monitoring, safeguarding the internal mass spectrometer from contamination while increasing process robustness.

Although currently implemented as a manual, laboratory-scale setup for single-cell testing, the measurement principle, data-processing workflow, and hardware architecture were developed with a clear scalability path in mind. The design is compatible with semi-automatic and fully automated solutions, allowing parallelization of measurements and integration into in-line quality-control stations on industrial battery manufacturing lines.

A measurement workflow for monitoring H₂S release from Li₆PS₅Cl exposed to controlled atmospheres was developed. A measurement bench was designed and fabricated, which allows testing the samples under a controlled atmosphere through the use of an integrated air treatment group and operando analysis of the gas generated through connection with a mass spectrometer. This methodology combines partial-pressure mass spectrometry, vacuum-controlled exposure, and quantitative threshold definition based on instrumental background noise analysis. The approach enables real-time and highly sensitive detection of gaseous byproducts arising from interactions between the electrolyte and environmental moisture. The results demonstrated a clear humidity-dependent degradation behaviour:

- exposures at dry-room-relevant humidity levels (≤ 470 ppm H₂O) lead to non-detectable H₂S signals, below the detection limit and leaving the electrolyte mechanically intact.

- exposure to ambient air (~40% RH) results in rapid and extensive chemical decomposition, accompanied by visible structural collapse of the material, preventing any further electrochemical use.

To assess the practical impact of such degradation, the exposed electrolytes were assembled into solid-state cells using a $\text{Li}_6\text{PS}_5\text{Cl}$ interlayer, an NMC-83 cathode and a pre-lithiated silicon anode. Electrochemical tests confirmed the spectrometric interpretation: cells corresponding to dry-room exposure conditions showed similar formation behaviour, capacity retention, and coulombic efficiency, while ambient-exposed samples were entirely unfit for assembly. Rate capability analysis further supported the conclusion that moderate humidity exposure does not critically impair mechanical or transport properties in early cycling. Finally, aging tests also confirmed these results, indicating that a production environment with dew point up to $-27\text{ }^\circ\text{C}$ is not detrimental for battery performance.

Finally, a study on the state-of-the-art performance and successive developments dedicated to the Marposh Electrode Expansion test bench (M-EET) was performed. The system combines precise thickness monitoring, controlled mechanical loading, and flexible electrode configurations (two- and three-electrode modes), together with a recently introduced gas-sampling capability designed to enable real-time analysis of electrolyte decomposition products during electrochemical cycling. These features address diagnostic needs that are becoming increasingly relevant as battery technologies evolve toward high-energy density chemistries.

The custom design of the sample holders and interchangeable components allows adapting the instrument to different cell architectures and material compatibility requirements. Moreover, the recently proposed integration of localized heating expands the applicability of the system to polymer-based solid-state electrolytes, which typically require operation near their glass-transition temperature. Although this enhancement is currently at the end of its design phase and not yet implemented in the existing sample holders, it represents a concrete next step toward enabling the analysis of next-generation chemistries using the same mechanical platform.

To evaluate the current performance of the M-EET, a validation procedure using benchmark graphite/Li cells was executed. Impedance and cycling results revealed that the electrochemical behaviour of cells tested in the M-EET configuration was not yet comparable to that obtained in commercial reference housings (EL-Cell). Supplementary

helium leak tests and post-mortem analyses indicated that these discrepancies were largely attributable to insufficient sealing of the sample holders, leading to unintended moisture ingress and consequent parasitic reactions such as gas evolution and dead lithium formation. While the operando dilatometry measure was shown to function as expected during the earliest cycles, stable electrochemical operation remains dependent on improving the isolation and mechanical integrity of the measurement environment.

Although the current configuration does not yet meet the performance criteria required for full validation, the work carried out has been crucial in identifying the limiting factors and defining clear engineering directions. Ongoing optimization efforts will focus on enhancing sample-holder tightness, refining pressure-distribution homogeneity, and improving reproducibility through controlled assembly protocols. Once these aspects are addressed, the M-EET will constitute a highly valuable tool for laboratory research and a promising candidate for future technology transfer toward industrially deployable metrology solutions.

In light of the results achieved throughout this work, the overarching objective of this thesis has been fulfilled: to provide Marposs with experimental evidence, methodological foundations, and technological directions that will support the development of proprietary metrology solutions tailored to the demands of future battery manufacturing. The advances demonstrated in helium leak testing, electrolyte tracing, and operando chemical diagnostics highlight how innovative quality-control tools can be effectively aligned with the evolving needs of next-generation battery chemistries. By combining a deep understanding of analytical requirements with clear insight into industrial process challenges, ranging from sealing integrity to moisture-sensitive materials handling, it is possible to design scalable, robust, and future-proof inspection equipment. As these innovative chemistries move from laboratory concepts toward industrial adoption, the technologies explored in this thesis will contribute to positioning the company at the forefront of a rapidly transforming sector, helping secure a competitive role for Europe in the global battery value chain.

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