SHIMADZU

Excellence in Science

LITHIUM ION BATTERIES: ANALYTICAL SOLUTIONS

SUMMARY

P.4 INTRODUCTION

P.6 WHY THE LITHIUM BATTERY AND WHY NOW

P.8 ELECTROLYTES AND EMISSION GASES

P.17 ELECTRODES AND COMPONENTS

P.20 BINDERS

P.22 SEPARATORS

P.26 FINISHED PRODUCTS

P.30 IN PRACTICE

INTRODUCTION

The concept of lithium batteries dates back to the 1980s and the first lithium-ion batteries were marketed in 1991. These batteries were quickly used en masse in the electronics industry. However, to meet the growing need for clean energy storage, these systems need to be further improved and their production must be perfectly controlled to ensure the safety of users and systems.

Since 2006, batteries and battery waste have been regulated at EU level by Directive 2006/66/EC on batteries and accumulators. These regulations must be modernised in order to meet current social and environmental challenges. The production, use, but especially the future of these batteries after use must be supervised as best as possible to ensure the safety of everyone. The stated objective is clear: Batteries placed on the EU and UK markets should become durable, safe and maintain high-performance throughout their life cycle.

In December 2020, the European Commission, therefore, proposed as part of the "European Green Deal" a draft regulation, which will have to be validated by the Member States and the European Parliament, and which will impose environmental criteria on the entire life chain of batteries, from the extraction of raw materials to recycling and production. In addition, the UK has also announced the target of cutting carbon emissions by 78% before 2035, compared with 1990 levels.

This project will be marked by key phases for which manufacturers must prepare.

CHRONOLOGY OF EUROPEAN PROJECTS

Airbus of batteries	The European battery innovation	Research project with about forty companies
End of 2019	26 January 2021	Until 2028

WHY THE LITHIUM BATTERY? AND WHY NOW?

The European Commission presented in December 2020 a draft regulation, which will have to be validated by the Member States and the European Parliament, to strengthen environmental criteria across the entire battery life chain.

To limit the carbon footprint of their production, manufacturers should measure and report the environmental impact starting from July 2024. This system will allow a fine traceability of the origin and processing of the materials used.

In January 2026, performance class labels will be introduced. Based on the collected data, maximum carbon footprint thresholds would be set at each level of the chain, from July 2027. Performance and safety criteria will also be defined.

The ecological criteria to be respected will focus in particular on the sustainability of the raw materials used, the use of recycled materials and the cleanliness of the energy consumed for manufacturing. The recycling component of the plan would come into effect as early as 2025.

The ecological criteria to be respected will focus in particular on the sustainability of the raw materials used, the use of recycled materials and the cleanliness of the energy consumed for manufacturing.

The recycling component of the plan would come into effect as early as 2025.

The objective to separate collection of portable batteries would then increase to 65% (then 70% in 2030), against current 45%.

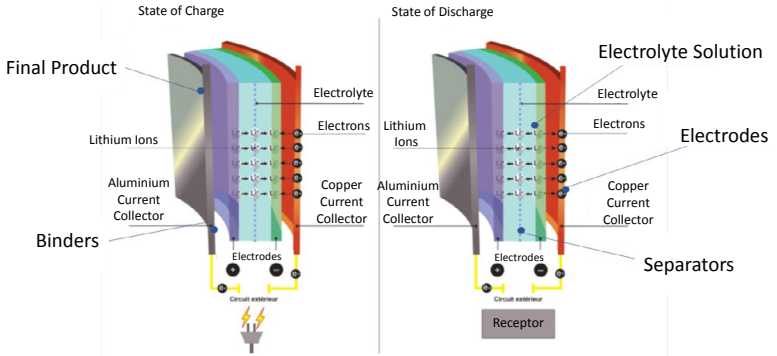
On 26 January 2021, the European Commission approved €2.9 billion in public support from 12 Member States, including Germany, France, Italy, and Spain, for a vast joint research project on next-generation batteries, called "The European battery innovation".

It completes the first European project called "Airbus of batteries", launched at the end of 2019 by seven States with €3.2 billion in state aid, which aims to launch the first European "giga factories" within two years. Within the UK, the initiative to build giga factories is backed by the government and private investments, with the first factory securing £1.7bn funding.

By 2028, the European battery innovation research project will bring together approximately forty companies, including the manufacturers BMW, Fiat-Chrysler and Tesla, the Swedish battery specialist Northvolt and the French chemist Arkema, to innovate throughout the value chain.

COMPONENTS OF THE LITHIUM BATTERY

A lithium battery is divided into 4 main parts:



Batteries use pairs of materials capable of exchanging positive electrons and ions easily and for a long time:

- When the battery charges, the lithium Li^+ ions leave the positive electrode (the cathode) and are stored in the negative electrode (the anode).
- When it discharges, i.e. when it produces the electric current, the Li^+ ions make the opposite motion.

SHIMADZU SYSTEMS

	GCMS-QP20NX RANGE	UHPLC NEXERA / ION CHROMATOGRAPHY RANGE	FTIR RANGE	TESTING MACHINES RANGE	TOC
SOLVENT	✓	✓	✓		
ELECTROLYTE		✓			
ADDITIVE	✓	✓			
BINDER			✓		
SEPARATOR				✓	✓
STRUCTURE				✓	✓
DEGRADATION	✓	✓	✓		
ELECTRODES				✓	✓

SHIMADZU
Excellence in Science

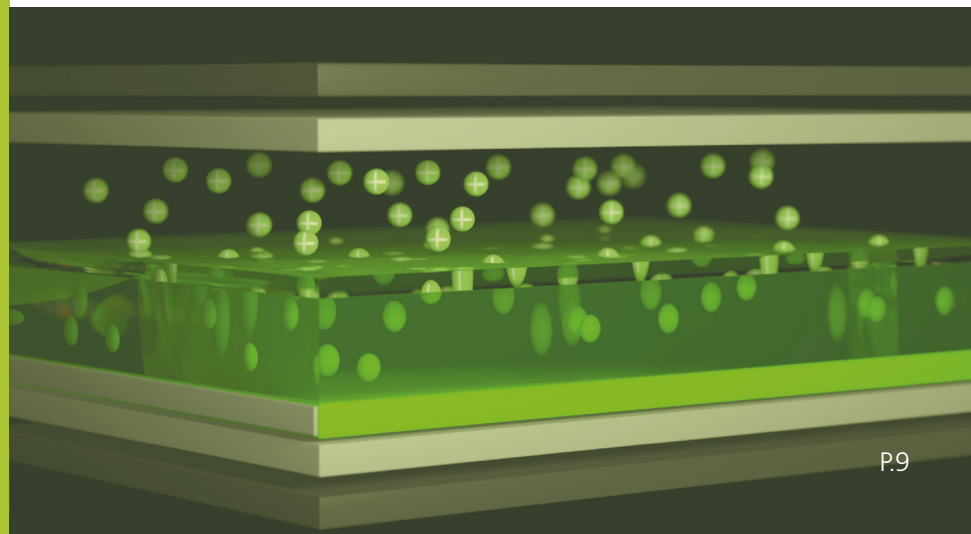
Electrolytes & Emission Gas

ELECTROLYTES

Electrolyte solutions have played a key role in lithium-ion batteries (LIB) acting as a lithium-ion transporter between the cathode and anode. High purity and battery-grade electrolyte solutions are therefore crucial for the performance of lithium-ion batteries.

The most common LIB electrolytes are derived from lithium salt solutions, such as $LiPF_6$ in non-aqueous solvents, such as alkyl carbonates. The performance of electrolyte solutions can be further modified with suitable additives.

SOLVENT + ELECTROLYTE + ADDITIVES = ELECTROLYTIC SOLUTION

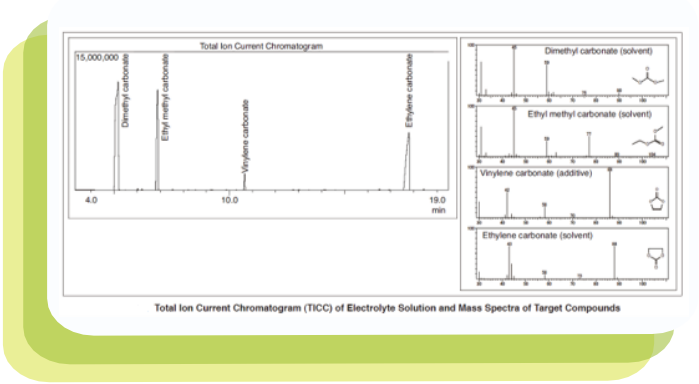


ELECTROLYTES AND LITHIUM BATTERY DEGRADATION PRODUCTS

How to analyse them?

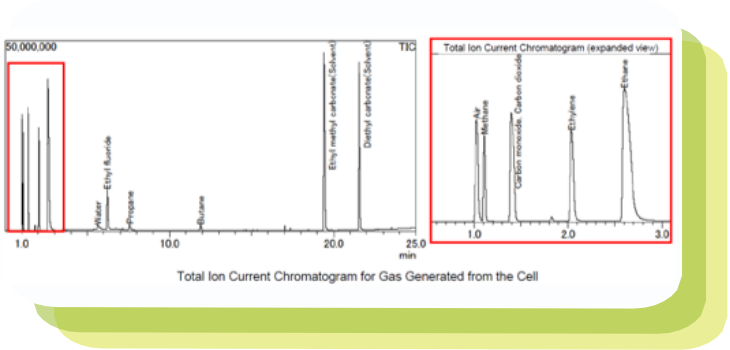
Gas chromatography coupled with mass spectrometry will make it possible to carry out a quantitative and qualitative analysis of electrolytes and degradation products of lithium batteries. This technique is based on the separation of compounds according to their affinity with a stationary phase present in a column and a mobile phase (gas) that will allow the circulation of compounds in this column. The analytes will be more or less retained according to their affinity with the stationary phase of the column. The analysis of all these compounds requires the implementation of analytical pathways on the same system:

> A "liquid" pathway allowing the analysis of liquid electrolytes and the monitoring of their evolution.



Total Ion Current Chromatogram (TICC) of Electrolyte Solution and Mass Spectra of Target Compounds

> A "gaseous" method allowing the analysis of gaseous degradation products.

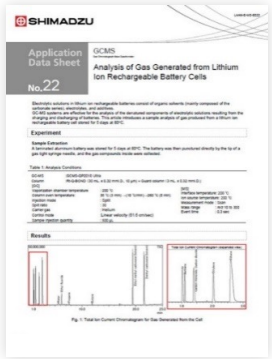


Total Ion Current Chromatogram for Gas Generated from the Cell

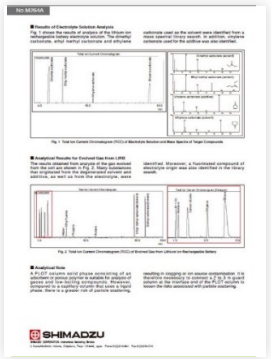
A simple comparison of spectra with a library, and the choice of ions specific to it, make it possible to identify the desired molecule in a safe way. Shimadzu has been working on developing analytical methods to meet these needs.

Focus:

The GCMS is adapted to this analysis, particularly for the electrolyte development phase in R&D. The GCMS will provide complete information on the composition of the electrolytes produced.


SHIMADZU
Application Data Sheet
GCMS
No.22
Analysis of Gas Generated from Lithium Ion Rechargeable Battery Cells

REQUEST MORE INFORMATION


SHIMADZU

GCMS QP2010 SE / 2020 NX

WHAT EQUIPMENT IS REQUIRED?

Equipment type: GCMS liquid and gas injections (2010 SE or 2020 NX)

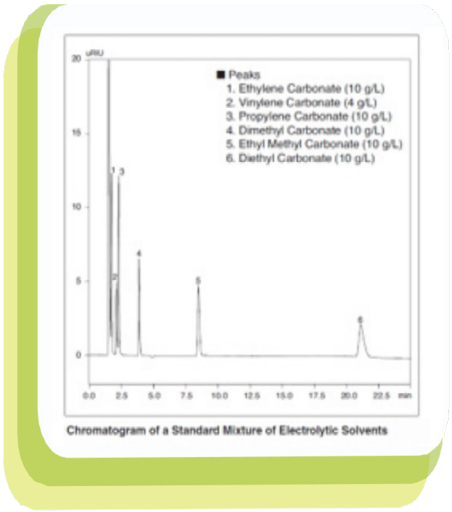
Level of expertise: Intermediate

ELECTROLYTES AND LITHIUM BATTERY DEGRADATION PRODUCTS

How to analyse the quality of the electrolytes produced?

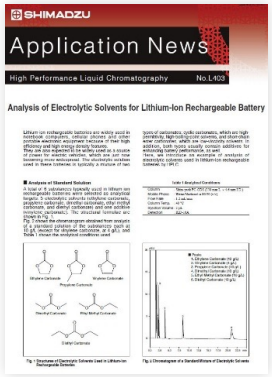
The recommended analytical solution for analysing the quality of carbonate-type electrolyte solutions is **liquid chromatography (HPLC)** coupled to a **refractometric detector**. Liquid chromatography is based on the same separation principle as gas chromatography. A liquid chromatography system contains a pump, an injector, one or more column(s) and one or more detector(s). The pump sends a liquid mobile phase into the system that will allow the circulation of analytes in the column where the separation will be done according to the affinity of the compounds for the internal coating of the column (stationary phase). At the column outlet, the type of detector may vary depending on the nature and optical properties of the analytes.

An HPLC coupled with a refractometric detector will allow for identification and quantification of compounds through the use of standard solutions.

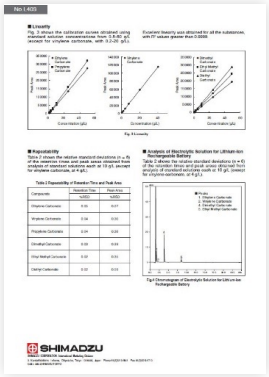


Chromatogram of a Standard Mixture of Electrolytic Solvents

ANALYSIS OF CARBONATE ELECTROLYTES BY LC-40


SHIMADZU
Application News
High Performance Liquid Chromatography No.L403
Analysis of Electrolytic Solvents for Lithium-Ion Rechargeable Battery

REQUEST MORE INFORMATION


SHIMADZU

HPLC RID

WHAT EQUIPMENT IS REQUIRED?

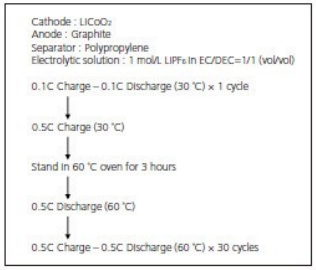
Equipment type: HPLC RID

Level of expertise: Beginner

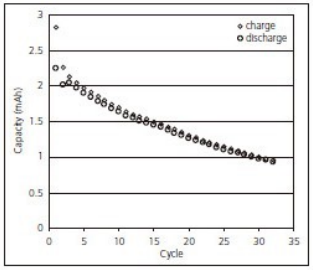
ANALYSIS OF DETERIORATION OF ELECTROLYTE SOLUTIONS BY ION CHROMATOGRAPHY

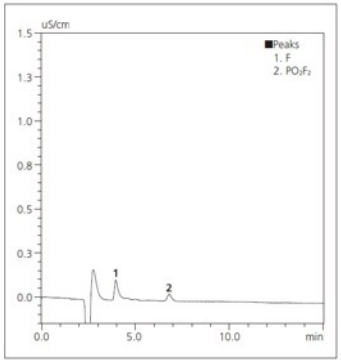
Electrolyte solutions, composed of lithium hexafluorophosphate, commonly used in the composition of lithium batteries, undergo degradation over time. Traces of water present in the electrolyte solution are responsible for the formation of fluoride ions that may affect battery performance. It is therefore important to control this degradation in the quality control process. This control can be done using **ion chromatography, where the** separation process is based on the ion charge of the solutes. The more the solutes are loaded, the more they will be retained in the column. The detection modes also change since this is not based on the optical properties of the solutes but rather on their ionic charge.

Shimadzu has developed an ion chromatographic method with the **Nexera HIC-ESP system** to analyse electrolyte degradation and quantify fluoride ions.

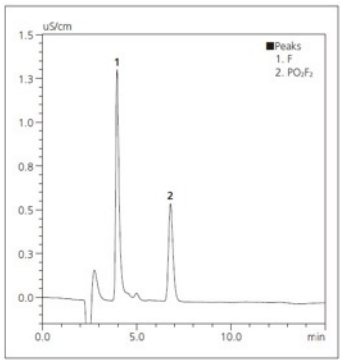


The figures show accelerated degradation tests of electrolyte solutions according to charge cycles.



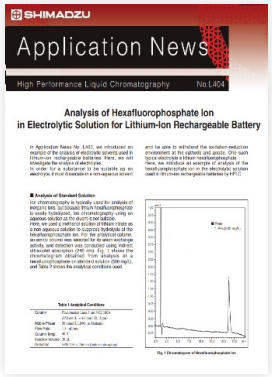


Chromatogram of Electrolytic Solution for Lithium-Ion Rechargeable Battery (New)



Chromatogram of Electrolytic Solution for Lithium-Ion Rechargeable Battery (Deteriorated)

The chromatograms on page 14 shows the profiles of an unused electrolyte solution and an electrolytic solution that has undergone the accelerated degradation test respectively. These results show a drastic increase in the amounts of difluorophosphate and fluoride ions in used electrolyte solutions. Each sample was diluted 100 times with purified water and then filtered with a membrane filter.



REQUEST MORE INFORMATION

WHAT EQUIPMENT IS REQUIRED?

Equipment type: Ion Chromatography

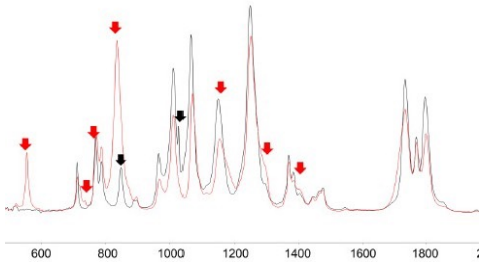
Level of expertise: Beginner

The degradation of electrolyte solutions by air and humidity can also be monitored using an **infrared spectrometer.**

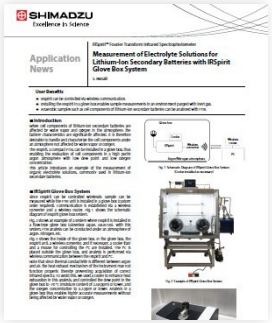
By combining the use of the FTIR inside a glove box it is possible to measure the degradation of an electrolyte according to the composition of the atmosphere to which it is subjected.

FTIR can also measure the difference between electrolyte solutions, which is especially useful when performing quality checks on samples.

Example of IRSpirit Glove Box System



Shows the difference in the Infrared Spectra of :
EC+DEC (3:7) Electrolyte Solution containing 1M LiPF6 (Red)
EC+DEC (3:7) Solution without LiPF6 (Black)


SHIMADZU
Excellence in Science

Application News

Measurement of Electrolyte Solutions for Lithium-Ion Secondary Batteries with IRSpirit Glove Box System

REQUEST MORE INFORMATION

WHAT EQUIPMENT IS REQUIRED?

Equipment type: FTIR IRSpirit

Level of expertise: Beginner

SHIMADZU
Excellence in Science

ELECTRODES & COMPONENTS

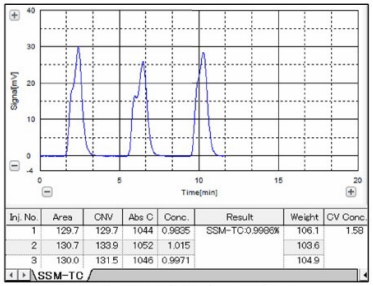
ELECTRODES

The electrodes are made of metallic materials. As such, it is important to control the purity of these components.

HOW TO ANALYSE THE METALLIC MATERIALS OF THE ELECTRODES?

In order to analyse the purity of the metallic materials, it is possible to track the concentration of carbon, in the metal powders, as a marker of organic pollution. Measuring the carbon concentration in metal powders is done simply by using **a total organic carbon analyser coupled with a solid sampling module**. This system makes it possible to degrade the sample and oxidize the carbon present by heating to 900 °C. The carbon is converted into CO_2, detected and quantified by an NDIR (non-dispersive infra-red) detector.

This technique makes it possible to obtain precise quantities of carbon present in a sample. This is shown in the example through the analysis of lithium cobalt oxide with different concentrations of glucose:



Sample: Lithium Cobalt Oxide + 1.0 % Glucose

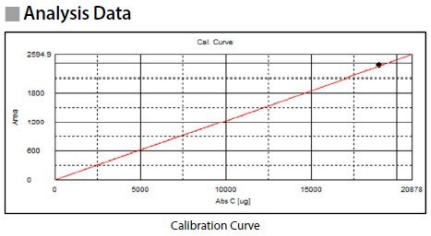


Table 2 Measurement Results

Sample	TC Measurement Value (%C)
Lithium Colbolt Oxide	0
Lithium Colbolt Oxide + 0.2 % Glucose	0.209
Lithium Colbolt Oxide + 1.0 % Glucose	0.999
Lithium Colbolt Oxide + 5.0 % Glucose	5.02


Application News
No. O72
Total Organic Carbon Analysis
Carbon Measurement of Metal Powder Battery Material

This application note presents an example of total carbon measurement of cobalt-lithium oxide, which is widely used as a positive electrode material in lithium-ion batteries, using the Shimadzu solid sampling system consisting of a TOC-LCPH total organic carbon analyser and solid sample combustion unit SSM-5000A.

REQUEST MORE INFORMATION

WHAT EQUIPMENT IS REQUIRED?

Equipment type: TOC-L + SSM 5000A

Level of expertise: Beginner

SHIMADZU
Excellence in Science

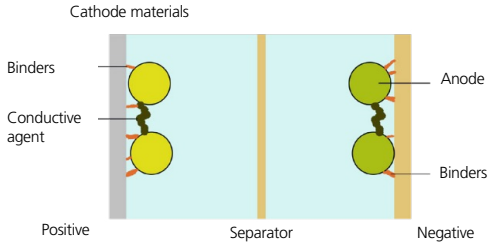
BINDERS

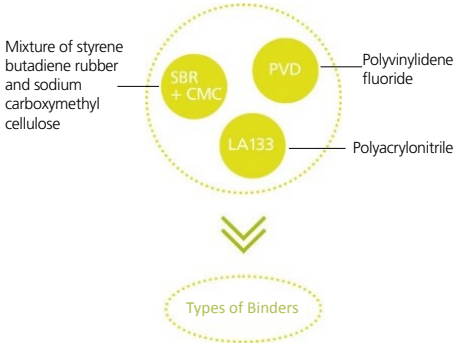
Electrode coatings in batteries facilitate the electrochemical reactions needed to provide electrical energy. The binders used in these coatings typically represent only a small percentage of a battery's total weight, but they are essential to building battery cells and offer a range of benefits, from safety and energy density improvements to capacity and more.

HOW TO ANALYSE BINDERS?

Fourier transform infrared spectroscopy (FTIR) can be used to confirm the chemical structure of the Binder.

When chemical compounds are irradiated with wavelengths of infrared light, functional groups can generate vibrations via a variety of ways such as stretching or bending. These vibrations and their intensity result in a FTIR spectrum by Fourier transform.





Since most of the mechanical properties of binders are derived from chemical cross-linking, new peaks appear in the FTIR spectrum indicating the formation of covalent bonds between the carrier and binders.

WHAT EQUIPMENT IS REQUIRED?

Equipment type: FTIR

Level of expertise: Beginner

SHIMADZU
Excellence in Science

SEPARATORS

HOW TO ANALYSE THE RESISTANCE OF SEPARATORS?

This parameter can be measured with **a universal testing machine (UTM)**, which allows for perforation measurements under controlled temperature to check the robustness of the separators.

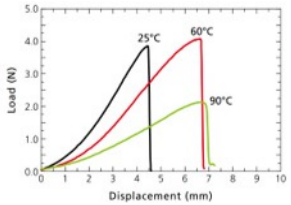
The measurement will make it possible to obtain the following curves which represent the forces necessary to be applied as a function of the temperature to degrade the separators.

Maximum Load Force and Maximum Displacement for Temperatures

Temperature	Maximum Load Force (N)	Maximum Displacement (mm)
25 °C	3.85	4.45
60 °C	4.07	6.63
90 °C	2.13	6.68

Images inside a Thermostatic Chamber

These results show that these separators are suitable for an operating temperature of 60 °C (red curve) since they have good resistance for a high maximum load.



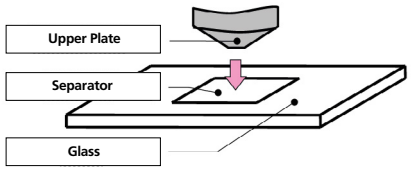
REQUEST MORE INFORMATION

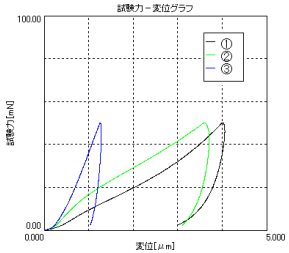
WHAT EQUIPMENT IS REQUIRED?

Equipment type: Universal Testing Machine with perforation module

Level of expertise: Beginner

Some tests of compressions can also be made on the separators with a micro-compression instrument, capable of accurately measuring reactions materials depending on the force applied.





The measurements made will make it possible to establish this type of curve, which compares the resistance of the different separators according to the force applied.

Maximum Test Force 50 mN, Compression Ratio is as following

Separator ① **>** **Separator** ② **>** **Separator** ③

Sample Name	Sample No.	Max Test Force [mN]	Displacement [μm]	Compression Ratio [%]
Separator	①	49.9	3.651	18.3
	②	49.9	3.371	16.9
	③	50.0	1.038	10.4

WHAT EQUIPMENT IS REQUIRED?

Equipment type: MCT Series

Level of expertise: Beginner

SHIMADZU
Excellence in Science

FINISHED PRODUCTS

Finished products must be checked in their entirety before marketing. The purpose of these tests is to assess the performance of the batteries in the context of normal use of course, but also after degradation.

The objective is to ensure the safety of the systems in use.

QUALITY CONTROL

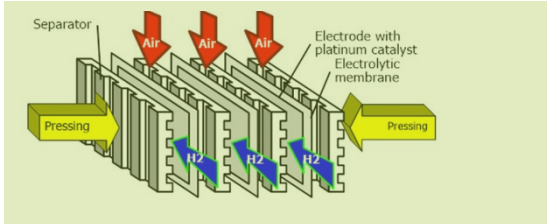
The analyses of finished products must verify the resistance of the batteries in use. Several mechanical tests must be carried out on the products:

To perform these tests, it is recommended to use a Universal Testing Machine (UTM)

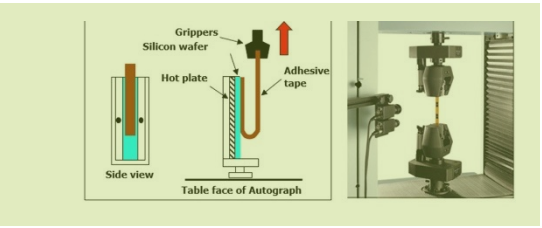
- Measurement of the electrical compression strength of the film
- Compression and bending of electrolyte membranes, separators
- Membrane Peel Test

Electrical compressive strength tests of the film

The battery is subjected to physical deformations: compression, bending... then undergoes cycles of loads and discharges in order to verify its performance after mechanical deformations.



Coat tests



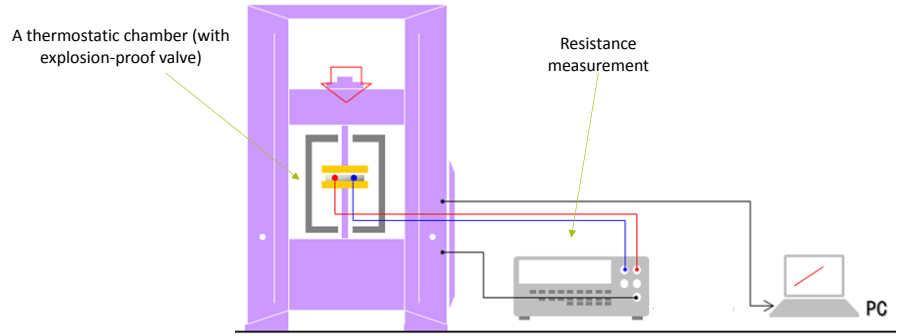
This test takes place on the electrodes and makes it possible to check the resistance of the adhesion of the electrode coating. This coating must meet the standards in force.

EXPLOSIVENESS TEST

Batteries may also be subject to conditions of use that are considered "abnormal". The manufacturer is responsible for defining the conditions of normal use but also for predicting the consequences of abnormal use.

It is important to ensure that the product will not become dangerous even in case of deterioration.

These tests can be done using a Universal Testing Machine, as shown above, equipped with a thermostatic chamber that will reproduce extreme conditions and evaluate the operation of the battery and the malfunctions caused by these conditions. This analysis makes it possible to evaluate the risks posed by the battery in case of degradation, to reduce them where possible and to inform users.



WHAT EQUIPMENT IS REQUIRED?

Equipment type: Universal Testing Machine with peeling module

Level of expertise: Beginner

SHIMADZU
Excellence in Science

IN PRACTICE

What are the existing solutions? What advice does Shimadzu provide?

BACKUP AND DATA INTEGRITY

Why secure data?

The environmental and social issues related to the storage of green energies are paramount. The European Union wants to change the regulations to introduce more control and traceability on the future of batteries and their components. The safety of everyone is guaranteed with increased traceability, strengthened data security and strict product composition.

As a supplier of analytical equipment in various scientific fields, particularly in the pharmaceutical and food industries, Shimadzu has developed software solutions to meet the following requirements:

> Recording of raw data in **a secure and tamper-proof space.**

> **Unique identifier** for each user and access to the functionalities necessary for the user's functions.

> **Traceability** of the actions carried out by each on the system.

> **Electronic signature** with identification of the signatory for each result.

Secure data

Several solutions exist to offer a high level of data security that best meets regulatory requirements in the context of audits, GMP or FDA regulations:

> The backup of raw data locally (on the control PC) in a secure and non-modifiable database.

> Backup of raw data in a network on a secure server with software running in network mode client/server mode.

Focus

> **A common software platform for Shimadzu instruments.**

> DB Labsolutions: software including a secure database for recording and preserving raw data.

> CS Labsolutions: client/server mode software for the secure transfer of data to a protected server.

SHIMADZU SYSTEMS

Shimadzu proposes **a full range of instrumentation to** meet the needs of the lithium battery industry. This offer covers both research and development as well as quality control analyses related to the production of these batteries.

GCMS QP 20 Range:

Designed to meet the needs of R&D and production, the Shimadzu GCMS range is a reference in the field. Reliable, efficient and accessible systems that adapt to the real needs of laboratories.

The +: Shimadzu GCMS are fitted with an inert source and dual filaments. This provides increased sensitivity and built-in redundancy for reliable, high-quality analysis.

TOC-L with solid samples module SSM:

A powerful and simple solution to quickly obtain information on possible contamination of the sample. The TOC-L and its robust module were designed to detect organic pollution quickly and with ease.

The +: combustion at 900 °C with the solid module that guarantees a total degradation of carbon in CO_2.

UHPLC Nexera LC-40 and Advanced i-Series:

Instruments designed for R&D and quality control. On the one hand, a modular design, on the other, a compact design in order to best adapt to the needs of the laboratories.

The +: smart features to ensure performance and results!

FTIR IRTracer or IRSpirit:

Excellent resolution, state-of-the-art tools, and ergonomics optimised for easy use. The tools Software Driving those systems allow one grip in main fast and routine use of this system by all!

The +: the compact size of the IR Spirit model allows easy use in a glove box.

Ion Chromatography - Nexera HIC-ESP

An intelligent, modular ion chromatography system with a robust and efficient electrolytic suppressor.

The +: a proven suppressor technology, ultra-efficient and with a low internal volume.

Universal Testing Machines:

Universal electromechanical test frames for electrode compression, separator perforation or peeling tests on finished products.

The +: These systems allow you to test all types of samples using the same frame. Powerful and versatile they are equipped with easy to use software.

Micro-compression MCT:

Micro-indentation technology for additional precision and robustness.

The +: the tablet sample visualisation kit.

LABSOLUTIONS SOFTWARE PLATFORM

Regulatory requirements on data integrity is becoming increasingly important and it is paramount for every laboratory to be able to meet them. The LabSolutions software platform, common to all instruments (excluding MCT) is a simple and accessible tool, developed to meet the productivity and safety needs of laboratories. This software meets the data integrity guidelines while remaining easy to use.

THE +

Service and support

The services and support are essential and are a long-term assurance during the capital investment of the purchase of an instrument for your laboratory. With our experience, knowledge and resources, Shimadzu provides you with the support you need to achieve the best results and optimal productivity.

Leasing

A lease purchase agreement would allow you to equip yourself with the instrumentation you require without impacting your budget or cash flow.
Shimadzu's finance partner would work with you to create a tailor-made package that suits your financial needs.

The combination of flexible lease agreements with cutting edge technology and market leading support ensure that Shimadzu customers are supported through every step of their new purchase.

SHIMADZU
Excellence in Science

Want to know more about Lithium battery analysis solutions?

Our experts answer your problems:

By email: info@shimadzu.co.uk

By phone: +44 (0)1908 552209

® Shimadzu Corporation First edition : January 2022

Shimadzu UK Ltd.

Mill Court, Featherstone Road,
Wolverton Mill South,
Milton Keynes, MK12 5RE
URL: www.shimadzu.co.uk