



NATIONAL UNIVERSITY OF  
SCIENCE AND TECHNOLOGY  
POLITEHNICA OF BUCHAREST  
FACULTY OF ENERGY  
ENGINEERING



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# Doctoral thesis

## SUMMARY

### Optimal solutions for electrical energy storage in Li-ion batteries

**Author:** Drd. Ing. Cosmin Giorgian UNGUREANU  
**Phd supervisor:** Prof. Dr. Ing. Horia NECULA

Bucharest  
2024

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### **Key words**

Li-ion batteries, Energy storage system, Energy density, High operating potential, Specific capacity, Coulombic efficiency, Cathode, Active material *NMC811*, Active material *LNMO*, Anode, Graphite, Electrolyte, Additive, *Pouch cell*, Test protocols.



## Extended summary

Modern society is still heavily dependent on fossil fuels, such as oil, natural gas and coal, which generated 83% of primary energy in 2020, contributing to pollution and increasing CO<sub>2</sub> emissions [1]. The largest emissions come from the energy and transport sectors, responsible for more than 50% of fossil CO<sub>2</sub> emissions in 2019. Many countries have started to take steps to reduce emissions, setting carbon neutrality targets by 2060, promoting electric vehicles for to replace internal combustion engines. Also, to support renewable energy sources such as wind and solar energy, the integration of energy storage systems (ESS) is necessary. Li-ion batteries (LIBs) are preferred due to their advantages, including energy density and superior efficiency, becoming a mainstream technology for electric and hybrid vehicles. However, challenges such as safety and issues related to operating conditions remain obstacles to the large-scale production of these batteries.

Although there are a variety of electrical energy storage technologies, Li-ion batteries have proven to be the most efficient solution in the short and medium term, due to their high storage capacity, optimal balance between power and energy, adequate lifetime and, in particular, due to the continuous decrease in costs, which make them competitive in various markets.

Considering the advantages of Li-ion batteries in numerous industrial and consumer applications, it becomes essential to explore solutions that further optimize their performance. In this context, the aim of this work is to address the existing challenges by developing electrodes that combine energy efficiency and electrolyte formulation with specific additives, to improve the thermal and cycling stability of Li-ion batteries.

The PhD thesis proposes the development of innovative solutions aimed at improving the performance of Li-ion batteries, focusing on the use of hybrid electrodes and safe electrolytes, including experimental and theoretical research on the design of electrodes and electrolytes, evaluating the electrochemical performances and cycling stability under various conditions of operation.

The content of the thesis includes experimental and theoretical research on the design of electrodes and electrolytes, evaluation of electrochemical performance, as well as cycling stability under different operating conditions. Through this approach, the paper aims to provide practical solutions for increasing the efficiency and durability of Li-ion batteries, thus contributing to the technological evolution in the field of energy storage. The relevance of this study derives from the urgent need to improve Li-ion battery technology, which plays a crucial role in supporting the transition to sustainable energy sources. As the adoption of electric vehicles and renewable energy systems continues to grow, the electrochemical performance of batteries becomes increasingly

important to ensure their reliability and sustainability.

The paper is structured in eight chapters, each with a clear and well-defined role in the analysis and presentation of relevant aspects in the field of energy, with a particular focus on energy storage in Li-ion batteries. The thesis addresses current trends, technological innovations, development strategies, cell safety, electrochemical performances, evaluated by galvanostatic tests and impedance measurements, as well as their practical implications.

*In the first chapter*, a detailed presentation of trends and innovations in the global energy sector is carried out. Technological transformations and their impact on the economy are emphasized, including energy policies and development strategies in the context of sustainability objectives and the transition to renewable energy sources. This chapter also describes the objectives of the thesis:

*Development of hybrid electrodes for energy applications:* A specific objective of the study is the realization and optimization of hybrid electrodes, using active materials such as *LNMO*, which provide high energy density and increased power. This approach not only improves the efficiency of energy storage systems, but also facilitates the integration of renewable energy sources into electrical networks. Furthermore, the potential of these hybrid electrodes extends to diverse applications, from electric vehicles and storage systems for solar or wind energy to use in wearable devices.

*Evaluation of electrode architecture:* Another direction of research focuses on the analysis of electrode architecture and their testing under operational conditions specific to the energy sector. This includes studies on the impact of electrode structure on efficiency and stability in energy storage applications, considering how each structural change can influence the overall performance of batteries in various operating environments.

*Improving the safety of Li-ion batteries:* Another main direction is to optimize the safety of Li-ion batteries using *NMC811* active material and advanced electrolyte formulation. In addition, the amount of cobalt, a material on the critical material list, is reduced, which not only improves safety, but also contributes to resource sustainability. The study includes adding additives and examining their impact on electrochemical performance, which promises to raise safety and efficiency standards in energy applications.

*Stability assessment:* The study analyzes the effects of additives on electrolyte stability, identifying optimal solutions for sustainable applications. The approach is critical to ensuring an efficient long-term energy supply, enabling batteries to keep pace with the ever-expanding demands of the sustainable energy and electric vehicle markets.

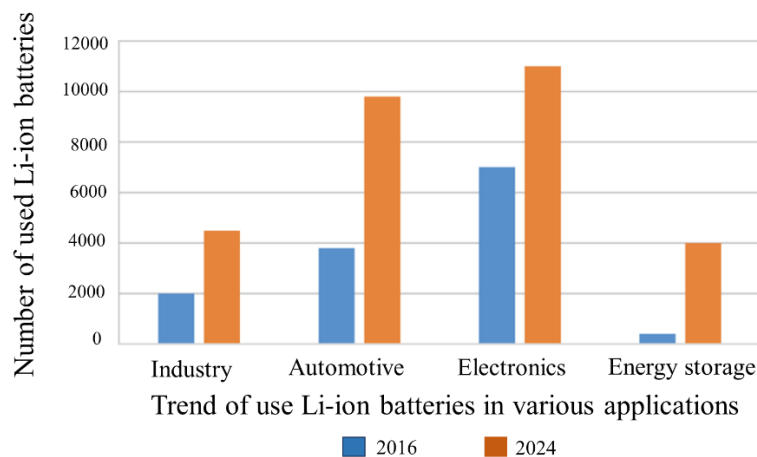
Through these objectives, the study not only aims to optimize the performance and stability of energy storage systems, but also highlights the vast potential of the applications of these Li-ion cells. This underlines the importance of innovation in the field, thus supporting the transition to a more



sustainable and secure energy system, which plays a crucial role in achieving global environmental goals.

*Chapter 2* provides an overview of energy storage solutions in Li-ion batteries. The study of these batteries, which began in the 1970, has seen accelerated development in recent decades, aimed in creating an efficient system capable of overcoming the issues related to the low gravimetric and volumetric energy density of contemporary rechargeable batteries. Current technologies used in the field of Li-ion batteries will continue to dominate this market in the near future, considering the significant investments already made in the stages of extraction, processing, and production. Active materials such as NMC, LFP, NCA, LMO, and LNMO serve as the foundation for applications utilizing Li-ion batteries, each having its own advantages and disadvantages, from energy storage in portable applications to use in mobile applications. The main issues include cracking of cathodes and dissolution of transition metal ions, affecting the solid-electrolyte interface (SEI) and the cathode-electrolyte interface (CEI). The development of long-lasting Li-ion batteries requires a thorough understanding of the degradation mechanisms that cause performance loss, especially in batteries for electric vehicles with nickel-rich NMC cathodes.

*Fig. 1.* illustrates the trend of Li-ion battery usage for various applications between 2016 and 2024 [2]. The ever-expanding adoption of hybrid and electric vehicles, along with promising energy policies promoting sustainable advancements, is driving market development.



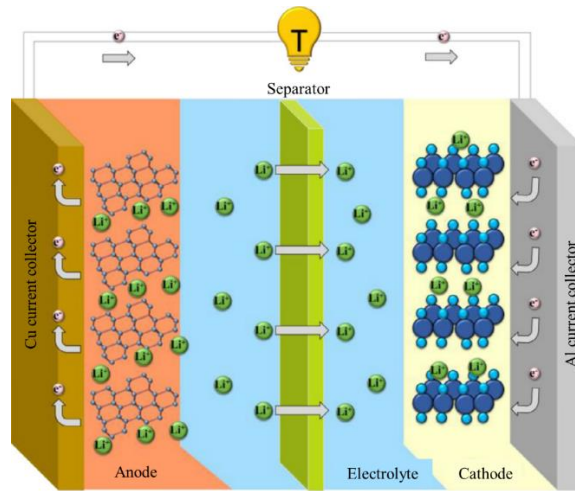
*Fig. 1. Trend of use of Li-ion batteries in various applications from 2016 to 2024. Adapted from ref. [2]*

The widespread use of Li-ion batteries in electric vehicles, portable electronic equipment, and storage systems is expected to drive market demand due to their high energy density and high level of safety [3, 4, 5]. The technological advances needed to reduce battery weight, cost, and increase their capacity yield are critical to driving industry growth. In addition, effective distribution channels will be a key factor in achieving a competitive advantage.

Also in this chapter are described the advantages of Li-ion batteries, such as high cell voltage, long life, high energy density, low self-discharge and simple charging methods. These features make

them preferred for commercial applications, especially in handheld devices. However, there are also disadvantages such as sensitivity to moisture that limit their expansion.

In *Fig. 2* the fundamental principle of operation is illustrated. During the discharge process,  $\text{Li}^+$  ions are extracted from the anode by electrochemical oxidation and intercalated into the delithiated cathode by electrochemical reduction. At the time of charging, the processes are resumed and the lithium ions are extracted from the cathode and reintroduced into the anode material. Being a reversible process, lithium ions move between anode and cathode during charge/discharge cycles.



*Fig. 2. Schematic diagram of the working principles of the LIB during discharge. Adapted from ref. [6]*

Heat loss and heat management issues are analyzed in detail. It also explores the risks associated with internal short-circuiting and the effects of mechanical, electrical and thermal abuse on battery performance.

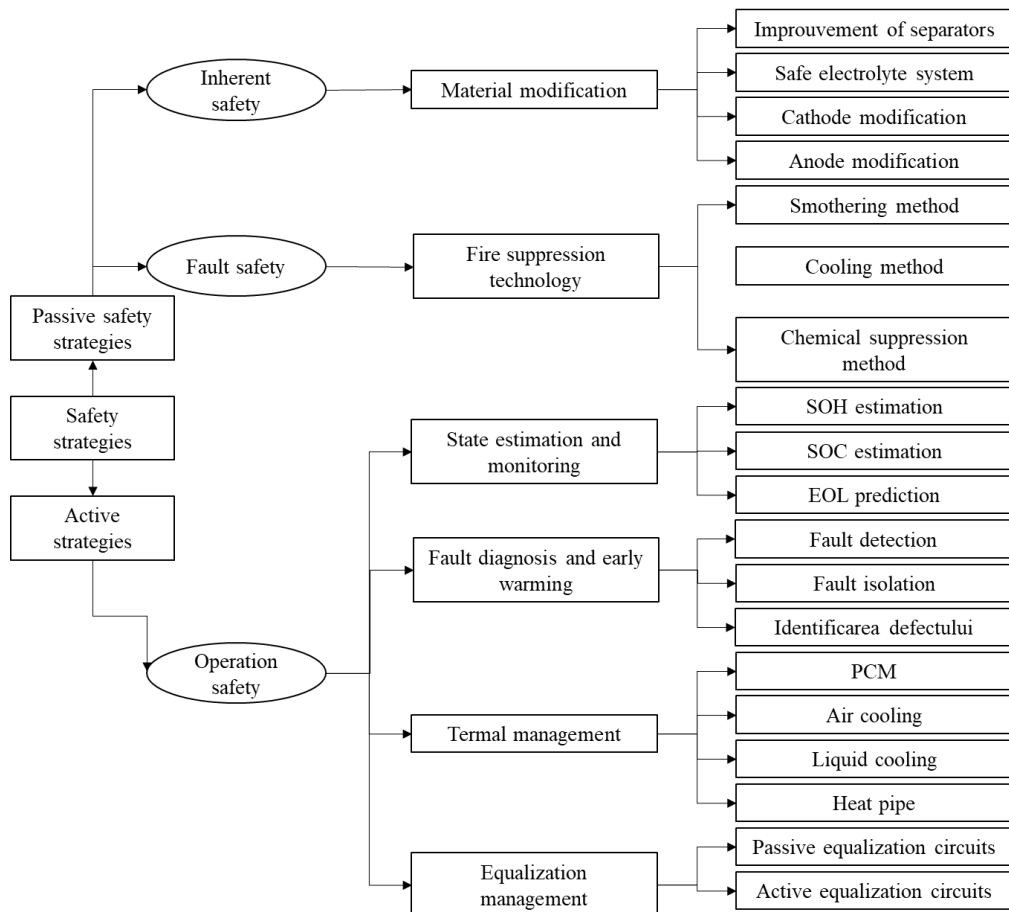
*Chapter 3* presents the advanced strategies for ensuring the safety of Li-ion batteries, structured in two categories: passive and active.

Passive strategies include material modification and fire suppression technologies aimed at reducing risks through safe battery design. However, the modification of materials is expensive and difficult to implement without affecting the electrochemical performance. Advances in electrode materials contribute significantly to increasing the safety of Li-ion batteries. Safety issues such as heat loss are caused by secondary reactions of materials under abuse conditions. Therefore, battery safety can be improved by modifying the cathode, anode, separator and electrolyte to reduce these reactions. Modification of the cathode material is essential to improve the safety of Li-ion cells, given that the decomposition temperature of cathode materials varies. Modification methods include surface coating and replacement of material structure elements. Cathode coating can prevent direct contact with the electrolyte, reducing heat generation and improving structural stability, reversible capacity, coulombic efficiency, and overcharge tolerance. Anode modification is equally important, as new high-capacity anode materials such as metal oxides and silicon-based anodes present

significant advantages. A notable example is LTO spinel, which offers thermal stability and high safety. The SEI layer plays a crucial role in anode performance, and improvements in this layer can contribute to thermal stability and reduction of side reactions. Mild graphite oxidation and anode coating techniques can greatly improve the electrochemical performance and thermal stability of Li-ion batteries. Electrolytes play an essential role in their safety, being the most thermally sensitive component. Currently, organic carbonates and  $\text{LiPF}_6$  salt are widely used due to their good conductivity and electrochemical performance. However, under conditions of abuse, they can generate flammable gases. Therefore, research is focused on the development of more stable and less flammable electrolytes, including non-flammable electrolytes, polymer and ceramic electrolytes, as well as solid-state electrolytes, which can eliminate the flammability risks associated with organic compounds. Isolators play an important role in preventing short circuits and fires. Multilayer separators, such as those made of polypropylene and polyethylene (PP/PE/PP) layers, provide increased safety by maintaining mechanical integrity at high temperatures, preventing short-circuiting between anode and cathode. For even greater safety, separator materials can be replaced with polymers with higher thermal stability, such as polyimide. Fire prevention and fighting technologies are also essential in the safety of Li-ion batteries, given the high risk of fire caused by internal thermal reactions. Extinguishing fires with water, dry chemical,  $\text{CO}_2$  or foam is the most common method, although water and  $\text{CO}_2$  have limitations. Experimental results show that  $\text{C}_6\text{F}_6$  - acetone can extinguish the fire of an LTO battery in 30 seconds, while the flame cannot be completely extinguished by continuous application of  $\text{CO}_2$  for 164 seconds.

Active safety strategies mainly include effective condition estimation and monitoring, fault diagnosis and early warning, thermal management and equalization management, which have been integrated into state-of-the-art BMS systems. In addition to the above functions, BMSs should also provide functions such as sensor data acquisition, data storage, charge/discharge control [7], communication with all battery components, and a user-friendly interface. Monitoring of Li-ion battery status parameters is an essential function of the battery management system - BMS. This includes measuring parameters such as currents, voltages and surface temperature using different types of sensors. However, certain parameters such as internal temperature, state of charge (SOC), degree of discharge (DOD), state of health (SOH) and remaining useful life (RUL) are more difficult to assess. Battery state estimation focuses on obtaining information about the internal states of Li-ion batteries based on external measurements. SOC, DOD, and SOH are the most important health parameters, each with precise definitions based on the battery's rated capacity. SOC estimation is done by various methods, including the OCV method and the Coulomb method, but these methods can be affected by measurement errors. The estimation of SOH is more complex due to the influence of several factors such as temperature and current. RUL is simply defined as the difference between

the estimated time to the end of battery life and the current time. Advanced fault diagnosis and early warning systems are essential for early detection of battery faults, preventing heat loss and other problems. Fault diagnosis includes problem detection, isolation and identification. Diagnostic methodologies can be classified into qualitative methods, which are based on accumulated knowledge, and quantitative methods, which include potential monitoring techniques and mathematical models. Temperature significantly affects the performance of Li-ion batteries, and thermal management is essential to maintain optimal temperature. Thermal management systems (BTMS) have the role of cooling or heating the batteries, thus preventing degradation and possible damage. Cooling systems can be passive or active, with active being more efficient, especially in extreme conditions. Performance equalization strategies to improve durability and efficiency involve grouping hundreds of Li-ion cells in series and parallel connections to meet the voltage and capacity requirements of large systems such as electric vehicles and energy storage systems. Inconsistencies between Li-ion cells are inevitable due to internal (manufacturing differences, impedances, self-discharge rate) and external (thermal, electrical and mechanical conditions) variations. These mismatches can lead to reduced system capacity and accelerated cell degradation, where the cell with the lowest maximum capacity ( $C_{max}$ ) risks being overcharged or overdischarged.



*Fig. 3. Overview of passive and active safety strategies for Li-ion batteries. Adapted from ref. [8]*

*Chapter 4* focuses on standardized protocols and advanced methods for optimizing the charging and performance of Li-ion batteries. This chapter reviews charging techniques, including constant and pulse charging methods, as well as the advantages and limitations of each method. Their impact on battery efficiency, safety and durability is also discussed, along with alternative charging protocols and innovative trends in this field.

The standard charging protocol for Li-ion batteries is CC\_CV (constant current / constant potential). Although many alternative protocols promise improvements in load storage and efficiency, few are supported by solid experimental data. Also, some methods are derived from simulations without experimental validation. The charging limitations of Li-ion cells are largely influenced by two factors: lithium plating at the anode and oxidation of the electrolyte solution, both of which lead to irreversible losses and affect cyclability. The main test protocols are detailed below, providing a description of them.

*Standardized protocols for efficient charging of Li-ion cells:* In general, optimized charging procedures aim to ensure the shortest charging time, good serviceability and high energy efficiency, all without affecting the life of that battery. Before introducing the various charging protocols, the basic limitations when considering Li-ion cell charging must first be established. The charging potential is limited by the oxidation of solvents in the electrolyte, which occurs at high cathode potentials (overpotentials). Overcharging a Li-ion cell promotes heat generation and produces irreversible reactions on the crystalline structure of the cathode, when the material from which the cathode is made is completely delithiated. This leads to further oxidation reactions that can promote gas production, unwanted pressurization of the cell, and ultimately lead to electrolyte leakage. Since the organic electrolytes used in Li-ion cells are highly flammable, their introduction into the atmosphere can produce undesirable effects such as local ignition or, in an extreme case, cell explosion. So conforming to the maximum potential of the cell is essential.

*Constant current and constant potential (CC\_CV) charging:* The standard protocol for charging Li-ion cells is CC\_CV charging. At first the cell is charged at a constant current  $I_{ch}$ , until the cell potential reaches the specified potential value  $V_{ch}$ . Then, the cell potential is kept constant at the  $V_{ch}$  value and the charging current gradually decreases. This phase, in which the cell is maintained at a constant potential, is terminated when the current value falls below a certain level  $I_{end}$  or until the predefined time allocated to the charge is exceeded. High currents and high charging potentials can damage a cell, so it is imperative that the values for the two quantities are chosen very carefully to minimize lithium plating and electrolyte breakdown.

*Multiphase constant current charging:* this type of charging, compared to the constant potential in the previous protocol, is replaced by a phase in which a current is applied constantly in several stages until its value drops below a set level ( $I_{ch1} > I_{ch2} > \dots > I_{chN}$ ). Each time the cell reaches

the charging potential  $V_{ch}$ , the charging current is reduced to the next level. The charging process ends when  $V_{ch}$  is reached at the lowest value of the charging current  $I_{ch}$ . This type of protocol reduces implementation costs because there is no need for additional circuitry or software for potential control.

*Pulse charging:* As an alternative to constant current or potential charging, several pulse charging profiles can be found in the literature. They are based on periodic changes in amperage or its direction of application. The charging current can be reduced, interrupted or replaced by short periods of discharge for a certain period of time.

*Combined constant current and pulse charging (CC\_PC):* pulse charging replaces the constant potential phase of the CC\_CV charging protocol. The Li-ion cell is charged with a constant current  $I_{ch}$  until a certain predefined potential  $V_{switch}$  is reached. Then the charging mode is changed to pulse charging: current pulses  $I_{ch}$  and duration  $t_{pulse}$  are applied to the cell. After each pulse, the current is cut off until the cell potential drops below a set potential. As the state of charge increases, the pauses become longer and longer. The charging procedure is terminated when the pause after the application of a current pulse exceeds a predefined time  $t_{pause, max}$ . This charging protocol can be implemented at very low cost, since it requires neither current control nor voltage control.

*Exclusive charging by pulses:* In addition to the previous protocols (CC\_PC) there are also PC protocols, where the entire charging procedure is controlled in pulses. During this PC protocol, the current alternates between  $I_{high}$  and  $I_{low}$ . The time period  $t_{total}=t_{high}+t_{low}$  and duty cycle  $D=t_{high}/t_{total}$  define the pulse shape. All parameters can change during the upload process. Reaching a predefined  $V_{end}$  charging potential ends the charging procedure. The combination of  $I_{high}$  and  $V_{end}$  determines the capacity utilization. The rationale for using the PC protocol is to reduce  $Li^+$  gradients and reduce bias concentration. Some studies report the beneficial effects of using PC for Li-ion batteries, such as reduced diffusion resistance, better utilization of the active material, improved lifetime and shorter charging times.

*Boost charging:* Boost charging is derived from CC\_CV (constant current / constant voltage) charging and features a CC or constant power range at the start of the charging process. This additional power range reduces charging time without damaging battery life, since batteries are less susceptible to lithium plating at lower state-of-charge values. The cell is initially charged with a high current  $I_{boost}$ , until a sufficiently large amount of charge is transferred to the cell.

*Alternative charging protocols:* Adaptation procedures are provided, which adjust the charging currents according to the properties of the Li-ion cells under certain conditions.

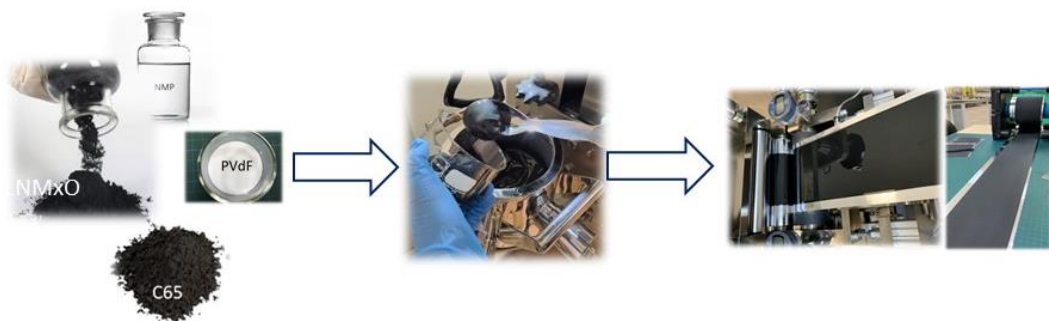
The charging procedures are based on the variation of the charging current, the procedure starting from high charging currents and as the charging takes place they decrease. Optimization methods are also used to achieve minimum charge times without exceeding certain potentials,

temperatures, stress levels or concentration limitations. Charge profiles are either determined experimentally or derived from simulated models to achieve maximum charge currents that can be applied without causing lithium plating or lithium deposits. This type of protocols have rarely been used in practical applications, since determining the maximum charging current is quite a complex matter, and also these currents vary with temperature and the degree of battery degradation. Charging protocols have been proposed that are no longer based on predefined charging currents, but follow a certain potential trajectory. This trajectory, which is actually the result of charging a new cell with a reference current profile, remains constant throughout the life of the battery. So, charging currents decrease with decreasing capacity, while charging time remains constant.

*Chapter 5* describes in detail the experimental part of the research, focusing on the performance evaluation of cathodes based on *LNMO* and *NMC811* in different configurations, such as half-cells and *pouch* cells.

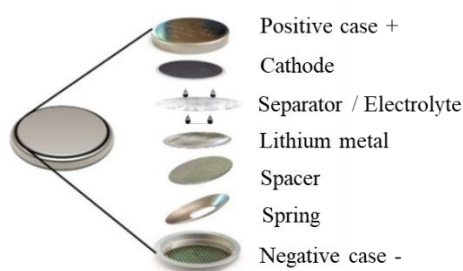
#### ***The experimental results of LNMO-based cathodes for Li-ion batteries***

The anode and cathode mixtures were prepared in a mixing unit for Li-ion battery active components, equipped with vacuum and a cooling jacket, through a multi-stage mixing process. Both mixtures were deposited via a continuous deposition process using a special roll-to-roll system. Copper foil was used for the anode and aluminum foil for the cathode. The technological process for obtaining *LNMO* - based electrodes is shown in *Fig. 4*. Subsequently, the electrodes were profiled, weighed, and calendered to a predetermined porosity using a specifically press dedicated to this process. Before assembling the *coin cell* and *pouch cell* types, the electrodes were dried in a vacuum oven. The specific capacity was determined through half-cell measurements. The two electrolytes used in these experiments were:  $1.2M LiPF_6$  in *EC:EMC (3:7) + 0.5 wt.% FEC* and  $1.2M LiPF_6$  in *EC:EMC (3:7) + 4 wt.% SA*, in all cell configurations.



*Fig. 4. Technological process for obtaining LNMO-based electrodes*

In *Fig. 5*, the components of a half-cell and the assembly method are illustrated, using a lithium metal chip as a reference.



*Fig. 5. Assembly of CR2032 half-cell*

After assembling the cells and filling them with electrolyte, they were hermetically sealed using a special system dedicated to sealing coin-type cells – *Fig. 6*.



*Fig. 6. Coin cell sealing system*

*Table 1* presents the components used to make a *half-cell*.

*Table 1. Components of Li-ion cells in CR2032 half-cell configuration with 2 electrodes*

<b>Reference electrode</b>	<b>Li Chips (Ø = 15mm, thickness = 1mm)</b>
<b>Working electrode</b>	Cathode - (Ø = 13mm)
<b>Active material</b>	LNMO
<b>Separator</b>	Glass Microfiber filters GF/D 150 mm / Whatman (Ø = 19mm)
<b>Electrolyte</b>	1.2M LiPF <sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC 1.2M LiPF <sub>6</sub> in EC:EMC (3:7) + 4 wt.% SA
<b>Cell type</b>	Coin CR2032

Before evaluating the effect of the additive in a standard electrolyte in *pouch cells* configuration, the development and testing of electrolyte formulations were carried out in coin cells type, using a *half-cell* configuration. The selected additives were combined in different concentrations with the standard electrolyte to observe their impact on electrochemical performance.

The first test conducted involved electrochemical impedance measurements performed over a frequency range of 500 kHz to 10 mHz, with a current amplitude of 5 mA. Four Li-ion cells were tested, two of which were calendered, while two remained uncalendered, using two types of electrolytes: *1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC* and *1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 4 wt.% SA*. The impedance measurement results for all cells are presented in Nyquist plots, both for the cells before and after galvanostatic testing, at different states of charge.



In Fig. 7, the contact resistances at different states of charge for the tested cells are represented, both before and after galvanostatic testing. In Fig. 7 a, it can be observed that the contact resistance at various states of charge is relatively constant, with values ranging from 3  $\Omega$  to 5  $\Omega$ . The lowest contact resistances were obtained at a state of charge of 60% as well as at a state of charge of 100%.

In Fig. 7 b, the contact resistance after galvanostatic testing at the same states of charge is represented. The values of the contact resistance vary between 7  $\Omega$  and 12  $\Omega$ , depending on the state of charge of the cell as well as the active material used and the electrolyte.

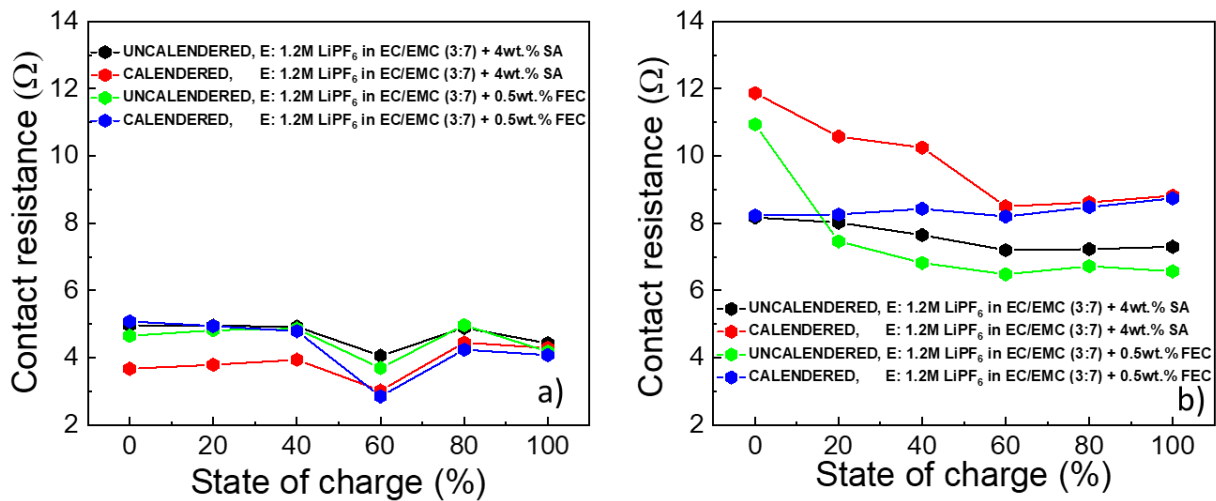


Fig. 7. Electrochemical Impedance Spectroscopy (EIS) - LNMO, showing contact resistance vs. state of charge: a) contact resistance for cells before testing, b) contact resistance for cells after testing

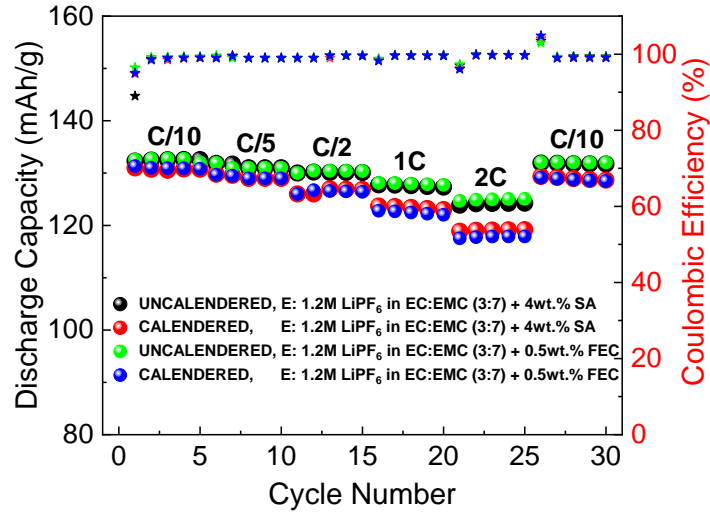
The contact resistances for the four tested cells are higher after galvanostatic testing at all states of charge, indicating degradation of both the electrode and the electrolyte.

Galvanostatic testing was performed in the potential range of 3.0 to 4.9 V, both for the performance of the cells at different rates and for their cycling stability, through two protocols:

*Rate Performance Protocol* – The cells were subjected to testing at different charge/discharge rates, starting with a current rate of C/10, gradually increasing the current rate up to 2C, after which the capacity was returned to its initial state, specifically C/10. Five charge/discharge cycles were performed at different rates - (C/10, C/5, C/2, 1C, 2C, C/10).

*Cycling Stability Protocol* – Following the performance protocol, the testing of the cells continued with the cycling stability protocol at a current rate of 1C for 500 charge/discharge cycles to determine the capacity over time.

Following the electrochemical rate performance protocol, very good capacities can be observed at low testing currents, both for the electrolyte with 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC and for the electrolyte 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 4 wt.% SA - Fig. 8.



**Fig. 8.** Electrochemical rate performance profile for calendared and uncalendered cathodes, based on the two electrolytes used, at different charge/discharge rates: 5 cycles at C/10, C/5, C/2, 1C, 2C, and C/10

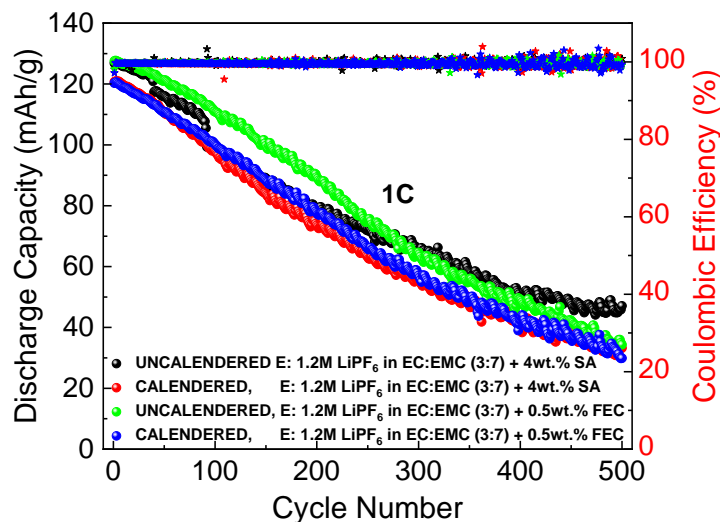
Higher capacities are highlighted for the calendared electrodes, both for the electrolyte  $1.2M LiPF_6$  in  $EC:EMC (3:7) + 4 wt.\% SA$  and for the electrolyte with  $1.2M LiPF_6$  in  $EC:EMC (3:7) + 0.5 wt.\% FEC$ , achieving capacities of 127 mAh/g at 1C, while the calendared electrodes achieved a capacity of 123 mAh/g. The coulombic efficiency for both electrolytes, as well as for the calendared and uncalendered electrodes, is over 99%, indicating very good charge transfer between the electrodes – [Table 2](#). The discharge capacity obtained in the last cycle at C/10 is very close to the discharge capacity achieved after the last C/10 cycle performed in the initial cycles, indicating good capacity reversibility.

**Table 2.** Values of discharge capacity (mAh/g) and coulombic efficiency (CE %) for the four tested cells, cycle 5 at different C-rates, based on the two electrolytes used and the type of electrode (calendered and uncalendered)

Electrolyte	Electrode type	Cycle 5 @ C/10	CE (%)	Cycle 5 @ C/5	CE (%)	Cycle 5 @ C/2	CE (%)	Cycle 5 @ 1C	CE (%)	Cycle 5 @ 2C	CE (%)	Cycle 5 @ C/10	CE (%)
1.2M $LiPF_6$ in $EC:EMC (3:7)+ 4 wt.\% SA$	Uncalendered	132.5	99.2	131.2	99.5	130.1	99.6	127.3	99.6	124.2	99.7	131.7	99.3
	Calendered	130.7	99.0	129.0	99.2	126.86	99.5	123.0	99.5	119.1	99.7	128.6	99.0
1.2M $LiPF_6$ in $EC:EMC (3:7)+ 0.5 wt.\% FEC$	Uncalendered	132.5	99.2	131.1	99.6	130.4	99.6	127.7	99.6	125.0	99.6	132.0	99.3
	Calendered	130.8	99.0	129.2	99.5	127.4	99.5	123.0	99.7	117.8	99.7	128.7	99.1

In [Fig. 9](#), the cycling stability after 500 cycles at a current rate of 1C vs. coulombic efficiency is represented. The best discharge capacity obtained was for the uncalendered electrode tested with the electrolyte  $1.2M LiPF_6$  in  $EC:EMC (3:7) + 4 wt.\% SA$ . After 500 charge/discharge cycles, the capacity obtained for the uncalendered electrode tested with the electrolyte  $1.2M LiPF_6$  in  $EC:EMC (3:7) + 4 wt.\% SA$  is 47 mAh/g; for the calendared electrode tested with the electrolyte  $1.2M LiPF_6$

in EC:EMC (3:7) + 4 wt.% SA, the capacity is 33 mAh/g; for the uncalendered electrode tested with the electrolyte 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC, the capacity is 34 mAh/g; and for the calendered electrode tested with the electrolyte 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC, the obtained capacity is 29 mAh/g – *Table 3*.



*Fig. 9. Cycling stability profile for calendered and uncalendered cathodes, based on the two electrolytes used, over 500 cycles at 1C*

*Table 3. Values of discharge capacity (mAh/g) and coulombic efficiency (CE %) for the four tested cells at cycles 1, 250, and 500 at a current rate of 1C, based on the two electrolytes used and the type of electrode (calendered and uncalendered)*

Electrolyte	Electrode type	Cycle 1 @1C	CE (%)	Cycle 250 @1C	CE (%)	Cycle 500 @1C	CE (%)
1.2M LiPF <sub>6</sub> in EC:EMC (3:7) + 4 wt.% SA	Uncalendered	126.8	98.0	71.9	99.8	47.0	99.9
	Calendered	120.6	97.1	63.1	99.4	33.2	99.4
1.2M LiPF <sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC	Uncalendered	127.5	98.1	75.0	99.9	34.3	99.0
	Calendered	120.2	97.1	65.8	99.3	29.8	99.4

The electrodes obtained from the deposition process were shaped using a dedicated system *Fig. 10*. The shaped electrodes were dried in a vacuum oven to remove any traces of solvent. The next step involved weighing the electrodes to determine their mass.



*Fig. 10. The profile system used in the production of electrodes*

*Pouch cells* (composed of anode, cathode, and separator) were assembled using the semi-automatic system *Fig. 11*. The attachment of the tabs to the current collectors was performed using an ultrasonic welding device.



*Fig. 11. Semi-automatic assembly system for pouch cells*

The aluminum casings were manufactured using the equipment shown in *Fig. 12*. After assembled the electrodes and connecting the two tabs, the next step involved inserting the assembled electrodes into the aluminum casings.



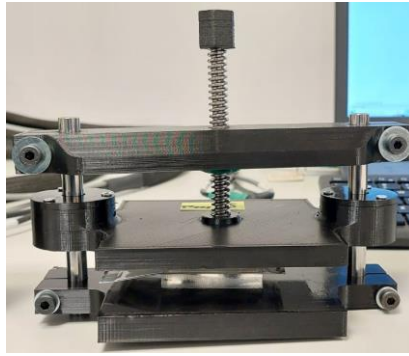
*Fig. 12. System for manufacturing casings for pouch cells*

The next step was to introduce the cells into a controlled atmosphere system for electrolyte filling, followed by the sealing stage, which ensured the cells hermeticity. This step was the final one in the manufacturing process of *pouch cells* *Fig. 13*.



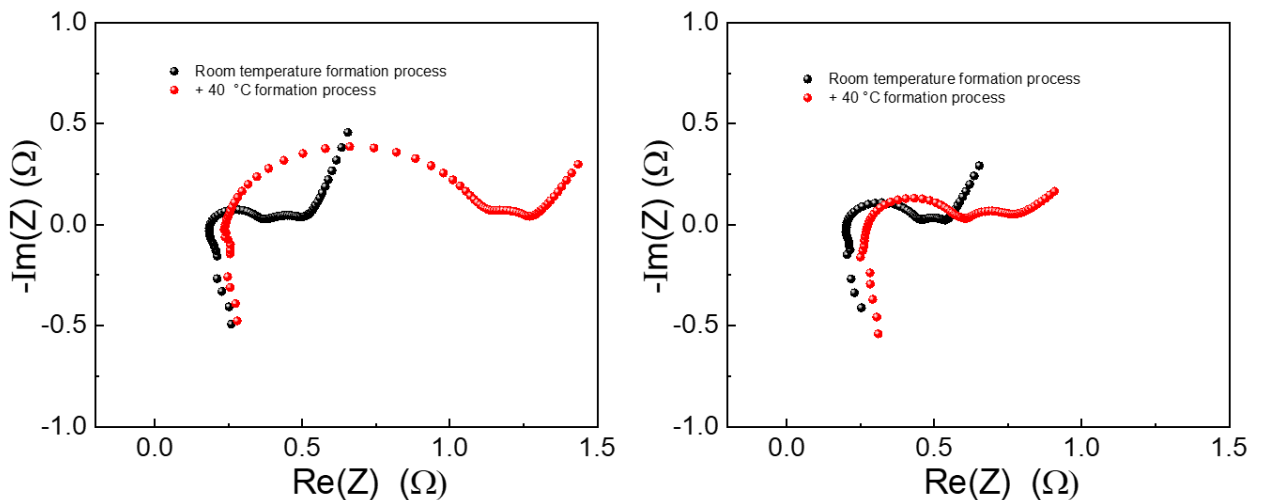
*Fig. 13. Controlled atmosphere system Glove Box*

In *Fig. 14*, the device used for pressing *pouch cells* is presented. This device allows for the application of a well-defined and established pressure on the cells.



*Fig. 14. Pressing device that applies uniform pressure on pouch cells*

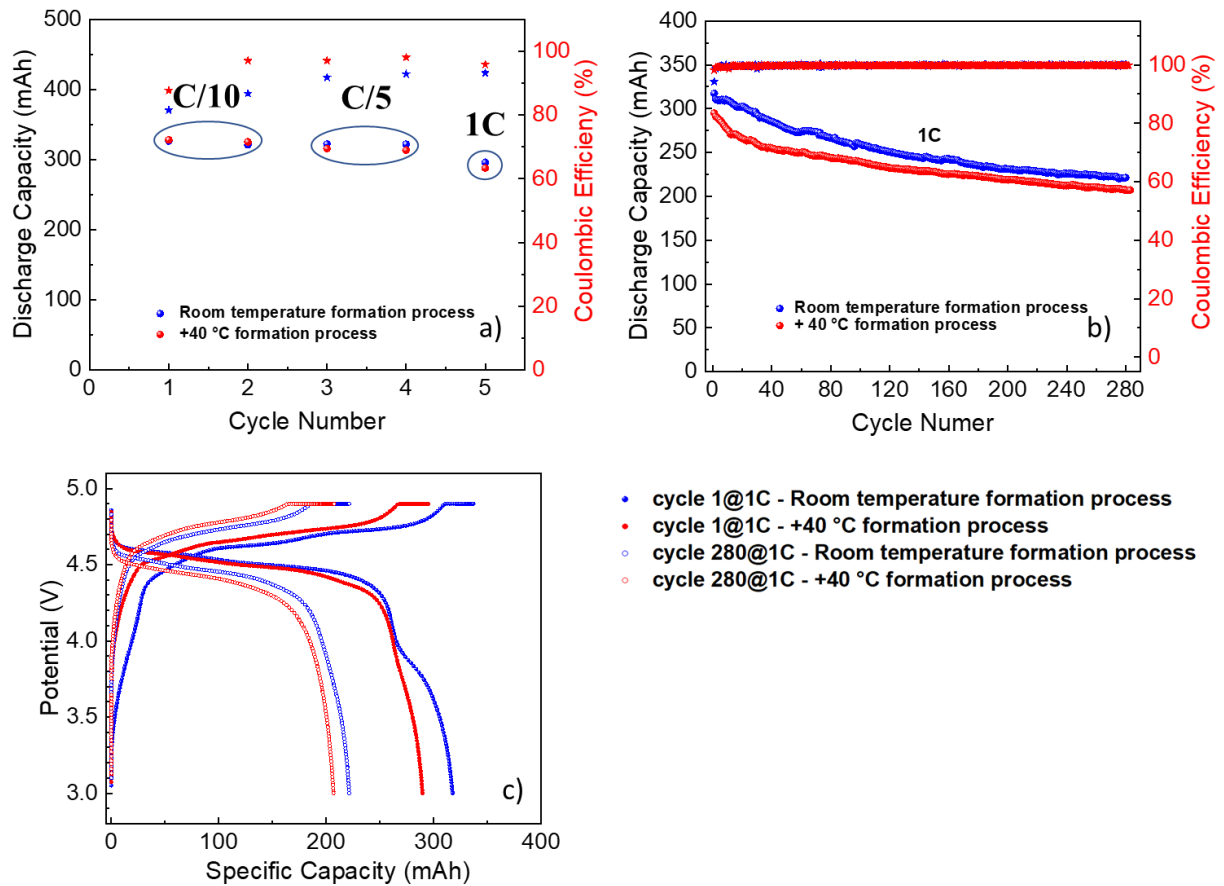
Thus, the manufactured cells were subjected to galvanostatic testing, being formation at room temperature and at a temperature of +40°C. Subsequently, after formation at different temperatures, galvanostatic tests were conducted, followed by impedance spectroscopy measurements. In *Fig. 15*, the graphs tested with the two electrolytes are overlaid:  $1.2M LiPF_6$  in  $EC:EMC (3:7) + 4 wt.\% SA$  and  $1.2M LiPF_6$  in  $EC:EMC (3:7) + 0.5 wt.\% FEC$ . In the cells formation at a temperature of +40°C, a significant increase in the internal resistance and contact resistance for both electrolytes is observed, suggesting a more pronounced degradation of the electrode/electrolyte interface compared to the cells formation at ambient temperature. This interface degradation may be caused by more intense electrochemical reactions occurring at higher temperatures, which can affect the structure and properties of the electrolyte.



*Fig. 15. Electrochemical impedance spectroscopy (EIS) for the pouch-type full-cell after galvanostatic testing: a) tested with the electrolyte  $1.2M LiPF_6$  in  $EC (3:7) + 4 wt.\% SA$ , b) tested with the electrolyte  $1.2M LiPF_6$  in  $EC (3:7) + 0.5 wt.\% FEC$*

The results of galvanostatic testing for the cells tested with the electrolyte  $1.2M LiPF_6$  in  $EC:EMC (3:7) + 4 wt.\% SA$  formation both at room temperature and at +40°C are overlaid in *Fig. 16*. The nominal capacity obtained at a current rate of 1C for the cell formation at room temperature is 296.07 mAh, with a coulombic efficiency of 93.1%, while for the cell formation at +40 °C, the obtained capacity is 287.9 mAh, with a coulombic efficiency of 95.8%. The cycling stability after

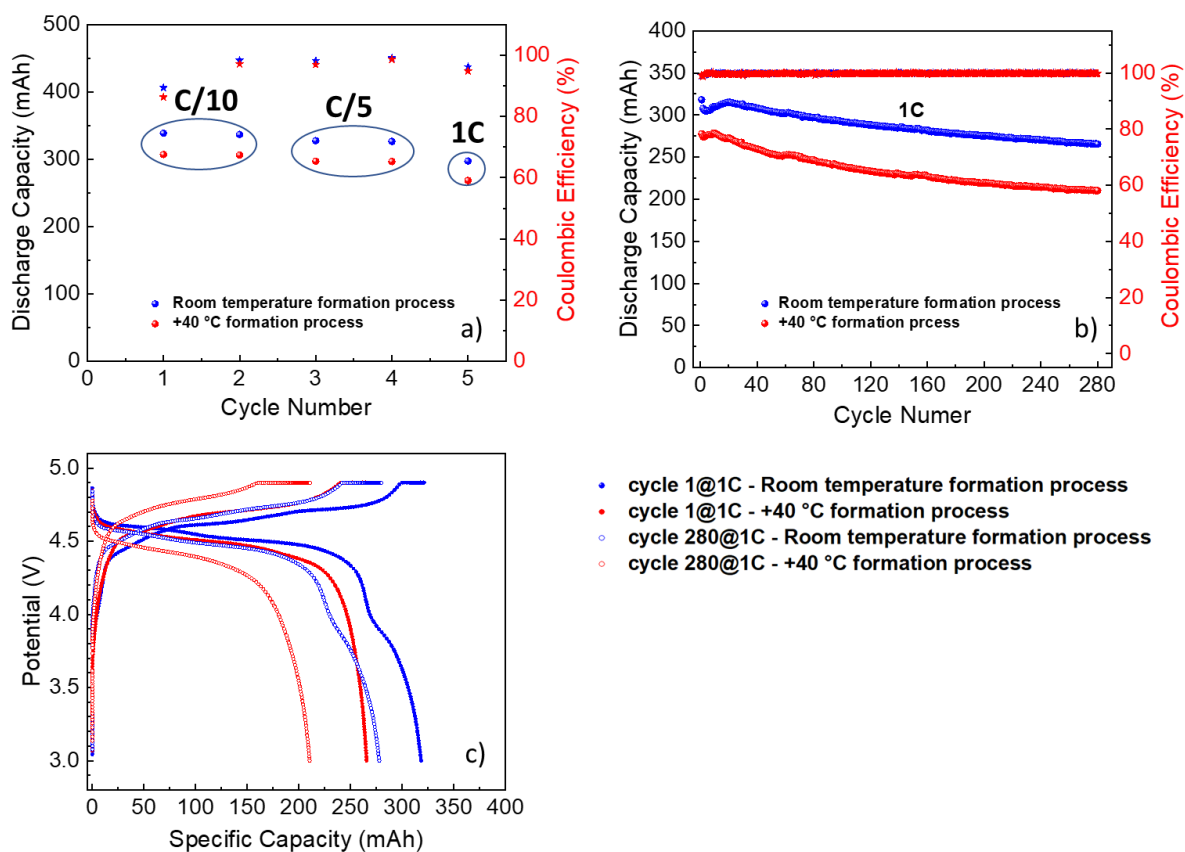
280 cycles at 1C is higher for the cell formation at room temperature, and the coulombic efficiency for both cells is approximately 100%. The capacity obtained after formation and gas removal at 1C for the cell formation at room temperature is 317.4 mAh, and after 280 charge/discharge cycles, it is 221.3 mAh, thus the capacity retention is 69.7%. Additionally, the capacity loss is 0.34 mA/cycle. The capacity obtained for the cell formation at +40 °C at 1C is 289.5 mAh, and after 280 cycles at 1C, the capacity decreased to 206.7 mAh, resulting in a capacity retention of 71.3% with a loss of 0.29 mA/cycle.



**Fig. 16.** Graphical representation for the pouch-cell formation at room temperature and at +40 °C: a) cell formation (2 cycles at C/10, 2 cycles at C/5, and 1 cycle at 1C), b) cycling stability over 280 cycles at 1C, and c) charge/discharge profile of the first cycle at 1C and the 280<sup>th</sup> cycle at 1C, tested with the electrolyte 1.2M LiPF<sub>6</sub> in EC (3:7) + 4 wt.% SA

Formation and electrochemical testing of the cells tested with the electrolyte 1.2M LiPF<sub>6</sub> in EC (3:7) + 0.5 wt.% FEC, formation at room temperature and at +40 °C, are presented in Fig. 17. Both the obtained capacity and cycling stability are higher for the cell formation at room temperature. Thus, the nominal capacity obtained at 1C for the cell formation at room temperature is 297.2 mAh, while for the cell formation at +40 °C, it is 268.8 mAh, with a coulombic efficiency of 96.2% and 94.7%, respectively. After 280 cycles at 1C, the capacity for the cell formation at room temperature is 277.7 mAh, and for the cell formation at +40 °C, it is 210.3 mAh. The capacity retention for the cell formation at room temperature is 87.2%, while for the cell formatted at +40 °C, it is 79.2%.





**Fig. 17.** Graphical representation for the pouch-cell formation at room temperature and at +40 °C: a) cell formation (2 cycles at C/10, 2 cycles at C/5, and 1 cycle at 1C), b) cycling stability over 280 cycles at 1C, and c) charge/discharge profile of the first cycle at 1C and the 280<sup>th</sup> cycle at 1C, tested with the electrolyte 1.2M LiPF<sub>6</sub> in EC (3:7) + 0.5 wt.% FEC

The results of the experiments are presented through the above graphs, which illustrate the variation of capacity, efficiency, and safety of the Li-ion cells as a function of formation temperature and the electrolyte used.

#### **Experimental results for NMC811-based cathodes for Li-ion batteries**

In this experimental section, the results obtained on *single-layer* and *multi-layer pouch cells* are presented. The technological process for producing NMC811 electrodes is similar to the process for producing LNMO cathodes. *Single-layer* cells were made from one cathode, one anode, and a separator, while *multi-layer* cells were made from four cathodes and five anodes, using the same separator as in the case of *single-layer* cells.

The preparation of electrolytes additive with TMSB was achieved by combining it in various concentrations with the standard LP30 electrolyte (1M LiPF<sub>6</sub> in EC:DMC 1:1) in a controlled argon atmosphere. In Table 4, different percentages of TMSB additive added to the electrolyte can be found.

*Table 4. Electrolytes used in single-layer and multi-layer pouch cells*

	<b>Electrolyte + additive</b>	<b>Cell name</b>
<b>NMC811/graphite</b> <i>Single layer</i>	1M LiPF <sub>6</sub> in EC:DMC 1:1 – LP30	Electrolyte std.
	1M LiPF <sub>6</sub> in EC:DMC 1:1 + 1 wt.% TMSB	Electrolyte std.+ 1 wt.% TMSB
	1M LiPF <sub>6</sub> in EC:DMC 1:1 + 3 wt.% TMSB	Electrolyte std.+ 3 wt.% TMSB
<b>NMC811/graphite</b> <i>Multi layer</i>	1M LiPF <sub>6</sub> in EC:DMC 1:1 – LP30	Electrolyte std.
	1M LiPF <sub>6</sub> in EC:DMC 1:1 + 1 wt.% TMSB	Electrolyte std.+ 1 wt.% TMSB
	1M LiPF <sub>6</sub> in EC:DMC 1:1 + 3 wt.% TMSB	Electrolyte std.+ 3 wt.% TMSB

After filling the *pouch cells* with electrolyte, its were sealed with a dedicated system for this stage. These steps were carried out within a controlled atmosphere system.

The formation and testing of the cells were performed using the Neware testing system *Fig. 18* at room temperature, which ranged between 22°C and 25°C.



*Fig. 18. Testing of pouch cells on the testing system*

The same protocol was used for all *single-layer* and *multi-layer* cells: two cycles at a current rate of 0.1C, two cycles at a current rate of 0.2C, and one cycle at a current rate of 1C, within the potential range of 3.0 V – 4.4 V. The gases resulting from the formation process *Fig. 19* were removed in the controlled atmosphere system. After the degassing process, the cells were resealed and prepared for galvanostatic testing.

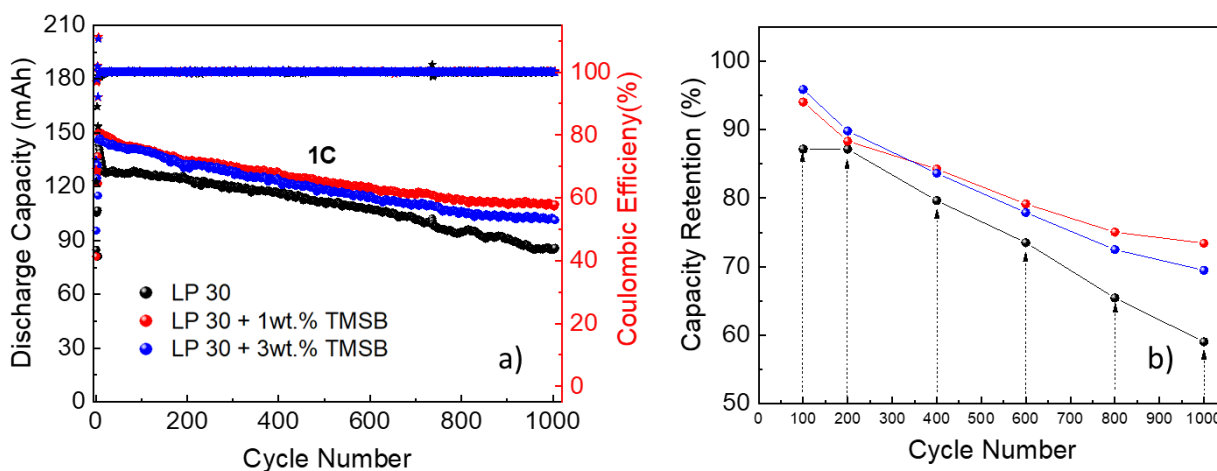


*Fig. 19. Multi-layer pouch cells NMC811/graphite after formation*



The testing of *single-layer pouch cells* was carried out simultaneously, with two cells being tested for the different percentages of additive. The *single-layer pouch cells* were tested using the cycling stability protocol.

In *Fig. 20 a*, the results obtained for the three electrolytes used in testing the *single-layer pouch cells* are presented. A higher cycling stability is observed for the cell tested with the *LP 30 + 1 wt.% TMSB* electrolyte, with a capacity retention of over 75% after 1000 charge/discharge cycles at a current rate of 1C *Fig. 20 b*. In the case of the cell tested with the *LP 30 + 3 wt.% TMSB* electrolyte, the capacity retention is approximately 70% after the same number of cycles, while the cell tested with the *LP 30* electrolyte without additive shows a greater capacity loss after 1000 cycles, reaching a capacity retention of below 60% after those 1000 cycles. The capacity loss for the cell tested without additive is 0.074 mA/cycle, for the cell tested with 1% additive in the electrolyte it is 0.049 mA/cycle, and 0.055 mA/cycle for the cell tested with 3% additive in the electrolyte.



*Fig. 20. The graphical representation for the single-layer pouch full cell NMC811 a) the cycling stability profile over 1000 cycles at 1C and b) the capacity retention after 1000 cycles, tested with the LP 30, LP 30 + 1 wt.% TMSB, and LP 30 + 3 wt.% TMSB electrolytes*

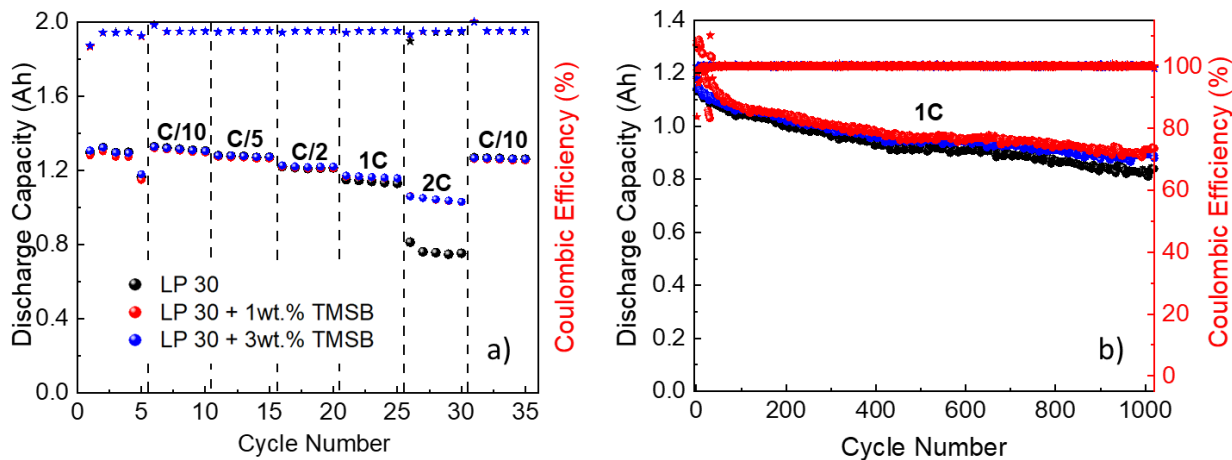
The testing of *multi-layer pouch cells* was carried out according to two protocols: rate performance protocol and cycling stability protocol. As with the *single-layer cells*, the same electrolyte was used, with the same percentage of *TMSB* additive added.

Through the rate performance protocol, the electrochemical behavior of the cells was evaluated based on the electrolyte and additive used at different current rates. The performance protocol consisted of 5 cycles at different rates: (C/10, C/5, C/2, 1C, 2C, C/10).

*Fig. 21 a* and *b* present the results of the galvanostatic testing for the different percentages of additives in the electrolyte within the two testing protocols: the rate performance protocol and the cycling stability protocol. The differences in capacity among the various percentages of additives are evident at a current rate of 2C. The *LP 30* electrolyte with 1 wt.% *TMSB* demonstrated the best

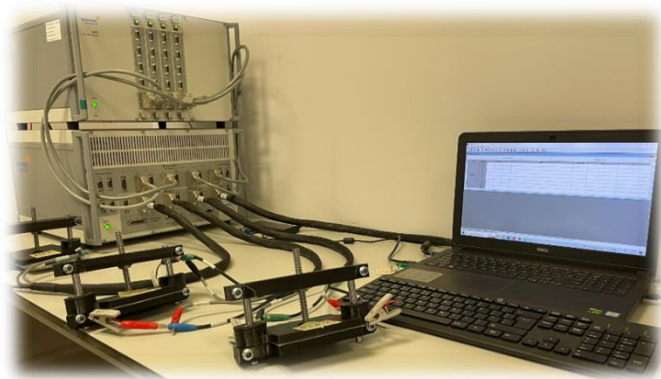
discharge capacity, followed by the *LP 30* electrolyte with 3 wt.% *TMSB*. In contrast, the most unstable electrolyte was the one without additive.

In the rate performance protocol, the electrolytes with 1 wt.% *TMSB* and 3 wt.% *TMSB* demonstrated the best discharge capacity at various current rates. Additionally, the highest cycling stability was observed after 1000 charge/discharge cycles for the electrolyte with 1 wt.% *TMSB*, while the electrolyte without additive recorded the lowest electrochemical performance.



*Fig. 21. Graphical representation for the multi-layer pouch cell NMC811: a) rate performance protocol at different current rates, b) cycling stability profile, 1000 cycles at 1C, tested with the LP 30, LP 30 + 1 wt.% TMSB, and LP 30 + 3 wt.% TMSB electrolytes*

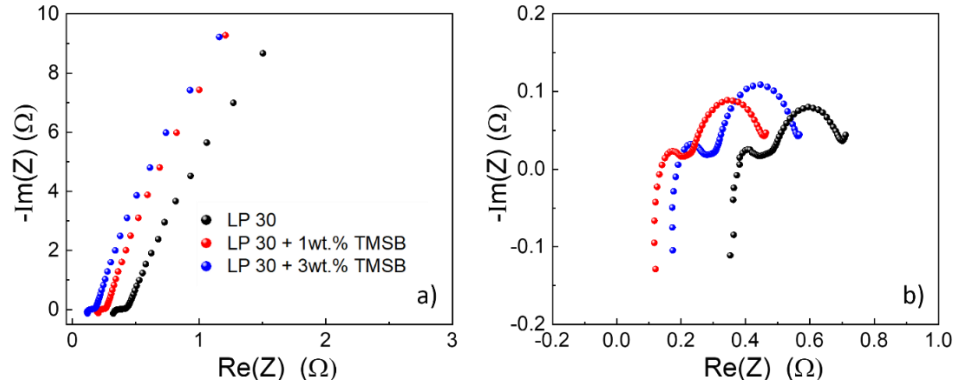
EIS measurements were performed using the Solartron testing system *Fig. 22* in a frequency range between 500 kHz and 100 mHz, with a current amplitude of 5 mA.



*Fig. 22. Testing of pouch cells was conducted using the testing system*

The results of the impedance experiment are graphically represented in the form of Nyquist plots, before and after galvanostatic testing *Fig. 23* for the *single-layer pouch cells*. The contact resistances obtained for the fresh cells tested with the *LP 30* electrolyte without additive, *LP 30 + 1 wt.% TMSB*, and *LP 30 + 3 wt.% TMSB* were 0.32  $\Omega$ , 0.12  $\Omega$ , and 0.11  $\Omega$ , respectively. After galvanostatic testing, these values increased to 0.35  $\Omega$ , 0.17  $\Omega$ , and 0.20  $\Omega$ , *Table 5*. An increase in contact resistance is observed after 1000 charge/discharge cycles. These results suggest the formation of a stable solid-electrolyte interphase and a more efficient lithium ion transfer for the

cells tested with the *LP 30 + 1 wt.% TMSB* and *LP 30 + 3 wt.% TMSB* electrolytes. In *Fig. 23 b*, the formation of two semicircles is observed, which are attributed to the reactions at the anode and cathode.

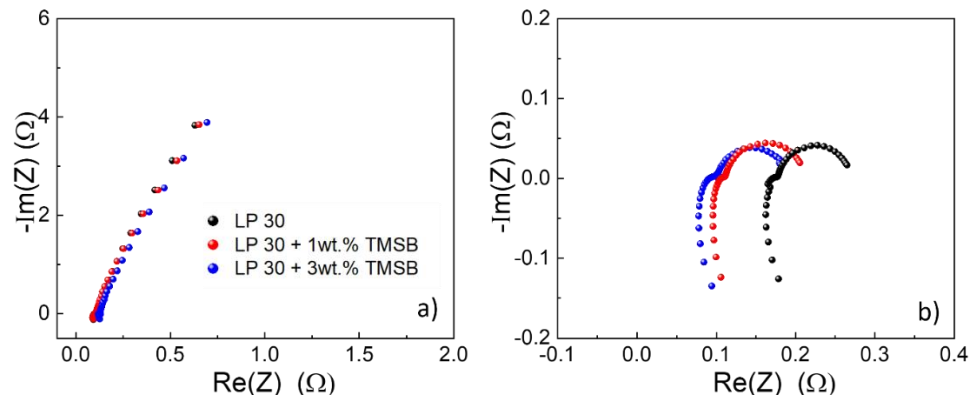


*Fig. 23. Electrochemical impedance spectroscopy for the single-layer pouch cell: a) before galvanostatic testing, b) after testing, using the LP 30, LP 30 + 1 wt.% TMSB, and LP 30 + 3 wt.% TMSB electrolytes*

*Table 5. Values of internal resistance at different states, both before and after testing, for single-layer pouch cells, depending on the electrolyte*

Electrolyte	Before testing (fresh cells)		After galvanostatic testing	
	Contact resistance ( $\Omega$ )	Resistance at a frequency of 1 kHz ( $\Omega$ )	Contact resistance ( $\Omega$ )	Resistance at a frequency of 1 kHz ( $\Omega$ )
<b>LP 30</b>	0.32	0.39	0.35	0.45
<b>LP 30 + 1 wt.% TMSB</b>	0.12	0.23	0.17	0.20
<b>LP 30 + 3 wt.% TMSB</b>	0.11	0.15	0.20	0.27

Impedance measurements for the *multi-layer pouch cells* were conducted under the same conditions as those for the *single-layer cells*. The results are graphically represented in the form of Nyquist plots *Fig. 24*, both before and after testing. The contact resistances obtained for the fresh cells tested with the *LP 30* electrolyte without additive, *LP 30 + 1 wt.% TMSB*, and *LP 30 + 3 wt.% TMSB* were 0.09  $\Omega$ , 0.09  $\Omega$ , and 0.12  $\Omega$ , respectively. After galvanostatic testing, the contact resistance values were 0.17  $\Omega$ , 0.10  $\Omega$ , and 0.09  $\Omega$ , *Table 6*.



**Fig. 24.** Electrochemical impedance spectroscopy for the multi-layer pouch cell: a) before galvanostatic testing, b) after testing, using the LP 30, LP 30 + 1 wt.% TMSB, and LP 30 + 3 wt.% TMSB electrolytes

**Table 6.** Internal resistance at different states, both before and after testing, for multi-layer pouch cells, depending on the electrolyte

Electrolyte	Before testing (fresh cells)		After galvanostatic testing	
	Contact resistance ( $\Omega$ )	Resistance at a frequency of 1 kHz ( $\Omega$ )	Rezistența de contact ( $\Omega$ )	Contact resistance ( $\Omega$ )
<b>LP 30</b>	0.092	0.103	0.178	0.094
<b>LP 30+ 1 wt.% TMSB</b>	0.092	0.101	0.105	0.107
<b>LP 30 + 3 wt.% TMSB</b>	0.125	0.120	0.094	0.174

In *Chapter 6*, the performances obtained from experimental tests and the potential use of Li-ion batteries in the *LNMO/graphite pouch cell* configuration are analyzed, with an emphasis on stationary and automotive applications. The study includes an evaluation of the *LNMO/graphite* material, highlighting its technical advantages, electrochemical behavior, and durability in various usage scenarios. Additionally, the significant potential of this material in the development of future energy solutions is assessed, emphasizing its capacity to improve efficiency and reliability in practical applications.

A series of *LNMO/graphite pouch cells* were electrochemically evaluated with various electrolytes, including *1.2M LiPF<sub>6</sub> in EC:EMC (3:7)*, *1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC*, *1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 2 wt.% FEC* and *1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 4 wt.% SA*, at different temperatures and testing protocols.

The cells underwent a formation process that included 2 cycles at rates of 0.1C and 0.2C, followed by a cycle at 1C. Subsequently, a rate performance testing protocol was applied at various rates, consisting of 5 cycles at rates of 1C, 2C, 5C, 10C, and 15C, *Fig 25 a*. After this protocol, the cells were tested for 100 cycles at a current rate of 1C at room temperature and another 100 cycles at the same current rate of 1C at a temperature of 50 °C. The next stage included 500 cycles at 1C at room temperature, followed by another rate performance test with 5 cycles at rates of 0.1C, 0.2C,

1C, 2C, 5C, 10C, 15C, and 0.1C. Finally, the cycle stability at 1C was evaluated to determine the number of charge/discharge cycles a cell can endure before reaching the end of its lifespan.

The cycling stability of the cells was investigated at temperatures of 23°C and 50°C. Fig. 25 b presents the discharge capacities after 130 cycles at a rate of 1C for different formulations, where the discharge capacities are 110.9, 115.1, 109.3, and 115.8 mAh·g<sup>-1</sup>, respectively. The observed increase in capacity during cycling at a current density of 1C is attributed to the wetting process and electrochemical activation. Therefore, the content of additives, especially 4 wt.% SA and 0.5 wt.% FEC, significantly contributes to faster kinetics, resulting in improved cell performance. Even after several cycles, the charge/discharge profiles of the cells with 4 wt.% SA and 0.5 wt.% FEC additives in the electrolyte show minimal degradation, demonstrating enhanced cycling stability.

The discharge capacities after 230 electrochemical cycles conducted at a current rate of 1C and tested at a temperature of 50 °C for the cells tested with the electrolyte 1.2M LiPF<sub>6</sub> in EC:EMC (3:7), 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC, 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 2 wt.% FEC and 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 4 wt.% SA additive in the electrolyte were reported at 91.5, 92.9, 76.3, and 67.5 mAh·g<sup>-1</sup>, respectively. It is observed that all cells exhibited a reduction in capacity, primarily attributed to the high testing temperature [10, 11, 14].

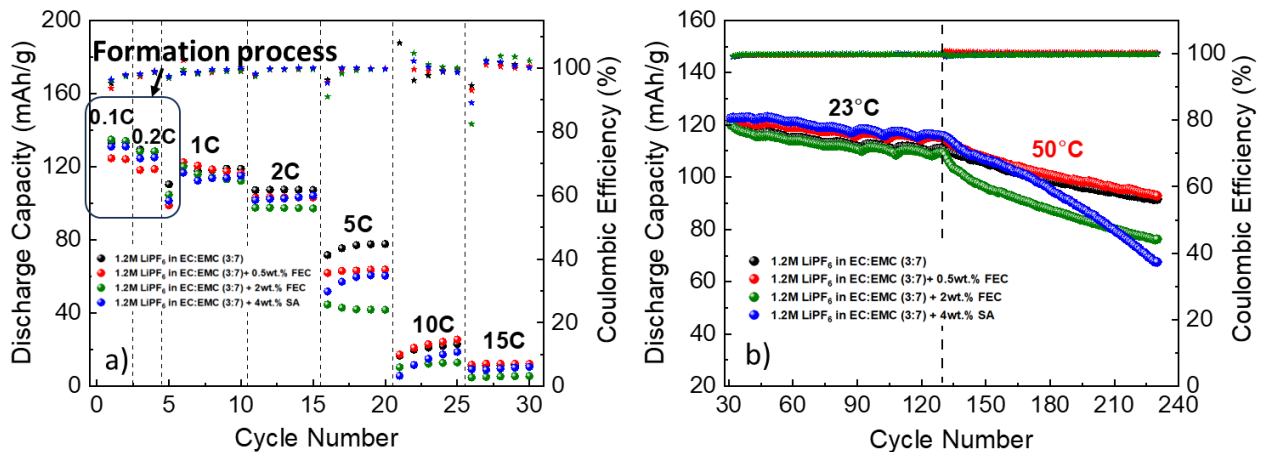
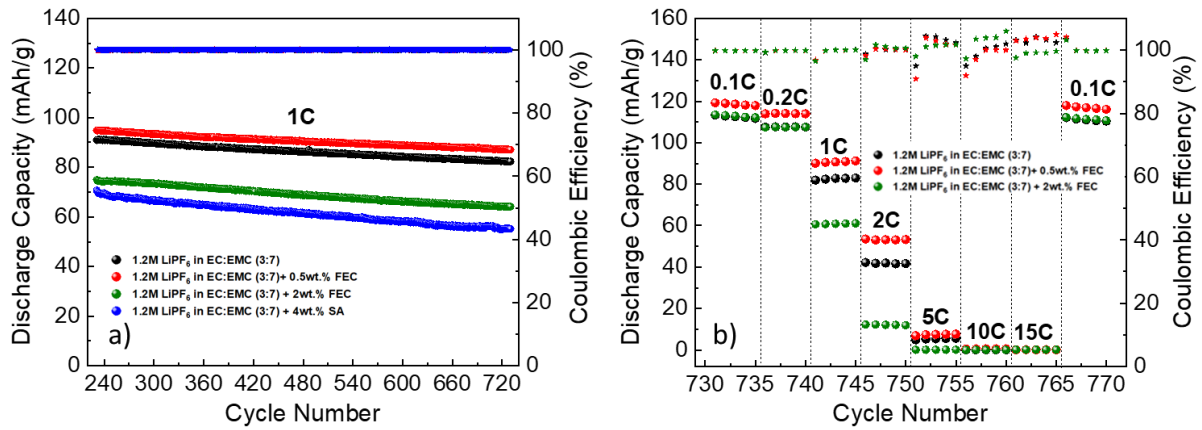


Fig. 25. a) The formation process and capacity test at different rates, and b) the cycling stability at room temperature and at 50°C at 1C rate

An additional evaluation of the cycling stability was conducted for all four types of cells. After undergoing 730 cycles at a rate of 1C, the cells exhibited minimal capacity loss, as shown in Fig. 26 a. The cells with 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC and the 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) electrolyte demonstrated higher capacity compared to those with 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 2 wt.% FEC and 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 4 wt.% SA. Fig. 26 b presents another capacity test involving 5 cycles at various rates (0.1C, 0.2C, 1C, 2C, 5C, 10C, 15C, and 0.1C). There is a good capacity reversibility observed during the retest at 0.1C. This suggests that the interface between LNMO and the electrolyte remains stable and that there is no significant decomposition of

the *LNMO* material and/or the electrolyte during performance tests, indicating their robust stability [12]. Cells containing 0.5 wt.% *FEC* additive in the electrolyte demonstrated the highest capacity achieved at different rates.

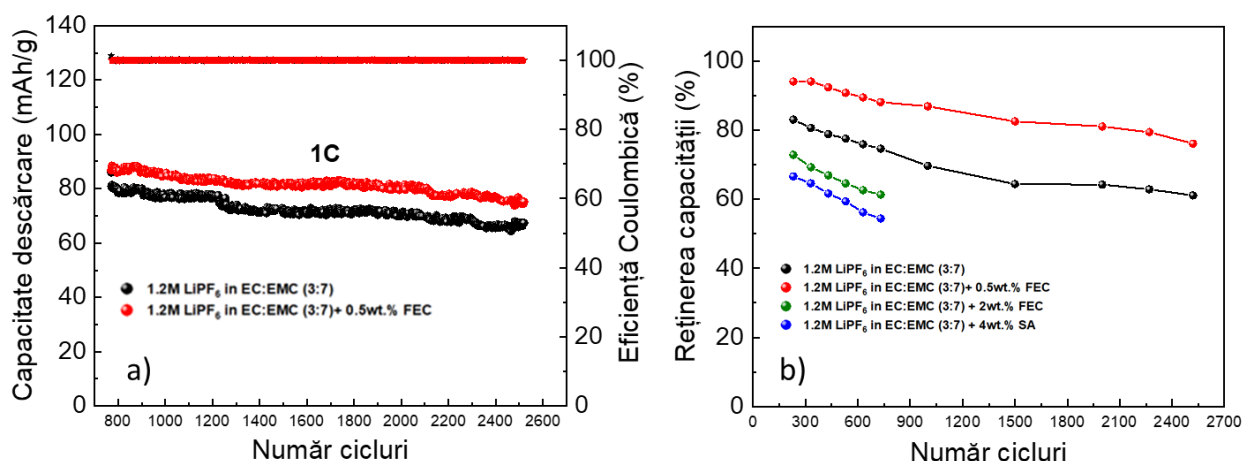


**Fig. 26.** a) Cycling stability at 1C and b) capacity at different rates: 5 cycles at 0.1C, 0.2C, 1C, 2C, 5C, 10C, 15C, and 0.1C

In *Fig. 27 a*, another analysis was conducted over 2500 cycles at a current rate of 1C for cells with the electrolyte *1.2M LiPF<sub>6</sub> in EC:EMC (3:7)* and for cells with *1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC* additive in the electrolyte. It was observed that the cells containing 0.5 wt.% *FEC* exhibited the highest capacity among all tested cells. These results regarding the extended cycles of the cells with the 0.5 wt.% *FEC* additive highlight the effectiveness of the additive in the electrolyte by increasing capacity and long-term cycle stability [13].

Cells utilizing 0.5 wt.% *FEC* additive in the electrolyte demonstrate remarkable capacity retention exceeding 80% even after undergoing 2500 cycles across various testing protocols and also tested at a high temperature of 50 °C. The cell using the electrolyte *1.2M LiPF<sub>6</sub> in EC:EMC (3:7)* shows a slightly lower capacity retention of 70% under the same conditions as the cell tested with *1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC* additive in the electrolyte. However, cells with 2 wt.% *FEC* and 4 wt.% *SA* additives in the electrolyte formulation exhibit capacity retention below 80% after the initial 300 charge/discharge cycles - *Fig. 27 b*.





**Fig. 27.** a) Cycling stability for the 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) and 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC at 1C, b) capacity retention for the electrolyte 1.2M LiPF<sub>6</sub> in EC:EMC (3:7), 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 0.5 wt.% FEC, 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 2 wt.% FEC and 1.2M LiPF<sub>6</sub> in EC:EMC (3:7) + 4 wt.% SA additives in the electrolyte

Chapter VII summarizes the main conclusions of the research, highlighting the original contributions made in the Li-ion batteries. The results of the research obtained during this period of the study are presented, along with potential future development perspectives.

### Overall conclusions

Safety is a primary concern in large-scale Li-ion battery-based applications, such as power sources for electric vehicles and energy storage systems in power grids. These systems contain numerous Li-ion batteries configured in complex series and parallel connections to achieve the required voltage and capacity.

Failures in Li-ion battery-based systems can occur from a variety of factors, including aging and abuse conditions such as mechanical, electrical and thermal abuse. Abuse conditions can usually lead to sudden failures, while aging results in gradual failures. Once a Li-ion battery fails, a series of side reactions are triggered, such as the breakdown and regeneration of the solid electrolyte film, melting of the PP/PE-based separator, and breakdown of the cathode, electrolyte and anode. These events lead to decreased capacity, reduced power, swelling and thermal losses, which can lead to emissions of smoke, fire and explosion. The most common cause of thermal losses is internal short-circuit, a mechanism that is not yet fully understood and requires further research. Mechanical abuse conditions include mechanical shocks, falls, collisions and vibration, while electrical abuse manifests itself through external short-circuits, overload and over-discharge. Thermal abuse, which can include global overheating due to high ambient temperature and localized overheating due to poor contact, is a direct cause of thermal losses.

Given the variety of failures and the complexity of their mechanisms, it is essential to adopt effective strategies to improve the safety of large Li-ion battery-based systems in order to reduce the

risk of thermal loss and/or fires. Safety strategies can be divided into two main categories: passive and active strategies. Active safety strategies focus on preventing abuse conditions that can lead to thermal loss, while passive strategies aim to improve safety by modifying materials and reducing the risks associated with failure. In this context, material modification is the most fundamental approach to enhance the internal safety of Li-ion batteries. However, low-cost material modification without jeopardizing electrochemical performance remains a challenge.

Several test protocols have been developed to evaluate the safety, reliability and performance of these batteries. Some of the advantages of these protocols are:

*Enhanced safety:*

Test protocols are designed to evaluate the safety of Li-ion batteries under various operating and environmental conditions. These include tests such as overload, overvoltage, short circuit and extreme temperature to identify and prevent the risk of fire, explosion or other accidents. Rigorous testing according to protocols establishes that Li-ion batteries are safe to use in a variety of applications, from personal electronic devices to electric vehicles and energy storage systems.

*Improved reliability:*

The protocols are developed to evaluate the reliability of Li-ion batteries under normal and extreme conditions. These tests may include repeated charge and discharge cycles, electrochemical impedance spectroscopy analysis, and other methods to assess long-term cell performance and durability. By identifying and eliminating potential problems in the early stages, testing protocols help to increase the reliability and durability of Li-ion batteries, thereby reducing maintenance and replacement costs.

*Benchmarking and traceability:*

The test protocols provide a standardized framework for evaluating Li-ion batteries, making it easy to compare performance and characteristics between different products and technologies. This benchmarking is important for the industry, allowing developers to evaluate their products objectively.

*Improving innovation and efficiency:*

Test protocols can stimulate innovation and technology development by setting high standards for performance, safety and reliability. By rigorously testing to these protocols, developers are encouraged to continuously improve their products, optimize production processes, and bring innovations leading to more efficient and reliable Li-ion batteries. Test protocols are essential to ensure the safety, reliability and optimal performance of Li-ion batteries. They contribute to improving industry standards, stimulate innovation and give consumers confidence in the products that they are using.



*LNMO*-based Li-ion cells are a promising candidate to become one of the main energy storage technologies due to their multiple advantages, including high energy density, high potential, zero cobalt in the composition, which contributes to lower production costs and increase the long-term sustainability of the batteries.

The performance improvement of *LNMO*-based active material for Li-ion batteries is strongly influenced by the formatting process, that can be optimized by a careful and integrated approach. In addition to temperature, other factors such as charge/discharge parameters, electrolyte composition and electrode architecture play an important role in determining the results of the formatting process.

Experimental studies on *LNMO/graphite pouch cells* have demonstrated that the formation temperature has a significant impact on cell performance. Higher temperatures lead to faster formation processes, but can cause degradation of the active material and electrolyte, with negative effects on cell capacity and durability.

Studies suggest that the optimal formatting temperature for Li-ion cells with active *LNMO/graphite* material is between 20°C and 25°C. At this temperature, optimal cell performance with high capacity and efficiency can be achieved. Operating temperatures outside this range can have a negative effect on performance and can lead to irreversible changes in Li-ion cells.

Also, *NMC811/graphite pouch cells* in different *single* and *multi-layer* configurations were electrochemically tested using *LP30* standard electrolyte with different percentage of additive - *trimethylsilyl borate (TMSB)*, and tested by galvanostatic and impedance measurements.

The cycling stability of *single layer* cells after 1000 cycles at 1C, demonstrated a loss of 0.049 mA/cycle for the cell tested with 1 wt.% *TMSB*, compared to a loss of 0.074 mA/cycle and 0.055 mA/cycle for cells tested without additive and with 3 wt.% additive in the electrolyte, respectively. Studies performed on *multi-layer* cells demonstrated that 1 wt.% *TMSB* and 3 wt.% *TMSB* give the best results at high current rates. In terms of cycling stability, the same percentage of 1 wt.% *TMSB* additive in the electrolyte had the best performance in terms of electrochemical stability.

The experimental results suggest that *TMSB* is an efficient additive for *NMC811/graphite* configuration, improving cycling stability by forming a thin and tough protective layer at the electrode-electrolyte interface. *TMSB* also helps to reduce gas formation as a result of electrolyte decomposition. In the case of the *NMC811/graphite* system, for both cell configurations, after 1000 cycles at 1C cycling rate, the presence of the 1 wt.% *TMSB* additive led to a significant improvement in the retention capacity, performance and cycling stability of the cells, independent of the electrode number.

From these results, the tested cells with *LNMO/graphite* active material as well as the cells with *NMC811/graphite* active material have the potential to accelerate the development of safer, more sustainable and more efficient energy solutions. The additives considerably improved cell

performance by stabilizing the interfaces: the solid electrolyte interface, the electrolyte-cathode interface but also ameliorated the reduction of electrolyte and electrode degradation effects.

The main objective of this study was to develop hybrid electrodes combining both power and energy efficiency for use in next-generation Li-ion batteries. The research aimed to develop innovative electrodes to optimize battery performance in different applications, from portable electronic devices to electric vehicles and renewable energy storage systems. By combining advanced materials and different testing protocols, the goal was to create efficient, sustainable and low-cost solutions capable of meeting the demands of the global energy market. The results of the study provide significant contributions towards the development of more efficient energy storage technologies, thus advancing sustainability and innovation in the energy sector.

In conclusion, both *NMC811* and *LNMO* cells are promising energy storage technologies with the potential to transform the way we manage and consume energy. By continuously improving these technologies, we can move towards a more sustainable and efficient energy system. Continued research and innovation in these technologies is essential to improve performance and expand applications. The motto of turning today's challenges into opportunities will lead to the development of improved solutions to meet future energy demands.

### ***Original contributions***

*Development of new cobalt (Co) free hybrid electrode materials and architectures:* The focus was on the identification and use of innovative materials that would eliminate the use of costly and environmentally problematic cobalt. The aim was to create electrodes that offer superior performance in terms of lifecycle stability without compromising material sustainability and affordability.

*Improving the environmental impact and environmental sustainability of batteries:* The study aimed to reduce the environmental footprint of Li-ion batteries by using environmentally friendly materials and adopting eco-friendly recipes, replacing organic solvents with aqueous solvents for graphite-based anode processing.

*Optimization of manufacturing processes and development of new testing protocols:* Another step was to improve electrode manufacturing processes. This included the development of new testing protocols designed to ensure optimal battery performance under various conditions of deployment. The new testing protocols were designed to better assess battery durability, stability and safety.

*Development and optimization of LNMO/graphite pouch Li-ion cells:* by combining an innovative hybrid electrode design with a considerable improvement over the current state of the art in Li-ion technology.

The development of *NMC811/graphite pouch cells* by introducing an innovative, thermally

safer electrolyte system based on *LP30 (1M LiPF<sub>6</sub> in EC 1:1)* and the additive tris(trimethylsilyl)borate (*TMSB*). The use of this boron-based additive *TMSB* compatible with the electrode-separator assembly has improved electrochemical performance at high voltages. The development of *NMC811/graphite pouch cells* is an economical solution to reduce the risk of ignition and swelling of *pouch cells*, which are essential for energy storage applications and automotive applications.

### ***Dissemination of research results***

The research study includes contributions of the author, among which the following can be mentioned:

- 1 scientific paper submitted for publication in the UPB journal, *Series C Electrical Engineering and Computer Science*, as the principal author.
- 5 scientific papers published in ISI - listed journals as co-author.
- 2 scientific papers published in BDI - listed journals, as co-author.
- 1 participation in a national conference.
- 41 participations in international conferences.
- 4 co-authored patent applications.

Research team member in 10 national and 2 international projects on different technologies: Li-ion, Na-ion, Li-S and solid-state batteries.

### ***Prospects for future applications and development directions***

The research will continue to focus on advancing energy storage technologies, in particular to improve the performance of Li-ion and post-lithium batteries. It is essential to explore innovative solutions that meet growing market demands such as energy density, safety and durability.

*Improving graphite anodes:* A promising direction will be the insertion of silicon into graphite anodes to increase their capacity. This combination has the potential to significantly increase the energy density and overall efficiency of storage systems.

*Advanced electrolyte studies:* Further research on electrolytes will be crucial. The impact of different concentrations of additives on the electrochemical behavior of the batteries will be assessed and the evolution of the resulting gases during formatting will be monitored.

*Implementing advanced monitoring technologies:* One innovative direction concerns the integration of optical sensors into the developed *pouch*-type Li-ion cells. This will enable real-time monitoring of critical parameters such as charging level, temperature and battery health. Continuous monitoring will facilitate prompt intervention if problems are detected, thus improving safety and reliability.

*Optimize charging and discharging algorithms:* Using advanced monitoring data to refine algorithms for managing the charge and discharge cycle will maximize battery lifetime. This

optimization will have significant benefits in applications requiring increased reliability, such as electric vehicles and energy storage systems.

*Environmental Impact Assessment:* An important direction will be the assessment of the environmental impact of new battery technologies, thus ensuring new, environmentally friendly cathode processing methods.

*Applications:* A promising application for developed cells will be the development of next-generation drones. These batteries, due to their high energy density and durability, will enable drones to operate over longer distances and remain airborne for extended periods of time. This will broaden the possible uses of drones in various fields such as commercial supplies, environmental monitoring, infrastructure assessment and emergency response. Also, the integration of optical sensors and advanced technologies will enable new functions such as autonomous navigation and real-time data analysis, making drones more versatile and efficient.

*In the last chapter,* the bibliography of the thesis is presented, providing a solid base of references that supported the development of this research.

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