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Electrochemical and Post-Mortem Study of Pyrrolinium-Based Ionic Liquid on a Single-Layer Pouch Cell

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Abstract

Ionic liquid (IL)-based electrolytes have garnered significant interest for enhancing lithium-ion battery (LIB) safety due to their non-flammability, thermal stability, high conductivity, and broad electrochemical stability. We propose novel pyrrolinium-based ionic liquids to enhance lithium-ion mobility and address safety concerns in LIBs. This study investigated LiTFSI in [Pyr13] [FSI] ionic liquid for Li-ion batteries. The cyclic stability and rate performance of single-layer full cells with commercial graphite anode and NMC532 cathode were examined for the electrolyte required per cell and compared to those using a carbonate electrolyte (LP30). Electrolytes containing LiTFSI/[Pyr13] [FSI] exhibited satisfactory rate performance and stable cycling for 100 cycles. The reversible capacity was maintained at over 22 mAh for a cycle period of 100 cycles with an electrolyte loading of 161.8 $\mu\text{L}/\text{cm}^2$. These electrolytes exhibited the highest oxidation stability, surpassing 5.3 V compared to that of the Li^+/Li reference electrode. Long cycle life of up to 1000 cycles was conducted, showing 80% capacity retention. Post-mortem analysis using scanning electron microscopy (SEM) and micro-Raman spectroscopy allowed observation of LiTFSI/[Pyr13] [FSI] effects on cathode and anode active particle stability, and reduced formation of secondary reactions between the IL and battery electrodes.

Keywords: Li-ion batteries; ionic liquid; separator; LiTFSI; FSI; Pyrrolinium based ionic liquid; binary ionic liquid; LiTFSI-PPY₁₃FSI



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1. Introduction

Investigations into energy conversion and storage systems for small- and large-scale devices have concentrated on lithium-ion batteries (LIBs) due to their balanced rate performance and long cycling life [1,2]. To increase the total energy density of cells, numerous types of electrode materials with high working voltages and specific capacities have been developed [3–9]. This will enable LIBs to have broader applications in the future. Extensive studies have focused on the anode, cathode, and electrolyte, which are the three fundamental components of lithium or lithium-ion batteries. Since the inception of lithium-ion batteries, graphite has been the predominant anode material due to its unparalleled combination of attributes. These attributes encompass its relatively low cost, abundance, high energy and power density, and exceptional cycle life. Natural and synthetic forms of graphite facilitate the reversible insertion of lithium ions at voltages proximate to that of

lithium, achieving a maximum theoretical lithium storage capacity of 372 mAh/g [10–14]. Cathode materials generally consist of transition metal oxides that are capable of undergoing oxidation to higher valences upon the removal of lithium [15,16]. The oxidation of the transition metal can preserve the charge neutrality within the compound; however, significant compositional alterations frequently result in phase transitions. Therefore, it is essential to utilize crystal structures that exhibit stability over broad compositional ranges. Conventional cathode materials can be categorized by structure into layered LiMO_2 (where $\text{M} = \text{Co}, \text{Ni}, \text{Mn}$, etc.), spinel LiM_2O_4 (where $\text{M} = \text{Mn}$, etc.), and olivine LiMPO_4 (where $\text{M} = \text{Fe}, \text{Mn}, \text{Ni}, \text{Co}$, etc.). Studies have predominantly focused on these materials and their derivatives. Recently, there has been a growing interest in new structural intercalation materials, including silicates, borates, and tavorite [15–21].

Electrolyte solutions also should be designed optimally to ensure peak performance within the electrochemical system. The electrolyte is essential for lithium-ion conduction between the electrodes, as it must facilitate rapid ionic transport and create stable, conductive passivation layers on the electrodes. Furthermore, it should be capable of enduring both oxidative and reductive decomposition [22–24]. As LIB systems progress towards enhanced power and energy densities, electrolyte solutions encounter the challenge of supporting faster rate capabilities across wider voltage ranges, especially with increasingly demanding electrode materials. The choice of electrolyte composition, including lithium salts, solvents, and additives, plays a crucial role in determining rate capabilities, capacity, energy, cycle life, and safety. Standard electrolyte solutions typically consist of 1.0 M lithium hexafluorophosphate (LiPF_6) combined with a mixture of ethylene carbonate (EC) and one or more of the following: ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), diethyl carbonate (DEC), in addition to various performance-enhancing additives [3,22,25]. Compared to other lithium salts like LiClO_4 , LiBF_4 , and LiAsF_6 [22], LiPF_6 does not have the best lithium-ion mobility or any other remarkable traits; instead, it offers a mix of balanced qualities. However, there are significant safety concerns with LiPF_6 . These include thermal instability at high temperatures, separation into gaseous PF_5 and LiF , and hydrolysis leading to the creation of HF [26]. The second chemical is extremely poisonous and damages the solvents used in the electrolyte and the active materials used in the electrodes. Lastly, it has been claimed that extremely harmful fluoroethanol derivatives can be produced when ethylene carbonate and LiPF_6 react at high temperatures with cathodes based on transition metals, which may raise concerns for a thermal runaway, either by an internal short or by external damage [8,23,27,28]. Consequently, the development of a more robust lithium salt is unquestionably a crucial strategy for enhancing the safety of lithium-ion battery electrolytes. Studies indicate that LiTFSI offers several benefits, including excellent thermal and chemical stability, a high thermal decomposition point (360 °C), resistance to moisture, superior ionic conductivity, and a broad electrochemical window (5.0 V vs. Li^+/Li , using glassy carbon as the working electrode). Furthermore, LiTFSI finds extensive use in innovative battery designs, where it can create a stable SEI layer on graphite anodes, significantly mitigating the dendrite issue on lithium anodes. As a result, LiTFSI shows promise as a potential replacement for LiPF_6 [29,30].

There are numerous advantages to using ionic liquid (IL) electrolytes in electrochemical processes, including their low flammability, wide electrochemical window, and excellent thermal stability. After its discovery in 1985 by Armand and Moursli, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) quickly rose to the top of the list of potential possibilities. For lithium-ion and lithium metal batteries, pyrrolidinium-based ILs with bis(trifluoromethylsulfonyl)imide [TFSI] and bis(fluorosulfonyl)imide [FSI] anions have been extensively studied because of their stability at very high electrochemical window (5–6 V versus Li/Li^+) [31,32]. It has been found that these ILs can prevent dendrite de-

velopment on lithiated graphite and lithium metal by creating a stable solid electrolyte interphase (SEI). This allows for rechargeable high-energy-density batteries to be cyclable for a long time [33–38]. The practical challenges with Li^+ mobility and the rate performance of batteries with ILs stem from the poor conductivities and high viscosities of IL electrolytes containing Li^+ [23,39,40]. The ultimate objective is to entirely substitute frequently employed organic carbonate-based liquid electrolytes with non-flammable and leak-proof systems that possess high Li^+ -ion mobility and little reactivity towards other cell components. An example of this would be the successful demonstration that the integration of ILs leads to an enhancement in ionic conductivity. As per the literature, very few researchers demonstrated pouch cell prototypes with ionic liquids as electrolytes; Yamagata et al. [41] demonstrated the normal cycling data under extreme vacuum conditions, Raghibi et al. [42] characterized the evaluation of gases formed by comparing different electrolytes with ILs, indicating less gas formation using LiTFSI ionic liquids, Moreno et al. [43] demonstrated that the introduction of ternary electrolyte is capable of functioning through the utilization of high-voltage NMC cathodes and graphite anodes. Takahashi et al. [44] demonstrated the performance of NMC/Gr pouch cell with increased lithium salts concentration in ILs with increased rate capability, and Chancelier et al. [45] produced an LTO/NMC coin and pouch cells with imidazolium-based electrolytes to mainly highlight the electrochemical and thermal stability with organic carbonate electrolytes over 50 cycles indicating they are highly thermally stable and less stable for over-charge conditions.

Pyrrolidinium-based ionic liquids (ILs), including N-butyl-N-methyl pyrrolidinium bis(trifluoromethylsulfonyl)imide ($\text{Py}_{14}\text{TFSI}$) and N-propyl-N-methyl pyrrolidinium bis(fluorosulfonyl)imide ($\text{PYR}_{13}\text{FSI}$), have been identified as effective electrolyte components for improving interfacial stability in lithium-based batteries. Their elevated electrochemical and thermal stability, non-flammability, and low volatility render them suitable for inhibiting dendrite growth and enhancing cycle life. When utilized with fluorinated anions such as FSI^- or TFSI^- , these ionic liquids decompose during electrochemical cycling, resulting in the formation of durable, LiF-rich solid electrolyte interphases (SEI) on lithium metal anodes and cathode electrolyte interphases (CEI) on high-voltage cathodes. Research indicates that mixed-anion systems (TFSI/FSI) produce thicker and more uniform solid electrolyte interphases (SEI) of approximately 110 nm, which improve lithium plating and stripping behavior while mitigating parasitic reactions [46,47]. $\text{PYR}_{13}\text{FSI}$ -based electrolytes on the cathode side stabilize CEI layers and reduce oxidative degradation, especially in high-voltage materials (>4.5 V) such as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [48,49]. Recent advancements in gel-based quasi-solid-state electrolytes that include $\text{Py}_{14}\text{TFSI}$ and lithium salts have demonstrated effective formation of SEI/CEI and stable lithium cycling under challenging conditions [50]. The findings underscore the multifunctional role of pyrrolidinium ionic liquids in enhancing the safety and performance of lithium battery systems, as stated in Table 1 below.

Table 1. Pyrrolidinium ILs roles and mechanisms for the formation of stable SEI and CEI.

Role	Mechanism
Electrochemical stability	High anodic stability restricts decomposition at the cathode; stability against reduction safeguards the anode [48].
LiF-rich layer formation	The decomposition of $\text{FSI}^-/\text{TFSI}^-$ results in the formation of stable, ion-conductive LiF at the solid electrolyte interphase (SEI) and the cathode electrolyte interphase (CEI) [46].
Uniform deposition of Li	Stable solvation contributes to the reduction in dendrite growth [50].
Suppression of side reactions	Creates thick interphases that obstruct solvent/electrolyte access to electrode surfaces [48].
Temperature tolerances	Elevated thermal stability facilitates a consistent interphase at high temperatures [50].

The details discussed above effectively highlight the significance of ionic liquids (ILs); however, a more detailed explanation regarding the selection of 1.3 M LiTFSI in Py₁₃FSI as the electrolyte is warranted. The selection of this system can be supported by a number of considerations. Initially, employing a lithium salt that possesses the same anion (TFSI[−]) as the ionic liquid minimizes ion–ion mismatch, mitigates unfavorable clustering, and enhances salt solubility and ion mobility [51,52]. The pyrrolidinium cation (Py₁₃⁺) is well-known for its outstanding electrochemical stability, extensive electrochemical window, thermal resilience, and non-volatility, which renders it especially appealing for lithium-based systems. Moreover, elevating the concentration of Li salt typically leads to higher viscosity and lower conductivity; however, a concentration around 1.3 M offers a suitable compromise: adequate Li⁺ carrier density while maintaining optimal ionic conductivity. The Py₁₃FSI/LiTFSI system has been noted for its advantageous Li⁺ transference numbers and enhanced interfacial stability with electrodes, which lead to improved SEI formation and cycling performance [53,54]. Ultimately, electrolytes based in IL demonstrate enhanced safety characteristics owing to their non-flammable nature and reduced volatility. Additionally, the presence of the bis(fluorosulfonyl)imide anion (FSI[−]) contributes to the suppression of crystallization and expands the liquid range [54]. Collectively, these factors validate the choice of 1.3 M LiTFSI in Py₁₃FSI for this study.

Our study investigates the design parameters, electrolyte loading of binary mixtures of ILs, with 1.3 M lithium bis (trifluoromethylsulfonyl)imide (LiTFSI) in 1-Methyl-1-propylpyrrolidinium bis(fluorosulfonyl)imide (Py₁₃FSI) as an electrolyte for our single-layer pouch cell comprising NMC532 as cathode, graphite as anode, and GF/D separator at room temperature (RT) with capacity of 40mAh. Furthermore, a standard organic electrolyte, consisting of 1.0 M lithium hexafluorophosphate (LiPF₆) in a mixture of ethylene carbonate and diethyl carbonate (EC: DMC, 1:1 by volume), was evaluated for comparative analysis. Formation cycles effect, cycling results, electrolyte loading, comparison of different separators effect on the cell, and electrolyte degradation in open air were evaluated for their electrochemical performances. In addition, we performed the post-mortem analysis of the electrodes using scanning electron microscopy (SEM) and micro-Raman spectroscopy to better understand the structural, composition, and surface morphologies of the cycled electrodes.

2. Experimental Section

2.1. Materials

The commercial graphite and NMC532 electrode sheets obtained from NEI (NEI Corporation, Somerset, NJ, USA) which have nominal specific capacity values of around 372 mAh/g and 165 mAh/g, ionic liquid (IL) consisting of 1.3 M lithium bis (Trifluoromethylsulfonyl)imide (LiTFSI) in 1-Methyl-1-propylpyrrolidinium bis(fluorosulfonyl)imide (Py₁₃FSI) from IoLiTEC (IoLiTec-Ionic Liquids Technologies, GmbH), Germany, and LP30 (1M LiPF₆ in EC: DMC, 1:1 by volume) from Sigma-Aldrich, battery grade were used for making a single-layer pouch cell of 40 mAh capacity. Whatman GF/D was used as a baseline separator due to improved wettability against ionic liquids. The anode consists of 4.2 × 5.2 cm graphite, cathode is 4 × 5 cm NMC532, and the separator with 4.5 × 5.5 cm sizes were used for the pouch cell fabrication. The N/P ratio of the cell was maintained at 1.1. Different separators, named the ceramic-coated separator, were used in the pouch cell, whereas Celgard membrane (Celgard2500, Celgard company, Selestat Cedex, France) cellulose and polyamide from Sartorius, Germany, were used in CR2032.

2.2. Electrochemical Characterization

Full and half cells in coin cell configurations were assembled within an argon-filled glove box, where the levels of oxygen and moisture were maintained below 1 ppm. The assembly utilized stainless steel CR2032 coin cell components sourced from MTI. The coin cells were tested for high C-rates of 1 C and 2 C. The pouch cells underwent manufacturing processes within the controlled environment of the dry room. Graphite and NMC-532 electrodes functioned as the anode and cathode, respectively, with a diameter of 15 mm. Separators are composed of polyamide, cellulose, and Celgard 2500. All cells were saturated with an electrolyte solution. Following construction, cells containing IL electrolyte were maintained at room temperature for a duration of 12 h prior to testing.

The electrochemical stability window (ESW) was evaluated at room temperature (25 °C) using linear sweep voltammetry (LSV). Lithium symmetric cells (Li/Li) and stainless steel (SS)/IL/CR2032 coin-type cells were assembled systematically, utilizing 15 mm diameter lithium metal foil for both the working and counter electrodes, with a glass microfiber separator (Whatman GF/D) positioned in between and conducted using VSP-3B-100 (Biologic, Seyssinet-Pariset, France) galvanostat/potentiostat system with an applied sweep rate of 10 mV s^{−1}. The charge–discharge tests and cyclic voltammetry (CV) measurements were carried out on BCS-805 (Biologic) with a C-rate of 0.1 C and scan rate of 0.05 mV·s^{−1}. Table 2 shows the operation conditions for the formation of cycling and charge–discharge protocol.

Table 2. Operating conditions for the pouch cell.

Operating Voltage Window		2.7–4.2 V
Operating Temperature		RT
Formation Cycles	5 cycles	CCCV(C/30)
Cycling Tests	100 and 1000 cycles	0.1 C(C/10) charge and discharge

The investigation of rate capability was conducted at various current densities ranging from 0.05 C to 2 C (0.05 C → 0.1 C → 1 C → 2 C → 0.1 C). The current density was altered after five cycles at each C-rate, maintaining a consistent cut-off voltage of 2.7–4.2 V. Following assembly, cells with conventional and IL electrolytes were stored at room temperature for 12 h before testing to assess electrolyte degradation in open air. One side of the pouch cell is cut open and exposed to the external atmosphere while monitoring the daily weight variation in the cells over the course of a week.

2.3. Post-Mortem Preparation

The pouch cells were first cut on the side, and then each layer was “peeled” with non-conductive tweezers to cut small samples from all parts. In all cases, the separator was too wet to be measurable and would not dry even after treatments at 70 °C during various days. Filter paper was used to cover the electrodes and very lightly pressed for a couple of seconds; this resulted in a significant reduction in IL, noticeable to the naked eye. After this, samples were dried/stored at 60 °C for at least a day. Scanning electron microscopy (SEM) analysis was performed in a Thermofisher Prisma-E SEM. Micro-Raman spectroscopy was carried out in a Horiba Jobin–Yvon LabRaman Hr800 confocal microscope, using a 633 nm focused He–Ne laser as an excitation source.

3. Results and Discussion

In the initial experiments, the electrochemical stability windows (ESWs) were established using linear sweep voltammetry (LSV), revealing that ionic liquid (IL) electrolytes

begin to decompose at voltages of 5 V or higher versus $\text{Li}^+/\text{Li}^\circ$ (Figure S1). The anodic and cathodic thresholds of ionic liquids (ILs) are dictated by the anion's oxidation and the cation's reduction, respectively [55–60]. The high anodic stability at 5.3 V and 4.48 V of the ionic liquid electrolytes is consistent with the findings of Haojun et al. and Perez et al., which indicate anodic stabilities of TFSI and LiTFSI-Py₁₃TFSI at or above 5 V relative to $\text{Li}^+/\text{Li}^\circ$ at room temperature [61–64]. The cycling performances of Gr//NMC pouch cells (approximately 40 mAh) were examined using two different electrolytes: conventional electrolyte and 1.3 M LiTFSI in Py₁₃(FSI), at a temperature of 25 °C. The tests of pouch cells were conducted through three methods: (i) comparison of the formation cycle between LP30 and IL, (ii) stabilization of the SEI via formation cycles, and (iii) quantification of electrolyte (IL) loading (mL/cm^2). In the experiments (i & ii), the batteries underwent charging at a rate of C/30 until they reached 4.2 V and discharging at the same rate down to 2.7 V. In the third set of experiments, the batteries underwent a charge–discharge cycle at a C/10 rate, ranging from 4.2 V to 2.7 V. Simultaneously, the currents necessary for sustaining the cell voltage and the cell volumes were quantified. A subsequent series of experiments were conducted to assess electrolyte degradation by measuring the weight of the cell under open air conditions. The electrode surfaces were analyzed post-mortem using scanning electron microscopy (SEM) and Raman techniques.

3.1. Comparison of Formation Cycle Between Electrolytes and Electrolyte Degradation

The formation process involves the growth of surface interfaces, which serve to stabilize the electrolyte in relation to the lithiated graphite. The electrolyte undergoes decomposition on the surface of the newly formed graphite anode, leading to the creation of the solid electrolyte interface (SEI) layer. This layer serves as a passivation barrier, exhibiting electrical resistance while allowing the conduction of lithium ions [12,53,65,66]. The SEI layer serves as a protective barrier, inhibiting ongoing electrolyte decomposition and solvent co-intercalation within graphitic layers during subsequent cycles [67]. Most formation processes employ three or more cycles at C/20 or C/30 charge and discharge rates. In this study, we suggest the comparison and stable formation protocol for IL electrolytes.

The batteries underwent galvanostatic cycling for a total of two cycles during the formation process. The program included two cycles at a C/30 rate for pouch cells, followed by cycles at a C/10 rate as detailed in Table 2. The cycling performances of Gr-NMC pouch cells were examined using the two electrolytes: 1 M LiPF₆ [EC: DMC, 1:1 by volume], also known as LP30, and 1.3 M LiTFSI in Py₁₃(FSI).

Figure 1 shows the Coulombic efficiency (CE) profile of NMC 532/graphite cells for the two-cycle formation protocol. The discharge capacities were below 24 mAh and 38 mAh in the first discharge, yielding a first cycle. Coulombic efficiency (CE) was around 51% and 82% for LP30 and IL. The low Coulombic efficiency during the initial formation cycle is anticipated due to electrolyte reduction occurring at the anode, leading to the formation of the solid electrolyte interphase (SEI) [12,13,68]. The results indicate that the ionic liquid demonstrates superior performance in comparison to the commercial electrolyte as LP30 did not have any additives included in it for better performance, concluding that the solvent decomposes with cycling [8]. Additionally, there is a likelihood of an increased number of formation cycles, which contributes to the establishment of a stable solid electrolyte interphase (SEI) layer, thereby minimizing the cumulative irreversible capacity loss (ICL) throughout all formation steps. A similar trend was followed during the second cycle. The stable SEI for LP30 takes after some cycles as per the literature, which makes an SEI thick layer for the time being, due to the continuous Li plating, SEI layer formation, and some other factors that affect the LP30 electrolyte [69]. As for ILs, formation of stable SEI, higher transport conductivity, and suppressed dendrite formation leads to

higher CE than commercial electrolytes; this was not certain till now, and further studies and characterizations need to be conducted in order to establish completely ILs-based commercial cells.

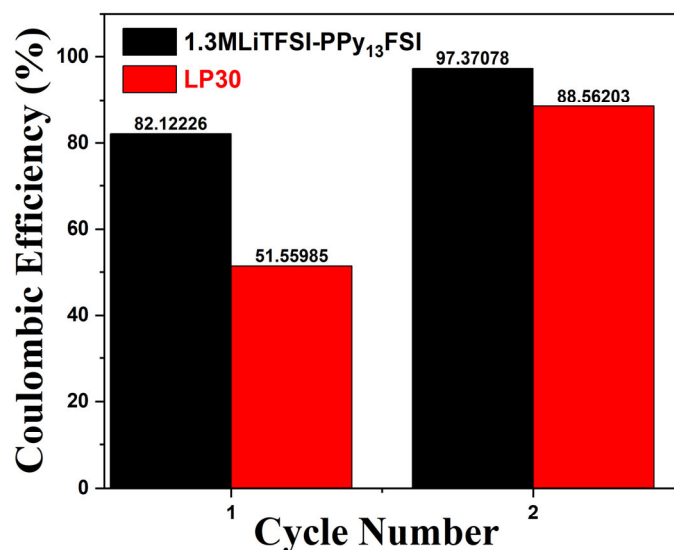


Figure 1. Effect of electrolyte formation of LP30 and IL for 2 cycles at 25 °C.

3.2. Stabilizing the SEI by Formation Cycles

When electrons may move freely through the electrolyte and the electrolyte is subjected to a wide voltage swing, two distinct phases—the anode solid electrolyte interphase (SEI) and the cathode electrolyte interphase (CEI)—can emerge. At lower potentials on the anode, reduction reactions cause electrolyte breakdown and precipitation, whereas at high potentials on the cathode, oxidation reactions do the same. After the first charge/discharge cycle, the capacity loss caused by electrolyte interphase formation is at maximum (ca. 10% in the case of a graphite anode), then it drops dramatically after the second cycle, and finally it drops to less than 0.05% after the third cycle and so on. The ratio of negative to positive capacity, particle surface area, operating circumstances, etc., all have a role in the irreversible capacity loss [68,70–72]. As the anode and cathode currently lack passivation layers that provide electrical protection from the electrolyte, the majority of the electrolyte interphase develops during the initial charge/discharge cycle. The preformed interphase layer from the initial charging cycle obstructs the diffusion of solvent molecules to the electrode surface and impedes electron transfer between the electrode and electrolyte. As a result, if the anode graphite is not substantially exfoliated after the first cycle, subsequent cycling leads to a marked reduction in electrolyte interphase formation [73,74]. The formation process is the step during which the surface interfaces are grown to stabilize the electrolyte against the lithiated graphite [75].

Figure 2 shows the formation cycles and CE profiles for two and five cycles. During formation cycling, the discharge capacities for stabilizing the solid electrolyte interphase (SEI) exhibit a slight increase of 1% charge efficiency (CE) per cycle, stabilizing around the fourth cycle. A similar trend is observed in the fifth cycle, with approximately 98% CE (Figure 2b). This indicates a reduced loss of active lithium during the critical formation stages, which may have contributed to an increase in parasitic reactions, electrolyte decomposition, and SEI growth during the initial cycle. The protocols align with conservative formation strategies that utilize multiple full cycles at low C-rates, enabling them to last several days [67,72,75,76]. The processes of Li intercalation and deintercalation induce volume changes and mechanical stress in the Gr particles [10,77]. This phenomenon leads to a break-and-repair mechanism that also impacts the SEI surrounding the particles. Con-

sequently, several cycles may be necessary to achieve a stable layer. The results indicated that a similar mechanism was observed in the multiple formation cycle strategy, which facilitated stable and smooth cycling in subsequent stages. strategy for stable SEI formation, which enables stable and smooth cycling later.

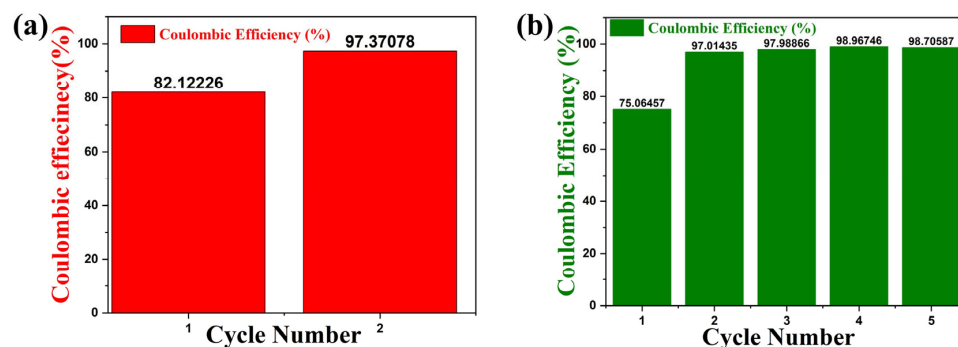


Figure 2. Single-layer Gr-IL-NMC532 pouch cell formation for (a) 2 cycles and (b) 5 cycles for standardizing the SEI layer and electrochemical performance at 25 °C.

3.3. The Effect of IL Loading

The electrolyte loading is defined as a volumetric factor (v_f), indicating the ratio of electrolyte volume to the total pore volume of the anode, cathode, and separator. However, the optimal v_f is not consistently defined, as it may differ based on the cell design and material system employed. Research on various Lithium–Nickel–Manganese–Cobalt–Oxides (NMC) indicates that the optimal v_f values range from 1.4 [78] to 1.9 [79], depending on the proportions of nickel, manganese, and cobalt. Prior research in this domain has concentrated on evaluating cell performance and its impact on energy density. The mechanism by which the electrolyte filling volume affects performance remains inadequately understood. Research examining the relationship between aging phenomena and variations in v_f is insufficiently represented in the literature [78,79]. The filling process consists of multiple stages where electrolyte liquid is dosed into the cell, succeeded by the intermediate wetting of the cell components. The volume of electrolytes affects both the wetting rate of the electrodes and separators, as well as limits the cell's capacity and impacts the battery's lifespan. Excessive electrolytes constitute dead mass and diminish energy density [78].

Figure 3 illustrates the cell formation protocol throughout the lifetime test, contingent upon the volumetric factor. The cells with v_f 60, 80.8, 121.2, 161.8, and 202.02 $\mu\text{L}/\text{cm}^2$ show not much change during the formation cycling, as they are performed at lower C-rates [78,79]; however, there is already a sharp drop in capacity for v_f 60, 80.8, and 121.2 $\mu\text{L}/\text{cm}^2$ over the 100 cycles, the loss of their efficacy owing to a lack of electrolyte inside the cells, which can be seen in Figure 4. Yang et al. [80] distinguished between linear and non-linear aging behavior. The increase in SEI, mainly at the cost of electrolyte, is the critical element during the linear phase. Non-linear aging acts as an indicator for lithium plating, which is initiated by pronounced local electrolyte gradients at the anode and the interface with the separator [80]. It is assumed that the capacity that could not be recovered during discharge will be assigned to a subsequent phase of SEI development, as shown by the efficiency in Figure S2. In addition to the solid electrolyte interphase (SEI) recreation caused by cracking during operation, an additional SEI is formed as unwetted regions draw electrolyte from already wetted areas, which is a consequence of a shift in the existing balance of forces. As electrolyte depletion advances, the ionic conductivity within the pores of the separator diminishes, ultimately leading to the cessation of the cells' functionality. The depletion of the electrolyte and the subsequent lithium plating are identified as the failure mechanisms of the cells [73].

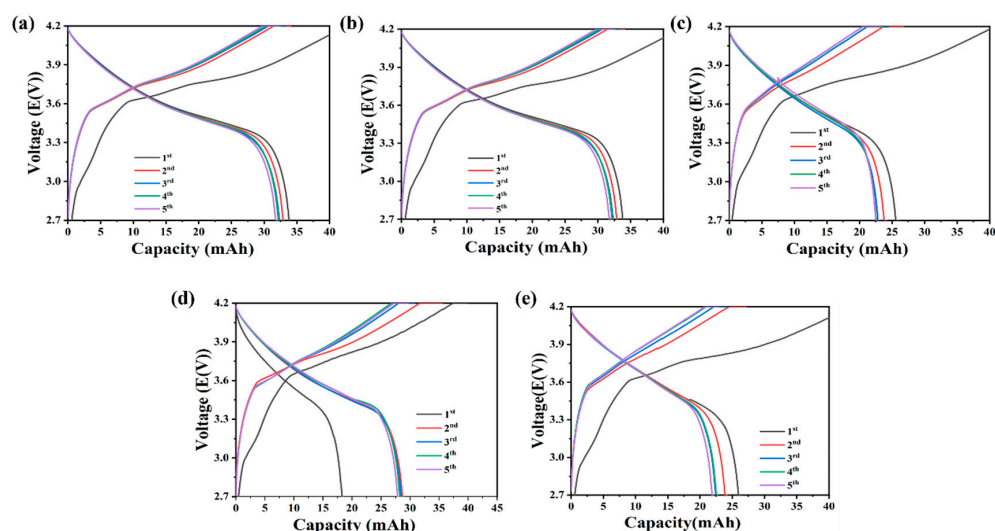


Figure 3. Effect of amount of IL at (a) 60 $\mu\text{L}/\text{cm}^2$, (b) 80.8 $\mu\text{L}/\text{cm}^2$, (c) 121.2 $\mu\text{L}/\text{cm}^2$, (d) 161.8 $\mu\text{L}/\text{cm}^2$, and (e) 202.02 $\mu\text{L}/\text{cm}^2$ on formation of Gr-IL-NMC532 single-layer pouch cell performed at C-rate of 0.1 C at 25 °C.

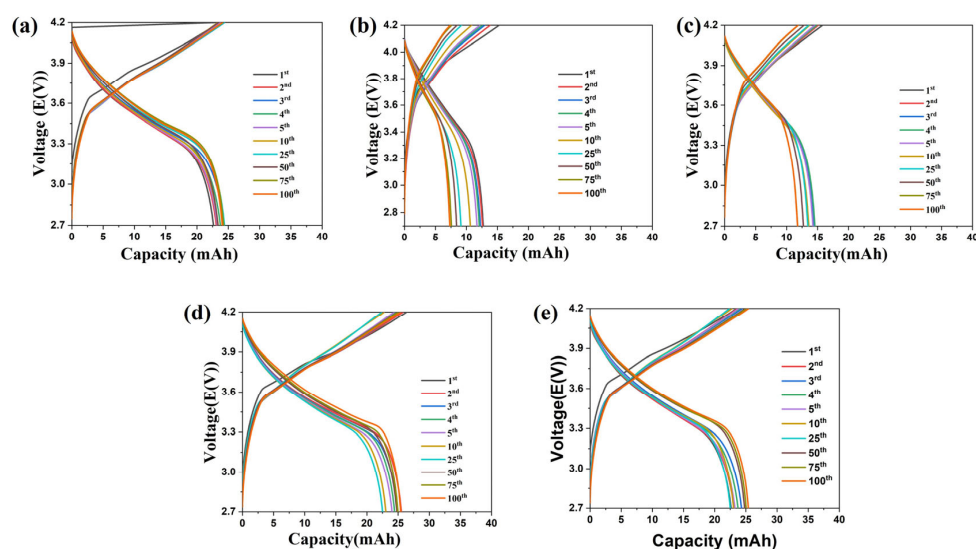


Figure 4. Charge–discharge profile performed at a C-rate of 0.1 C for IL addition of (a) 60 $\mu\text{L}/\text{cm}^2$, (b) 80.8 $\mu\text{L}/\text{cm}^2$, (c) 121.2 $\mu\text{L}/\text{cm}^2$, (d) 161.8 $\mu\text{L}/\text{cm}^2$, and (e) 202.02 $\mu\text{L}/\text{cm}^2$ for Gr-IL-NMC532 single-layer pouch cell at 25 °C.

Increasing the electrolyte amount up to v_f 161.8 $\mu\text{L}/\text{cm}^2$ enhances cell performance as seen in Figure 4d, thereby reducing capacity loss over their lifespan. In larger quantities (v_f 161.8 and 202.02 $\mu\text{L}/\text{cm}^2$), a significant capacity loss is evident in the expanded depiction of the 100 cycles at 0.1 C, as shown in Figure 4d,e. Cells having a lower v_f cycle are worse than seen in Figure 4a–c. A moderate and linearly constant discharge capacity decline throughout the cycle illustrates this. Figure S3 indicates the discharge profile of all v_f in a single graph. When $v_f \sim 161.88 \mu\text{L}/\text{cm}^2$ is reached, the cell performance is only stable for ~ 1000 cycles, as in Figure S4, due to minimal surplus pore volume. A relatively advanced electrolyte consumption causes “roll-over failure” or “sudden death” capacity fading [81,82]. Due to electrolyte deterioration and immobilization, the cell becomes dry, reducing electrode active areas and cell capacity [81]. Increasing the electrolyte capacity to v_f 161.8 $\mu\text{L}/\text{cm}^2$ improves cell performance and removes severe degradation at the end of life; hence, raising the electrolyte volume over v_f 161.8 $\mu\text{L}/\text{cm}^2$ does not improve cell performance. Higher electrolyte contents lead to a faster reduction in discharge capacity

during the first 65 cycles, which is a disadvantage. As v_f increases, capacity decreases. Electrochemical data can be used to establish the optimal electrolyte filling volume for the cell system evaluated, resulting in the highest cell performance. This supports prior research by Günther et al. [78], An et al. [79,83], and Lechtenfeld et al. [84]. Their respective CE profiles are shown in Figure S2. Different types of commercially available separators (Celgard 2500, polyamide, cellulose, and ceramic-coated separators), along with the GF-D, have been used to test the compatibility of the IL, as in Figure S5. Compared to the ceramic-coated separator (Figure S5d), which shows a significant charge–discharge capacity of around 2 mAh capacity at 100 cycles, remaining separators are unable to obtain any electrochemical reactions in the cell which we reported as 0 mAh.

Figure S6 illustrates the dQ/dV , for better understanding of the SEI formation. Figure S5a illustrates the plots for formation cycling and Figure S6b illustrates the plots for 100 cycles of $161.8 \mu\text{L}/\text{cm}^2$ electrolyte loading for the single-layer pouch cell. During the formation cycling, the redox peaks show that there are four distinctive peaks, mainly 3.46 V, 3.64 V, and 3.78 V, indicating that there is an impedance growth in the cell. It can be seen that the polarization rose from initial cycle and then subsequently stabilized finally around fifth cycle. The observed peaks at 3.46 and 3.64 V during charging correspond to alterations in the crystal structure, specifically the transition from graphite C_6 to LiC_x , as well as the H1-M phase change in the NMC. During the initial charge and discharge cycle of the cell, a phenomenon occurs characterized by a reduction in capacity referred to as ‘irreversible capacity loss’, primarily associated with the formation of the solid electrolyte interphase (SEI) layer [79,84–86]. For the 0.1 C cycling, dQ/dV plots indicate two distinctive peaks around 3.61 V and 3.82 V related to complete stabilization of the SEI layer throughout the cycling [79,84].

The charge–discharge curves of graphite and NMC532 for the 1st, 2nd, 3rd, 5th, 10th, 50th, and 100th cycles are shown in Figure S7a,b. The discharge curves of graphite show multiple plateaus below 0.2 V corresponding to the formation of lithium–graphite intercalation [10,12,13,85] and the Li^+ . The specific capacities of both electrodes are 267 mAh/g and 150 mAh/g, respectively. Figure S7c displays the cyclic voltammograms of the graphite analyzed at a scan rate of 0.05 mV s^{-1} at the potential 0–3 V. Two reduction current peaks were observed in the graphite electrode, occurring at 0.71 V (peak I) and 0.06 V (peak II), respectively. The observed peaks indicate two distinct stages in the reductive decomposition of TFSI/FSI molecules, leading to the formation of an SEI [46,47,85]. The peak was observed only in the first cycle, indicating that the formation of the SEI film predominantly took place during this initial scanning phase, with no further appearances in the subsequent cycles.

Figure S7d displays the cyclic voltammograms of the NMC532 analyzed at a scan rate of 0.05 mV s^{-1} at the potential 2.7–5 V. The pristine NMC532 CV displays a singular pair of cathodic and anodic peaks at 3.59/3.89 V, these redox peaks correspond to the $\text{Ni}^{4+}/\text{Ni}^{3+}$ and $\text{Co}^{4+}/\text{Co}^{3+}$ redox couples [86,87]. The height and potential position of the oxidation peak in the initial voltammogram varies from those observed in the following voltammograms. The observed difference arises from the development of the cathode electrolyte interphase (CEI) on the cathode electrode’s surface during the initial cycle of delithiation [88,89].

To determine the utility of a Gr-NMC532 cell with 1.3 M LiTFSI in Py_{13} (FSI) electrolyte solution, charge and discharge capacity was observed at rates between 0.05 C and 2 C (Figure 5a). Changing the discharge rate up to 2 C during many low- and high-rate discharge cycles does not permanently reduce discharge capacity. This confirms the system’s strong cycling ability. As expected, capacity decreases with discharge rate, especially when comparing 0.1 C and (1 C, 2 C) data as shown in Figure S8a,b. The Coulombic efficiency is close to 98% across all discharge rates, so the capacity drop, especially at higher discharge

rates, is not due to damage but rather to lithium transport limitations between Gr-NMC532 electrodes [90]. The capacity at 0.1 C is around 25 mAh which aligns with electrolyte loading of $161.8 \mu\text{L}/\text{cm}^2$ (Figures 4d and S2d).

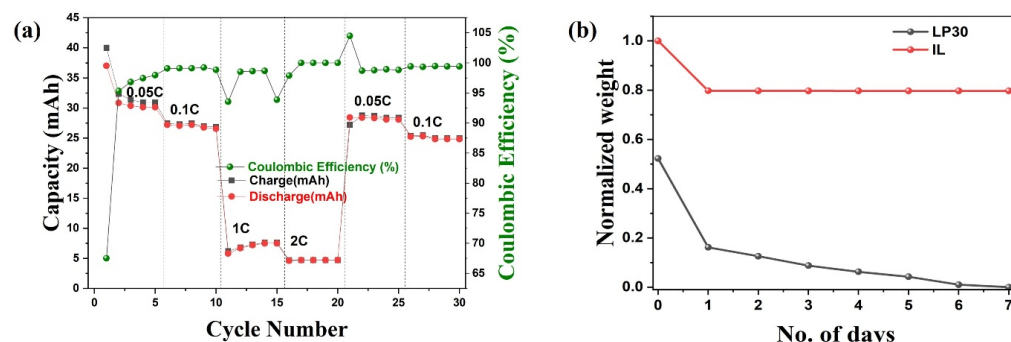


Figure 5. (a) Power cycle at 0.05 C, 0.1 C, 1 C, 2 C, 0.05 C, and 0.1 C at 25 °C for $161.8 \mu\text{L}/\text{cm}^2$ electrolyte loading and (b) stability of electrolyte degradation in open air conditions between LP30 and 1.3 M LiTFSI in $\text{Py}_{13}(\text{FSI})$.

In Figure 5b we can see electrolyte degradation in open air conditions within a week, where we can see that LP30 (black line) degrades day by day and forms precipitates as shown in Figure S9a,b. The results shown are normalized weight decay of electrolyte, indicating that there is a slow decay rate of organic compounds through the time period for LP30, while for IL it is stable around 0.8, indicating a very small amount of Li salt has been degraded and evaporated and is constant at room temperature (red line) as supported by the TGA results [69,91,92]. For LP30 the solvent evaporation takes place continuously, and the color of the electrolyte changes into pale yellow, as can be seen in Figure S9b, with white precipitate formation shown in the circled area (green color) (Figure S9a); this indicates further degradation of the LiPF_6 compound [91,93–95]. Figure S10 indicates that there might be a chance of an IL pouch cell performing an electrochemical reaction after 1 week of exposure to RT with less capacity obtained, around ~13 mAh capacity, for around 16 cycles. This might be due to loss of low boiling point solvents in the IL, for which further characterization is needed in the future. Depending on the electrochemical performances and its physical characterization, the IL properties are summarized in Table S1.

3.4. Post-Mortem Analysis

The post-mortem examination of cycled battery cathode and anode samples aims to uncover the main factors contributing to battery capacity reduction. Investigations are underway to identify and elucidate the formation of deposits, including layers, structural changes in cycled materials compared to their pristine electrodes, and the development of inactive components.

3.4.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is frequently utilized to examine the surface and internal morphological features of electrode materials. Using a scanning electron microscope (SEM), we may examine lithium plating, macroscale porosity, SEI thickness and shape, particle interconnectivity, fracture development, and particle size [14,96,97]. The analysis of the morphology of the SEI layer is of particular importance. One method to enhance surface morphological contrast with the electron beam involves imaging at a low electron acceleration voltage (approximately 1 kV). The thickness of the SEI can range from several to hundreds of nanometres, typically exhibiting greater thickness on the anode in comparison to the CEI on the cathode. Consequently, while an SEI layer is identifiable in SEM images of anode surfaces, distinguishing the CEI layer on cathode surfaces is generally

not feasible. The disassembled pouch cell is shown in Figure S11, where we can see through the naked eye that the graphite electrode is exfoliated more and formed some pits on the electrode surface [98].

Figure 6 shows the SEM images of pristine and cycled anode electrodes. From Figure 6b,c we can observe the presence of irregular thin layers, with dimensions ranging from few to tens of microns (marked in yellow arrows), deposited at the surface of the cycled samples, marked in the corresponding SEM images, which can be associated with the formation of the SEI layer. For the electrode with $161.8 \mu\text{L}/\text{cm}^2$ of IL (Figure 6d), flower-like structures (yellow circle) with dimensions of tens of microns are formed as well on top of the graphite particle. The electrode surface was coated with small particles due to the use of an IL-based electrolyte. The particle structure exhibited no loose aggregates, and the graphite electrode was enveloped by a compact and homogeneous polymer composite layer, which markedly enhanced the battery's capacity and cycle performance [99]. At the surface of other anodes with either higher (Figure 6b) or lower (Figure 6c) quantities of IL, $202.02 \mu\text{L}/\text{cm}^2$ and $80.8 \mu\text{L}/\text{cm}^2$ respectively, the presence of deposits and layered features at the surface of the samples, probably due to the formed SEI layer, appears to be lesser as a higher roughness is observed. This fact can be related to the morphology of the graphite used as active material, which could indicate a lower coverage and hence the formation of a thinner SEI layer at the anode.

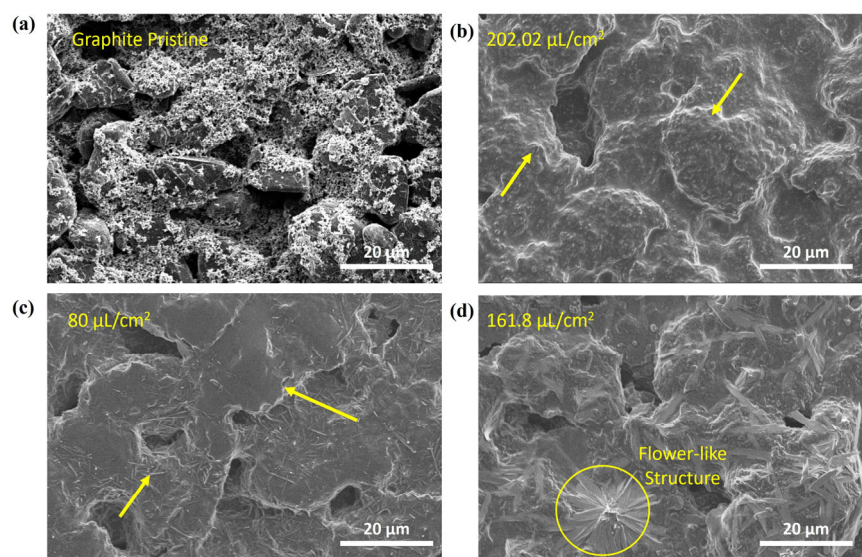


Figure 6. SEM images of Gr-IL-NMC532 single-layer pouch cells at 100 cycles. (a) Pristine graphite; (b) $202.02 \mu\text{L}/\text{cm}^2$, (c) $80.8 \mu\text{L}/\text{cm}^2$, and (d) $161.8 \mu\text{L}/\text{cm}^2$ of electrolyte loading.

The surface morphology of the pristine cathode electrode and cycled electrodes in the ionic liquid electrolytes were also analyzed by SEM. Figure 7a shows the surface of the fresh electrode. In that case, the NMC active material particles can be observed among the binder materials with no deposits present, as expected in the non-cycled sample. After cycling, the surface of the electrodes cycled using IL turned fuzzy and some deposits can be clearly observed (showed as yellow arrows), as shown in the corresponding SEM images (Figure 7b,d). As for the analysis of the anodes presented above, deposits and layered regions, possibly owing to the formation of SEI layer, are observed in all cathodes, being more homogeneous for the sample with an IL quantity of $161.8 \mu\text{L}/\text{cm}^2$ (Figure 7d), as indicated by the yellow color arrow insight. In that case, a thin layer covering all the active material (AM) particles is observed, which can be related to the CEI formation [96,98–100]. Samples with higher quantities of $202.02 \mu\text{L}/\text{cm}^2$ of IL show a thin layer on top of the

particles in addition to significant cracks, as observed in Figure 7b (shown in the yellow arrow), resulting in an incomplete coverage of the cathode. On the other hand, lower quantities of IL, $80.8 \mu\text{L}/\text{cm}^2$, appear to lead to particle dissolution and the formation of different deposits at the surface of the cycled cathodes (Figure 7c).

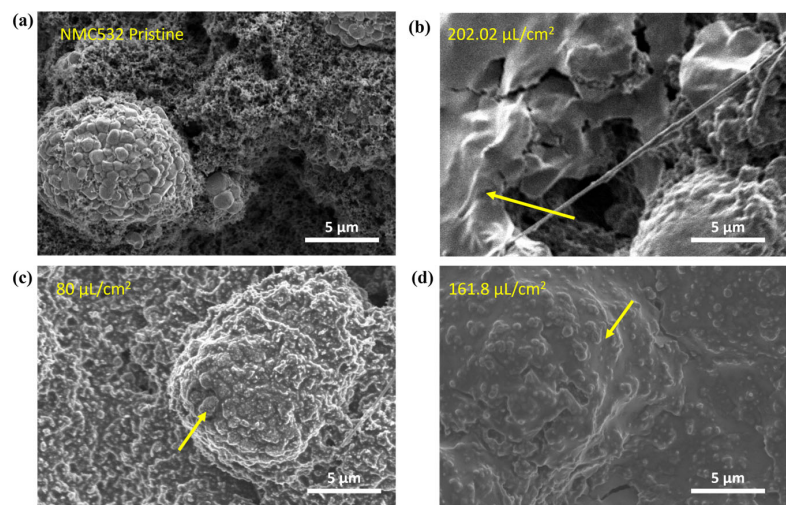


Figure 7. SEM images of Gr-IL-NMC532 single-layer pouch cells at 100 cycles of cathodes. (a) Pristine NMC532; (b) $202.02 \mu\text{L}/\text{cm}^2$, (c) $80.8 \mu\text{L}/\text{cm}^2$, and (d) $161.8 \mu\text{L}/\text{cm}^2$ of electrolyte loading.

3.4.2. Raman Spectroscopy

For the Raman spectroscopy measurements, at least ten measurements were performed at different points of the cleaned electrodes after cycling and averaged to obtain a statistically valid picture of their composition.

At the anodes, the average Raman spectra obtained presents a main region, at high frequencies of $1200\text{--}1500 \text{ cm}^{-1}$ (Figure 8a), related to the graphite and carbon compounds used for the electrode fabrication [79]. The 1340 cm^{-1} peak is usually named D and associated with disorder on the graphite structure, while the peak at around 1580 cm^{-1} is referred to as G and is typical of the perfectly ordered structure [101]. Variations in the ratio of the peaks have been observed and could be associated with different degrees of disorder. However, this association can be masked by the presence of varying carbon organic compounds such as the ones related to the binder or the IL itself.

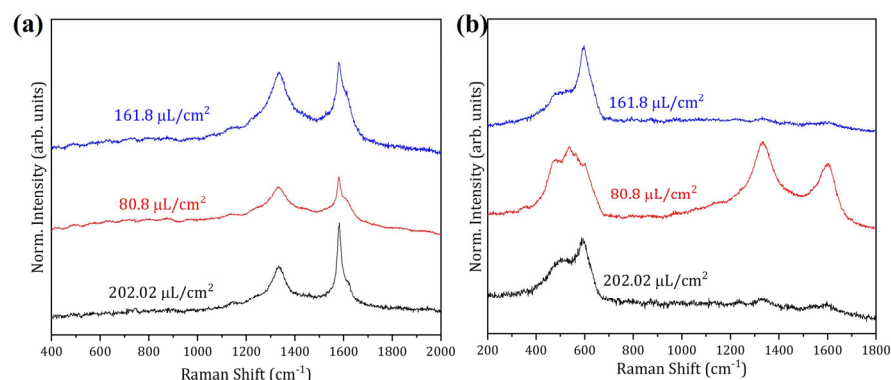


Figure 8. Micro-Raman spectroscopy measurements of Gr-IL-NMC532 single-layer pouch cells at 100 cycles with IL quantities of $202.02 \mu\text{L}/\text{cm}^2$, $80.8 \mu\text{L}/\text{cm}^2$, and $161.8 \mu\text{L}/\text{cm}^2$ of anodes (a) and cathodes (b).

For the dried cathodes, the average Raman spectra obtained can be divided into two clear regions (Figure 8b). The low frequency band at $400\text{--}700 \text{ cm}^{-1}$ is associated with

the NMC vibrational modes [102,103] and the high frequency band composed of two peaks at 1200–1500 cm^{-1} is related to the carbon compounds and IL used for the electrode fabrication that, for the anodes, presents the D and G peaks. Significant variation can be observed mainly for the cathode with low IL quantities with the significant modification of the NMC-related bands, probably due to the formation of spinel and other inactive phases during cycling [104], and the low intensity of this band compared to the one related to organic compounds. On the other hand, the higher presence of IL quantities appears to retain the NMC structure of the AM, as the vibrational modes correlate to that of typical layered NMC [103].

All in all, although the complex composition of the electrodes with the combination of active material, binders, and IL hinders a complete Raman spectroscopy analysis of them, the measurements appear to indicate a better retention of the cathode active material structure during cycling for the higher IL quantities, in correlation with the capacity retention observed in the electrochemical analysis.

4. Conclusions

NMC532/graphite cells made with binary mixture LiTFSI-PPY₁₃FSI ILE went through a prolonged charging/discharging protocol at 0.1 C between 2.5 V to 4.2 V at room temperature. This allowed for a thorough screening of the cells to determine which combination of formation protocol yielded cells with the least amount of capacity fade and stable SEI and CEI. These cells which are being tested can increase the volumetric and gravimetric energy densities of the Li-ion battery. Quantitative analysis of the ILE loading during and after cycling determined the composition changes through SEM and Raman analysis.

SEM surface morphological analysis and Raman spectroscopy indicated the formation of deposits and layered regions with micrometric dimensions at the surface of the cycled samples, especially for IL loading around 161.8 $\mu\text{L}/\text{cm}^2$, which could be associated with the formation of SEI and CEI layers. Moreover, the measurements confirm multiple formation cycling at five cycles is optimal for stable SEI for a long cycle life of around 1000 cycles. Further investigation into separators is warranted to improve wettability and facilitate their application in commercial pouch cell systems, thereby obviating the necessity for GF separators. Such advancements have the potential to enhance various electrochemical and thermal properties, particularly when a minimal quantity of IL is employed to wet the separator, thereby augmenting energy densities.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/batteries11110428/s1>, The supplementary data indicates some electrochemical characterization data and postmortem images of the pouch cell. References [10,12,13,83,87] are cited in the Supplementary Materials.

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Conflicts of Interest: The authors declare no conflict of interest.

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