



Development of safe, green and high performance ionic liquids-based batteries (ILLIBATT project)

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ABSTRACT

This manuscript presents the work carried out within the European project ILLIBATT, which was dedicated to the development of green, safe and high performance ionic liquids-based lithium batteries. Different types of ionic liquids-based electrolytes were developed in the project, based on different ionic liquids and polymers. Using these electrolytes, the performance of several anodic and cathodic materials has been tested and promising results have been obtained. Also, electrodes were formulated using water soluble binders. Using these innovative components, lithium-ion and lithium-metal battery prototypes (0.7–0.8 Ah) have been assembled and cycled between 100% and 0% SOC. The results of these tests showed that such ionic liquids-based prototypes are able to display high capacity, high coulombic efficiency and high cycle life. Moreover, safety tests showed that the introduction of these alternative electrolytes positively contribute to the safety of the batteries.

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1. Introduction

Lithium batteries (LBs) are nowadays one of the most popular energy storage devices. Depending on their cell chemistry LBs can show high energy, high power and high cycle life. For these characteristics, they dominate the consumer portable electronic and telecommunications market. In the last years, LBs have been indicated as the most promising option for the next generation of hybrid and electric vehicles (HV, EV) as well as an attracting candidate for the realization of high performance delocalized energy storage units. Clearly, the wide deployment of lithium batteries in these applications would have tremendous consequences on the

battery-market and it would further strengthen the central role of these systems in the field of energy storage. For that, considerable efforts are now focused on the development and realization of lithium batteries able to fulfil the requirement necessary for these applications.

When the present lithium ion battery technology is considered, the safety and the temperature range of use represents the main drawbacks holding the introduction of these systems in the new applications. As a matter of fact, the commercial systems nowadays available use electrolytes commonly based on organic carbonates (e.g. ethylene carbonate, EC, diethyl carbonate, DEC, ethyl methyl carbonate, EMC) but, since these electrolytes are flammable and volatile, their use poses a serious safety risk and strongly reduces the battery operative temperature range [1,2]. Moreover, liquid electrolytes are always a possible source of cell leakage. For that, alternative electrolytes with improved safety and able to work in a broader operative temperature range are today urgently needed. However, in order to be really effective, the introduction of such advanced electrolytes cannot lead to a reduction of the battery performance.

In the past, many R&D projects were devoted to the development of “solid” and “dry” polymeric electrolytes [3–6]. Polymer

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electrolytes have low volatility and flammability and thus they may be considered as safer than liquid organic electrolytes. Unfortunately, polymeric electrolytes show lower (for many applications insufficient) ionic conductivities than liquid organic solvent-based electrolytes [7]. More recently, the use of ionic liquids (ILs) as electrolyte for lithium batteries have jumped into the centre of interest. The main advantages of ILs towards organic solvents are the non-flammability, the negligible vapor pressure, the high chemical and thermal stability and, in some cases, hydrophobicity [8–11]. For these characteristics, ILs have attracted a large attention for use as “green” solvents and recently have been intensively investigated as electrolytes and/or electrolyte components for lithium batteries [12–21]. The results of these studies indicated ILs as promising electrolytes. However, when the performance of IL-based systems is compared with that of systems containing conventional electrolytes, further improvement appears still necessary. With the aim to combine the favorable properties of polymer electrolyte and ionic liquids, also the realization of polymer electrolytes containing ionic liquids has been investigated in the past. The results of these studies showed that the addition of ionic liquids to conventional polymer electrolytes increase dramatically their ionic conductivity, without negative effects of their mechanical stability [22–26]. However, also in this case, further improvement in term of ionic conductivity appears still necessary.

Considering the results of these studies, the replacement of organic electrolytes with ionic liquids based electrolytes (both, liquid or solid) certainly represents an attracting and promising strategy to improve the safety of the lithium battery technology. Nonetheless, further research is necessary to achieve the performance required for the next generation of batteries when these electrolytes are used.

In this paper we report about some of the results obtained within the European project ILLIBATT (2007–2010, contract no. NMP3-CT-2006-033181), which was dedicated to the development of green, safe and high performance IL-based lithium batteries. Four universities, two research centres and two industries from 7 different European countries were involved in the ILLIBATT Consortium (for more details, see Table 1).

Considering the limitation of the state of the art reported above, the scientific objectives of ILLIBATT project were:

- Synthesis and characterization of solid polymeric electrolytes, either formed by an Ionic Liquid (or a mixture of Ionic Liquids) integrated in a polymer matrix or being a Polymeric Ionic Liquid having properties (ionic conductivity, (electro-)chemical, and thermal stabilities) better than the present polymer electrolytes especially at ambient and lower temperatures. This included the synthesis and processing of novel ILs, polymers, and their composites.
- Synthesis of nano-structured metallic electrode materials, which are able to reversibly store lithium, via electroplating.
- Thorough investigation of interfacial reactions of commercial and newly synthesized cathode and anode materials with ILs and IL-based solid electrolytes.
- Realization of battery concept cells of lithium-ion and lithium metal configurations and investigation of their electrochemical performance and safety.

Following a comprehensive, manifold and multidisciplinary material approach (see Fig. 1), the ILLIBATT partners worked on four key objectives: (1) development of a green and safe solid-state electrolyte chemistry based on ionic liquids and unique ionic liquid-based composites with high performance; (2) use of novel nano-structured high capacity anodes, prepared with the help of novel ionic liquids; (3) investigation of the peculiar electrolyte properties and the specific interactions of these electrolytes

with advanced commercial and self-prepared electrode (anode and cathode) materials with the goal to understand and improve the electrode and electrolyte properties and thus their interactions; and (4) construction of rechargeable lithium cells with optimized electrode and electrolyte components.

The final goal of ILLIBATT was to realize rechargeable lithium batteries with high performance and safety. Specifically, the targets of the project were:

- optimize positive electrodes with specific capacities of at least 150 mAh g^{-1} of electrode active materials and 80 mAh g^{-1} of electrode composite layers;
- develop *all-solid-state* 1 Ah concept cell batteries operating at room temperature with specific energy up to 200 Wh kg^{-1} with respect to the overall weight of the concept cell;
- obtain a high coulombic efficiency in average higher than 99% during cycling at 20°C ;
- obtain a cycle life of up to 500 cycles with 20% maximum loss of capacity, cycling (at 20°C) between 100% and 0% SOC;
- evaluate the integration of the developed batteries in renewable energy sources, especially their use in combination with photovoltaic cells (PVs).

Several materials have been developed and tested during the ILLIBATT project. However, this paper focus mainly on the components materials (electrolytes and electrodes) used for the realization of the ILLIBATT prototypes. The performance of the ILLIBATT prototypes and the safety test carried on the developed batteries are also illustrated.

2. Experimental

2.1. Synthesis of electrolytes

N-Butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI) and *N*-butyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR₁₄FSI) room temperature ionic liquids were synthesized and dried as reported in Ref. [21]. All the compositions of the electrolytes containing PYR₁₄TFSI and PYR₁₄FSI are given as molar concentrations.

The polymer electrolyte based on cross linked poly(ethyleneoxide) and ionic liquid (cl-PEO–LiTFSI–PYR₁₄TFSI) was synthesized as reported in Refs. [27,28].

The pyrrolidinium-based polymeric ionic liquid (PIL) was synthesized as reported in Ref. [29]. The polymeric electrolytes based on PIL and ionic liquid (PIL–LiTFSI–PYR₁₄TFSI) was synthesized as reported in Ref. [30].

2.2. Electrode preparation

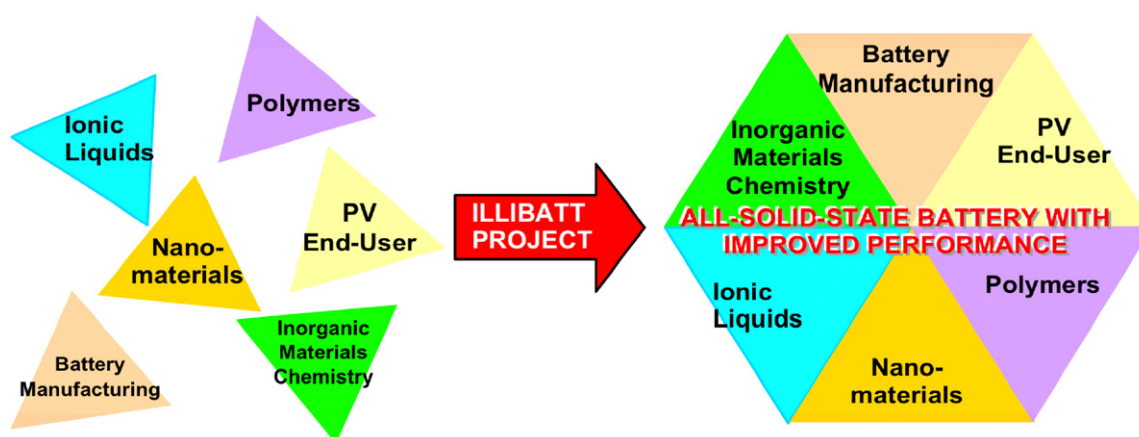
Graphite and silicon electrodes were prepared following the recipe reported in [31]. Lithium titanate (LTO) and lithium-iron phosphate (LFP) electrodes made using sodium-carboxymethylcellulose (CMC) water soluble binder, were prepared as described in [32]. LFP electrodes made using cl-PEO and PIL binders were prepared as described in Refs. [20,30], respectively. Tin electrodeposited electrodes were prepared following a procedure analogous to that reported in Ref. [33].

2.3. Electrochemical tests

The electrochemical tests referred to the characterization of PYR₁₄FSI are reported in [20]. The electrochemical tests referred to the characterization of cl-PEO–LiTFSI–PYR₁₄TFSI are reported in [28]. The electrochemical tests referred to the characterization

Table 1
ILLIBATT Consortium.

Participant organization name	Org. type	Country
Westfälische Wilhelms University of Münster	University	Germany
Graz University of Technology (2007–2008)	University	Austria
Agenzia per le Nuove Tecnologie, l'Energia e lo Sviluppo Economico Sostenibile	Res. Centre	Italy
Center for Electrochemical Technologies, CIDETEC	Res. Centre	Spain
Chalmers University of Technology	University	Sweden
Kiev National University of Technologies and Design	University	Ukraine
CEGASA	Industry	Spain
Sued-Chemie	Industry	Germany
Photowatt	Industry	France

**Fig. 1.** Scheme of the approach followed during the ILLIBATT project for the realization of all-solid-state batteries based on ionic liquids with improved performance.

of PIL–LiTFSI–PYR₁₄TFSI are reported in [29,30]. The electrochemical tests performed for the characterization of lithium titanate and lithium-iron phosphate electrodes are reported in Ref. [32].

2.4. Prototype preparation

The details relative to the realization and the testing of single small cells containing PYR₁₄FSI, cl-PEO–LiTFSI–PYR₁₄TFSI and PIL–LiTFSI–PYR₁₄TFSI electrolytes are reported in Refs. [28,30,32]. The details relative to the realization, the assembly and the testing of the prototypes are reported in Ref. [34]. The manufacturing of the lithium metal battery prototypes involved firstly the realization of double-face cathodic half-cells, each of them made by placing two LFP composite electrode tapes onto both the faces of the positive current collector (Al⁰) whereas two polymer electrolyte tapes were used to complete the double-face half-cell. Successively, the prototypes were fabricated by stacking, alternatively, twelve bipolar cathode half-cells and thirteen lithium metal tapes to achieve a theoretical capacity of 0.7 Ah. The lithium-ion battery prototypes (LTO/LFP) were manufactured by stacking, alternatively, fifteen bipolar LFP cathodes, twenty eight separators (glass fiber tapes) and fourteen LTO anodes. During the stacking, the separators and electrodes were progressively loaded with LiTFSI–PYR₁₄FSI electrolyte. Finally, the stacked LMPB and LIB prototypes were vacuum sealed in soft packages.

2.5. Safety tests

International standard protocols have been followed to test the safety of the battery concept cells. Concretely, altitude simulation, thermal cycling, overcharge and overdischarge abuse testing were performed following the indications given on the United Nations document, Recommendations on the Transport of Dangerous Goods; Manual of Tests and Criteria regarding lithium batteries (UN T1–T8) as well as International Standards IEC 62133 and IEC

62281 (harmonized with UN tests). Overcharge and overdischarge tests were carried using a multichannel potentiostat–galvanostat, that also monitored the voltage during nail penetration testing. During the experiment, the cell temperature was monitored using a thermocouple touching the external cell case and by thermal imaging using an infrared camera, which helps identifying points of high thermal stress in the cell.

3. Results and discussion

3.1. Electrolytes

Table 2 compares the physical and electrochemical properties of three different types of IL-based electrolytes:

1. Electrolyte (0.9PYR₁₄TFSI – 0.1LiFSI)
2. Polymeric electrolyte cl-PEO–PYR₁₄TFSI–LiTFSI
3. Polymeric ionic liquids PIL–PYR₁₄TFSI–LiTFSI

As indicated in the table, all electrolytes displayed very promising performance in terms of low vapor pressure and high thermal stability (from 150 °C of (0.9PYR₁₄TFSI–0.1LiFSI) to more than 300 °C for PIL–PYR₁₄TFSI–LiTFSI). Furthermore, their overall electrochemical stability window (ESW) at 20 °C was found higher than 5 V. The conductivity of (0.9PYR₁₄TFSI–0.1LiFSI) is of 3.2 mS cm⁻¹ at 20 °C, which is a value comparable with those of common organic electrolytes [20]. The cl-PEO–LiTFSI–PYR₁₄TFSI displays a conductivity of 0.37 mS cm⁻¹ at 20 °C. Even if this value is still lower than that of pure IL, it is important to note that the conductivity showed by this electrolyte is among the highest of PEO based systems. Moreover, it is to notice that such a polymer electrolyte is fully amorphous and highly adhesive, and displays very good mechanical stability and an elastomeric behaviour [28]. The PIL–LiTFSI–PYR₁₄TFSI electrolyte displays conductivity of

Table 2Comparison of physical and electrochemical properties of 0.9PYR₁₄TFSI–0.1LiFSI, cl-PEO–PYR₁₄TFSI–LiTFSI and PIL–PYR₁₄TFSI–LiTFSI electrolytes.

Electrolyte	No vapor pressure	Thermal stability	σ (mS cm ⁻¹) [20 °C]	ESW (V) [20 °C]	R_i (Ω cm ²) [20 °C]
0.9PYR ₁₄ TFSI–0.1LiFSI [20]	Up to 120 °C	150 °C	3.20	>5	50
cl-PEO–PYR ₁₄ TFSI–LiTFSI [28]	Up to 200 °C	>200 °C	0.11	>5	1000
PIL–PYR ₁₄ TFSI–LiTFSI [29]	Up to 200 °C	>300 °C	0.16	>5	1000

Table 3

Comparison of some properties of PVdF and CMC binders.

	PVdF	CMC
Solvent required during electrode preparation	Organic (NMP, etc.)	Aqueous
Disposability at the end of the battery life	Difficult	Very easy
Industrial cost	15–18 EUR kg ⁻¹	1–2 EUR kg ⁻¹

0.16 mS cm⁻¹ at 20 °C. This value, which is slightly lower than that of the cl-PEO systems, indicates that the use of PIL is an interesting strategy for the realization of solid polymeric electrolyte [29]. Very important, in addition to the above mentioned properties, all three electrolytes display very low and constant (for more than 100 days) interfacial resistance in contact with metallic lithium [20,28–30].

The properties of these electrolytes make them attracting candidates for use in lithium batteries. Considering the conductivity, ESW and thermal stability, the IL-based electrolyte (0.9PYR₁₄TFSI–0.1LiFSI) appears very promising for the realization of high performance and safe lithium-ion batteries. On the other hand, the properties of cl-PEO–LiTFSI–PYR₁₄TFSI and PIL–LiTFSI–PYR₁₄TFSI make these electrolytes as promising candidates for the realization of high performance and safe lithium-metal batteries.

3.2. Electrode binder

Table 3 compares the characteristics of the binders used in this project (CMC) with the standard materials in the state-of-art battery technology: polyvinylidene-di-fluoride (PVdF). PVdF is nowadays the most used binder in the commercial batteries. CMC, however, it is already used as binder for carbonaceous anodes [35–38].

As indicated in the table, the use of PVdF, even if it is largely diffuse, shows limitation related with the electrode preparation. As a matter of fact, PVdF requires the use of volatile organic compounds, often toxic like *N*-methyl-pyrrolidone (NMP), for the electrode coating. In addition, it is not easily disposable at the end of the battery life. To the contrary, CMC allows the use of aqueous slurries during the electrode preparation and it is easily disposable at the end of the battery life. In addition to that, the cost of PVdF is one order of magnitude higher than that of CMC (15–18 EUR kg⁻¹ for PVdF vs. 1–2 EUR kg⁻¹ for CMC). The same cost reduction is given by the solvent (0.1 EU L⁻¹ for water vs. 1 EU L⁻¹ for NMP).

Since for the development of green batteries not only the batteries components but also their preparation plays a crucial role, it is clear that the use of CMC binders appears more advantageous than that of PVdF. In the past the use of CMC was mainly restricted to anodic materials, but recently also the use of this safe binder in combination with cathodic materials was shown to be possible [39–43]. For example, lithium iron phosphate (LFP) composite electrode realized using CMC binder, displayed comparable performance with those realized with PVdF [43]. Moreover, it is interesting to note that the use of CMC allows the preparation of electrodes with lower porosity with respect to PVdF. This is an additional advantage related with the use of CMC since this characteristic would allow for a significant reduction or even the elimination of the post-coating treatment (roll pressing) during the

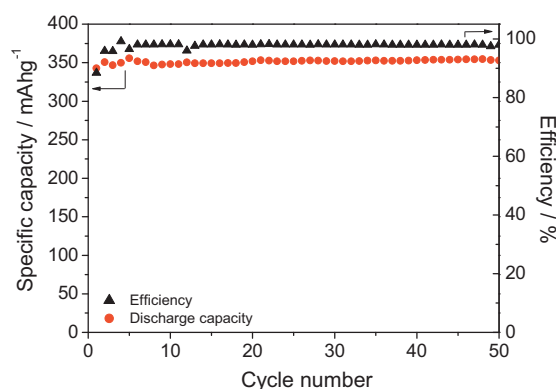


Fig. 2. Specific discharge capacity and coulombic efficiency of a graphite electrode (SLC 1520P from Superior Graphite Co., USA) in half cell configuration with 0.3 M LiTFSI in PYR₁₄TFSI + 20% of (EC:DEC:DMC, 1:1:1, w/w) electrolyte at RT. The cell was tested between 0.0 and 1.5 V at the current rate of 0.1 C, after two initial formation cycles carried out at 0.05 C.

manufacturing of the battery electrodes, with a consequent benefit in term of costs and production time.

3.3. Anodic and cathodic materials

3.3.1. Graphite based composite electrodes

The use of graphite in combination with ionic liquids based electrolytes has been intensively studied in the last years [16–20]. The reason of this interest is clearly related with the fact that graphite is the anodic material of choice in lithium ion batteries. Most of the work was focused on the growth of an effective SEI on the surface of graphite [1,2]. In order to build an effective SEI, a film forming agent is normally included in the conventional electrolytic solution in form of co-solvent (e.g. EC) or additive (e.g. vinylene carbonate, VC). Moreover, it is well known that lithium salt like lithium hexafluorophosphate (LiPF₆) also displays SEI film-forming ability. So far, several types of ILs have been used in combination with graphite electrode [16–20]. Among them, those based on the FSI⁻ anion appear the most promising since they display an intrinsic film forming ability [16,20]. However, in order to effectively use this kind of ILs in combination with graphite electrode, the presence of additives and a careful selection of the lithium salt appear of great importance. As a matter of fact, the presence of additives can reduce the initial irreversible capacity, while the lithium salt can strongly affect the cycling stability [19].

Even if the results obtained so far are promising, the performance of graphite electrode in ILs-based electrolytes appears still not fully competitive with that of conventional electrolytes, particularly at medium-high rate [16–20]. Recently, the use of mixtures of organic electrolyte and ionic liquids showed to be a convenient strategy for the realization electrolytic solutions with tunable properties [44,45]. Depending on the amount of IL present in the mixtures, viscosity, conductivity and flash point of these electrolytes could be properly varied.

Fig. 2 shows the performance of a graphite electrode (SLC 1520P from Superior Graphite Co., USA) in an electrolytic solution containing 0.3 M LiTFSI in PYR₁₄TFSI + 20% of (EC:DEC:DMC, 1:1:1 wt.) at RT. The cell was tested between 0.0 and 1.5 V at a current rate

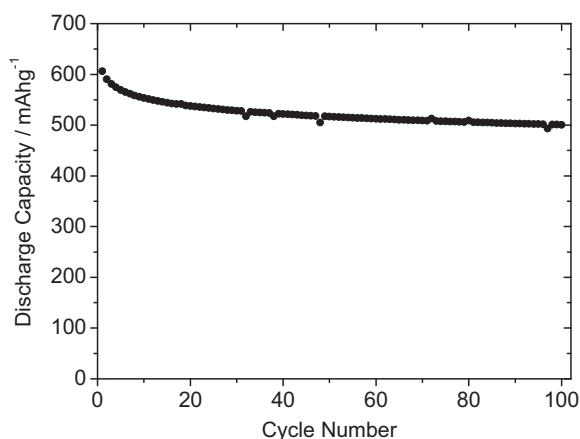


Fig. 3. Specific discharge capacity of silicon-graphite composite electrode tested in an electrolytic solution containing 0.3 M LiTFSI in PYR₁₄TFSI (50%) + (EC:DEC:DMC, 1:1:1, w/w) (50%) at RT. The cell was tested between 0.0 and 1.5 V at the current rate of 0.1 C.

of 0.1 C after two initial formation cycles carried out at 0.05 C. As shown in the figure, with this mixed electrolyte an electrode discharge capacity higher than 350 mAh g⁻¹ was achieved, which was extremely stable for 50 cycles. Very interestingly, the irreversible capacity of the electrode was quite low during the first cycles (in the order of 45 mAh g⁻¹) and the coulombic efficiency close to 100% throughout the cycling test. Considering these results, the use of such mixtures appears a promising strategy for the improvement of the graphite electrode performance in IL-based electrolytes.

3.3.2. Silicon based composite electrodes

Silicon represents today one of the most interesting materials for lithium-ion battery technology [46]. Silicon displays much higher theoretical capacity than graphite electrode (4200 mAh g⁻¹ vs. 372 mAh g⁻¹) and therefore its introduction in lithium-ion batteries could significantly improve the energy of these systems. However, because of the strong volume changes of the (inter)metallic hosts during lithium uptake and removal [46], the cycling stability of pure Si-based electrodes is limited with respect to that of graphite-based electrodes. In the last years several strategies have been proposed to improve the cycling stability of silicon electrode. Among them, the coating of silicon particles and the realization of composite electrode containing silicon and graphite resulted as the most effective [46]. In these latter composite electrodes, the graphite serves as a buffer for the silicon particle expansion, but it also contributes to the electrode capacity. Such kind of electrodes display lower specific capacity but higher cycling stability than pure silicon electrodes.

Fig. 3 shows an example of silicon-graphite composite electrode prepared using carbon shelled Si and graphite (SLC 1520P from Superior Graphite Co., USA) tested in an electrolytic solution containing 0.3 M LiTFSI in PYR₁₄TFSI (50%) + (EC:DEC:DMC, 1:1:1 wt.) (50%) at RT. The cell was tested between 0.0 and 1.5 V at a current rate of 0.1 C. As shown in the figure, the discharge capacity of the composite Si-graphite electrode was initially higher than 580 mAh g⁻¹. During the first 20 cycles the capacity rapidly decreased to ca. 550 mAh g⁻¹ but after that it is only slightly decreased for the remaining cycling test. At the end of the test, the electrode displayed a discharge capacity around 500 mAh g⁻¹. Even if these results are promising, the performance of such kind of electrode in mixtures of organic electrolyte and ionic liquids need to be further improved, particularly in terms of capacity fading during the initial cycles.

In spite of this, some recent work showed that the performance of pure silicon electrodes charged using a limited capacity

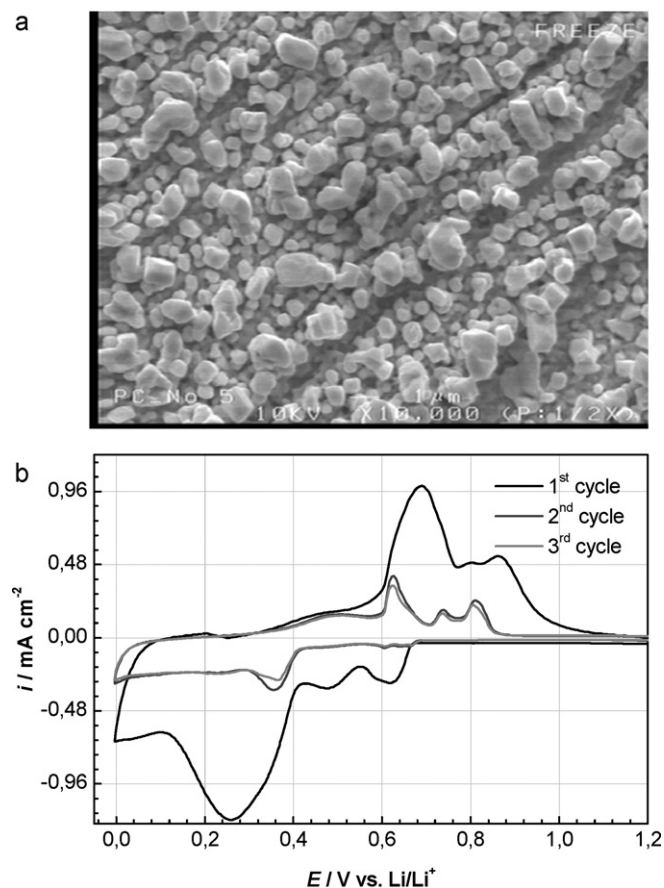


Fig. 4. (a) SEM images of a Sn electrode realized via electrodeposition in a solution of 1 M SnCl₄ in PYR₁₄TFSI. (b) CVs (scan rate of 500 μV s⁻¹) of the electrodeposited Sn electrode in 1 M LiTFSI in PC.

(1200 mAh g⁻¹) in PYR₁₄TFSI-based electrolytes is comparable with that of the same electrodes in organic solvent-based electrolytes [21]. These results indicate that pure silicon electrodes display higher compatibility with IL-based electrolytes than graphite electrodes. This is of course a promising indication for the use of silicon with IL-based electrolytes.

The electrodeposition of intermetallic anodes has been also investigated during ILLIBATT project. As mentioned earlier, intermetallic anodes (e.g. Si, Sn) are considered since many years attracting anodic material for the development of high energy lithium-ion batteries because of their high theoretical capacity. Several studies showed that nano-structured materials display much better cycling stability than coarse-structured materials [46–48]. Consequently, the development of nano-structured intermetallic anodes attracted great interest. Among the possible synthetic routes, the electroplating of metal has been indicated as one of the most convenient ways to realize such structures. However, due to electrolyte stability problems, electropositive metals, such as Al, Si, or Ge, cannot be plated from aqueous or other protic solutions. In order to carry out effective electroplating, electrolytes with wide electrochemical stability window and a very low reactivity with the electropositive metal are needed. The number of electrolytes able to display these properties is rather small, but several works showed that the electroplating of electropositive metal is possible from IL-based electrolyte [49]. Therefore, the realization of nano-structured intermetallic anodes through electrodeposition in IL appears a very attracting strategy for the development of high capacity nano-structured anodes. In fact, one of the advantages of such a process consists in tailoring the morphology of the deposit

by a proper variation of the plating conditions (including a variation of the ionic liquid electrolyte solution).

Fig. 4 reports an example of Sn electrode electrodeposited at RT from an ionic liquid electrolyte. The electrodeposition was carried out directly on a Cu current collector in a solution containing $\text{PYR}_{14}\text{TFSI}$ and 1 M SnCl_4 as precursor (saturated solution), following electroplating conditions similar to those reported in [33]. Fig. 4a shows the SEM image of the Sn electrode. In Fig. 4b are reported voltammetric curves carried out at $500 \mu\text{V s}^{-1}$ using the Sn electrode in a solution of 1 M LiTFSI in PC.

As mentioned above, the electrodeposition of nano-structured anodic material in ILs certainly represents an attractive possibility. One of the advantages of such electrodeposition process is the possibility to deposit the active materials directly on the desired current collector. However, for the realization of electrodes with high capacity and high cycling stability, further work is certainly necessary. Particularly, the optimization of the plating condition appears as the most critical parameter that needs here to be addressed.

3.3.3. LTO composite electrodes

Lithium titanate (LTO) is considered today as one of the most attractive anodic material for the realization of high power lithium-ion batteries which are currently considered for the realization of PHEVs [50]. LTO is thermally and electrochemically very stable, it can be charge-discharged at high rate and it is relatively cheap. Moreover, the process of charge-discharge of LTO takes place at 1.5 V vs. Li/Li^+ , a potential at which no electrolyte decomposition occurs and no SEI formation is necessary. It is important to note that the characteristics mentioned above make LTO one of the safest anodic materials currently available in lithium battery technology.

Recent work showed that LTO electrodes containing CMC as binder display high performance in IL-based electrolytes [32]. Fig. 5a shows an image of a CMC-based LTO composite electrode double coated on an Al current collector. Fig. 5b shows the voltage profile of the same electrodes in (0.9 $\text{PYR}_{14}\text{FSI}$ -0.1 LiTFSI) electrolyte during CC test carried out at 0.1 C rate and 20 °C. As shown in the figure, the specific capacity of the electrode was ca. 150 mAh g^{-1} with a coulombic efficiency of 100%. As reported in [32], such electrode was able to display a constant and high specific capacity for more than 100 cycles. It is important to note that the specific delivered capacity as well as the cycling stability obtained with this electrode is comparable with those obtained with LTO-based composite electrodes, made using PVdF as the binder, in conventional, organic solvent-based electrolytes.

Considering the results of these tests, LTO appears as the anodic material currently able to display the highest performance in pure IL-based electrolytes. This high performance in ionic liquids is most likely related with the intrinsic characteristics of LTO, particularly with the low volume changes and the value of lithium insertion-deinsertion potential. Because of these characteristics, when an IL with high conductivity and low viscosity (e.g. $\text{PYR}_{14}\text{FSI}$) is selected as electrolyte, the performance of such a material is comparable with that obtained in conventional electrolyte. However, it is important to note that the use of non-flammable, non-volatile, ionic liquids electrolytes (such as 0.9 $\text{PYR}_{14}\text{FSI}$ -0.1 LiTFSI) has the important advantage to further improve the safety of the battery systems in which this anodic material is used.

3.3.4. Metallic lithium

Lithium metal batteries (LMB) display high theoretical gravimetric energy and high power densities and for these characteristics they have been intensively investigated in the past [7]. Several studies, however, showed that for the realization of safe and high performance LMB the use of organic solvent-based electrolytes is not adequate. As a matter of fact, the high reactivity of organic

solvents (carbonates) with Li-metal results in poor performance and uneven (dendritic) anode deposition. In the last years, several works showed that the introduction of IL-based electrolyte in LMB can improve not only the safety, but also the performance since these electrolytes display high compatibility with metallic lithium [22–26].

As reported in the paragraph dedicated to the electrolytes, all three considered IL-based electrolytes display very promising values of interfacial resistance when tested in symmetric lithium cells (see Table 2). Moreover, the interfacial resistance of all these systems was found to be extremely stable over time. Of course, these properties make these electrolytes attractive candidates for the realization of LMB.

Fig. 6 shows a comparison of the behaviour of the three IL-based electrolytes during lithium plating-stripping test. The tests were performed using asymmetric Li/Ni cells with (0.9 $\text{PYR}_{14}\text{FSI}$ -0.1 LiFSI) electrolyte [20] and symmetric Li/Li cells for cl-PEO- $\text{PYR}_{14}\text{FSI}$ - LiTFSI [28] and PIL- $\text{PYR}_{14}\text{FSI}$ - LiTFSI [30] electrolytes. For all tests, the plating-stripping time was 1 h. In Fig. 6 the overvoltage vs. time profile of a few selected cycles is reported for each electrolyte. As shown in the figure, more than 1000 consecutive plating-stripping cycles were successfully performed using these electrolytes without major changes in the voltage profiles [20,28,30]. For all systems a very low overvoltage was observed and the efficiency of the plating-stripping process for all the duration of the tests was higher than 99%. Additionally, as indicated by impedance measurements (see insert in panels b, d and f), no major decomposition of the electrolytes and no significant changes in the charge transfer resistance occurred during these tests for all considered systems [20,28,30]. The results of these tests promise that lithium metal anodes might be used with IL-based electrolytes for the realization of LMB with good performance and the advantage of having very reduced flame hazards.

3.3.5. LFP composite electrodes

Lithium iron phosphate (LFP) is today considered one of the most attracting cathodic materials for the realization of high safety batteries. As a matter of fact, the presence of P-O covalent bonds in its structure reduces drastically the risk of oxygen release and give to LFP an intrinsic safety. Moreover, LFP is more environmentally friendly and cheaper than LiCoO_2 (state-of-art in Li-ion systems). Even if LFP suffers from a high intrinsic resistance, the use of carbon coating processes has been proved to be an effective way to overcome this limitation and several works showed that carbon-coated LFP electrodes display high capacity at high rate and high stability during prolonged cycling. For these reasons, LFP is already introduced in commercial batteries used in power tools and PHEVs [50].

Fig. 7 compares the performance of three LFP electrodes in cells employing Li as the negative electrode, tested in combination with different IL-based electrolytes. In panel A is reported the performance of a LFP electrode based on CMC as the binder, tested in (0.9 $\text{PYR}_{14}\text{FSI}$ -0.1 LiTFSI) electrolyte [32]. Like in the case of LTO, also for LFP electrode the use of CMC as the binder has been proved to be a viable approach to further improve the overall safety of such composite electrode [32,43]. As indicated in the figure, during charge-discharge tests carried out at a current density corresponding to 0.1 C rate and 20 °C the electrode displays a delivered capacity of ca. 165 mAh g^{-1} , stable for more than 100 cycles [32]. This performance is comparable with that showed by the same electrode tested in conventional organic electrolytes, indicating the ability of LFP to display high performance in IL-based electrolytes. The second panel (B) illustrates the performance of an LFP electrode tested in combination with cl-PEO- $\text{PYR}_{14}\text{FSI}$ - LiTFSI electrolyte [28]. The same electrolyte was also used as a binder to form the electrode.

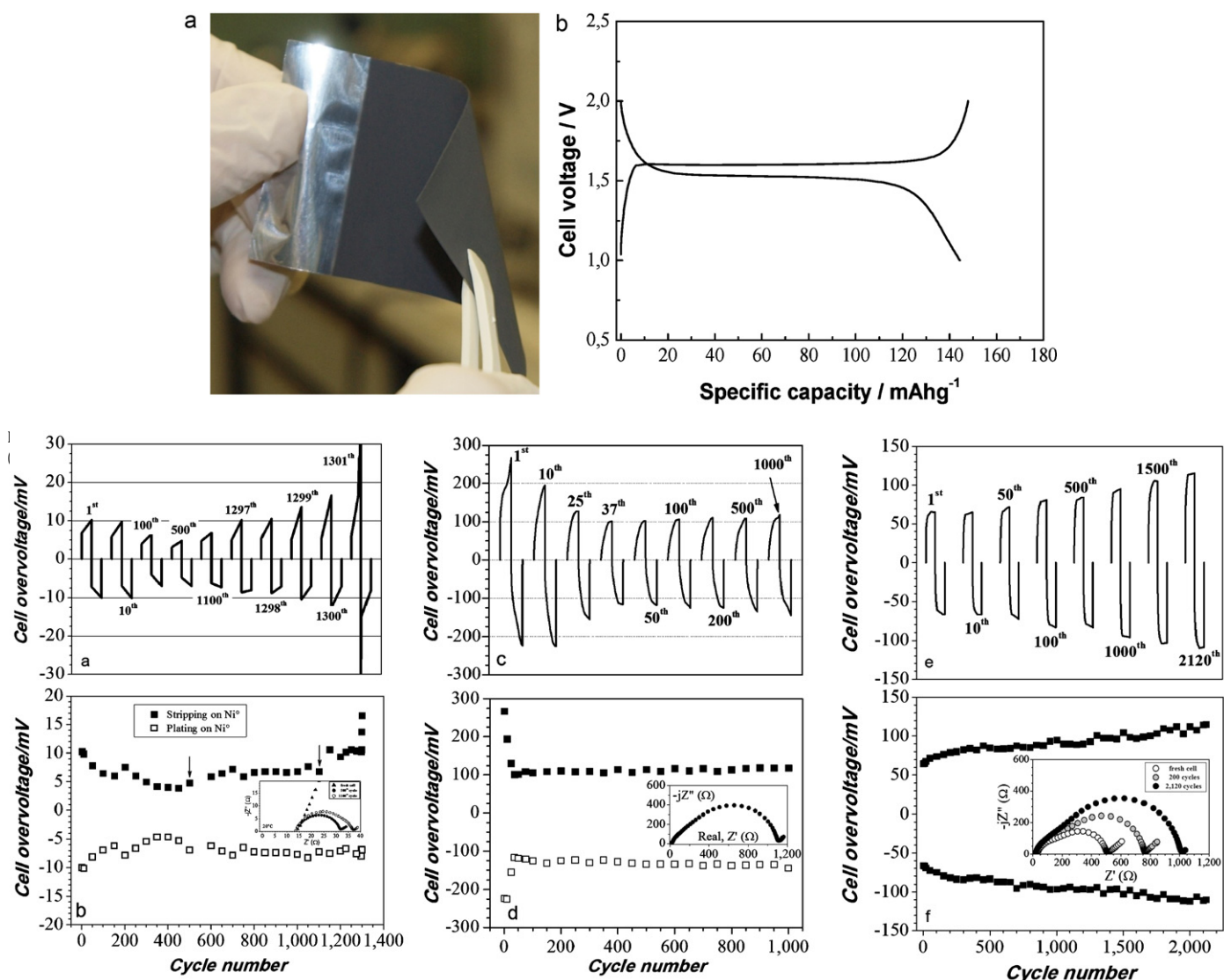


Fig. 6. Selected plating stripping cycles and overvoltage evolution profile measured at the end of each semi cycle during the cycling of: (a, b) a asymmetric Li/(0.9PYR₁₄FSI-0.1LiTFSI)/Ni cell at 20 °C [20]; (c, d) a symmetric Li/PEO-PYR₁₄TFSI-LiTFSI/Li cell at 40 °C [28]; (e, f) a symmetric Li/PIL-PYR₁₄TFSI-LiTFSI/Li cell at 40 °C [29].

In this case the charge–discharge tests were performed at a current density corresponding to 0.1 C rate at 40 °C. As indicated in the figure, during this test the LFP electrode displays a delivered capacity of almost 160 mAh g⁻¹ and a very high cycling stability for more than 400 cycles [28]. Although these values appear to be lower when compared with the previous system, it is important to note that in this case the electrode was used in an all-solid-state battery and for such a reason the results can certainly be considered as extremely promising. The performance of a third LFP composite electrode tested with the PIL-PYR₁₄TFSI-LiTFSI electrolyte [29] is reported in panel C. Once more, the electrolyte was used as a binder to produce the composite electrode. Also in this case the charge–discharge tests were performed at a current density corresponding to 0.1 C rate at 40 °C. As shown in the figure, during this test the LFP electrode shows a delivered capacity of ca. 150 mAh g⁻¹ and a very good cycling stability during 70 cycles [30]. The specific capacity delivered by LFP electrode is only 10% lower than that delivered by a similar electrode in combination with the cl-PEO-PYR₁₄TFSI-LiTFSI electrolyte. Considering the fact that this system can be further optimized, these results are seen as a promising indication about the use of PIL in lithium batteries.

3.4. ILLIBATT prototypes: selection of cell chemistry and concept cell design

Considering the results reported in the previous sections, several cell chemistries could be implemented for the realization of safe and high performance IL-based batteries.

Regarding the electrolyte composition, all three types of electrolytes described in this paper appear promising. The (0.9PYR₁₄FSI-0.1LiTFSI) electrolyte displays high conductivity and it appears therefore suitable for the realization of lithium-ion batteries. On the other hand, the electrochemical and mechanical properties of cl-PEO-PYR₁₄TFSI-LiTFSI and PIL-PYR₁₄TFSI-LiTFSI make these polymeric electrolytes suitable for the realization of all-solid-state lithium polymer batteries.

Regarding the anodic materials, the performance obtained with graphite and silicon electrodes in IL-based electrolytes still do not appear fully comparable with that obtained in conventional electrolytes. For these anodic materials, the use of organic electrolyte–ionic liquids mixtures appears at the moment the most convenient strategy to obtain high performance. However, considering the properties of ILs and the intense research work which

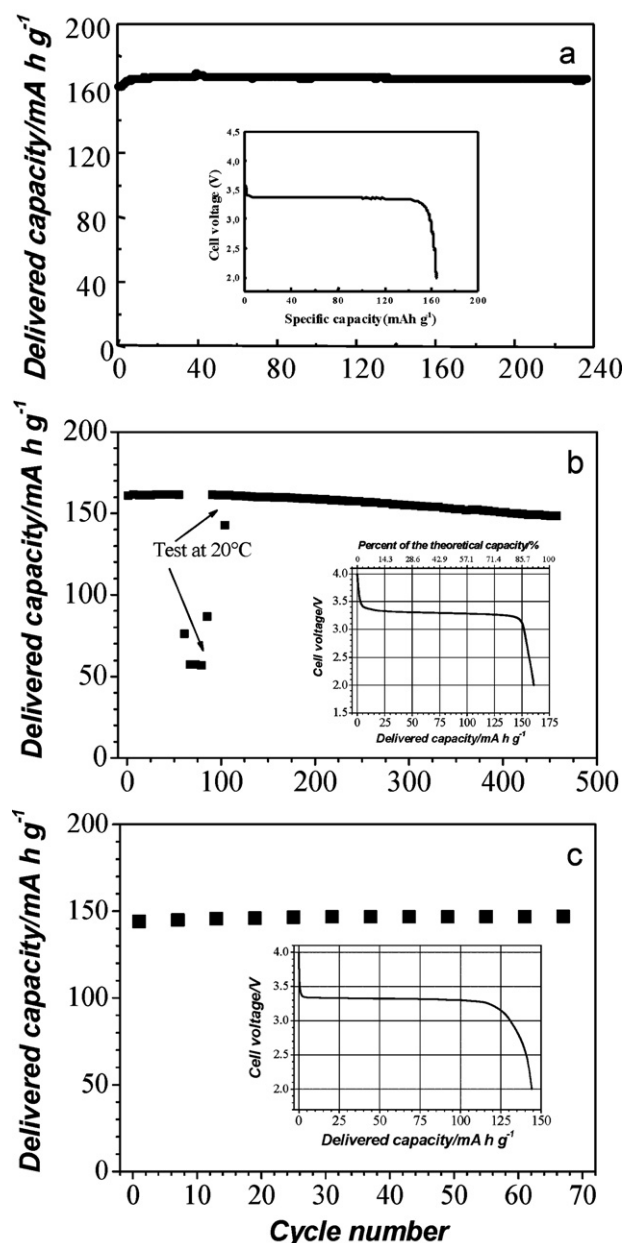


Fig. 7. LFP electrode in half cell (Li anode) configuration with: (a) 0.9PYR₁₄FSI–0.1LiTFSI electrolyte at 20 °C; (b) PEO–PYR₁₄TFSI–LiTFSI electrolyte at 40 °C; (c) PIL–PYR₁₄TFSI–LiTFSI electrolyte at 40 °C. For each electrode, the delivered capacity vs. cycle number and the voltage profile vs. specific capacity of a selected cycle are reported.

is currently in progress, it is presumable that, in a near future, these two anodic materials could also display high performance in IL-based electrolytes. Nonetheless, the results reported earlier indicate LTO as the best anodic material candidate for the realization of ILs-based lithium-ion batteries. As a matter of fact, the performance of LTO in (0.9PYR₁₄FSI–0.1LiTFSI) electrolyte are comparable with those normally observed in conventional organic electrolytes. Finally, as indicated by the lithium-plating stripping tests, also the use of metallic lithium in combination with IL-based polymer or liquid electrolyte appears certainly attractive in view of the realization of high performance lithium metal batteries.

Regarding the cathodes, the high performance obtained with LFP electrode in combination with all ILs-based electrolytes here investigated clearly indicates this material as a natural

Table 4

ILLIBATT prototypes: short name, nominal capacity, nominal voltage and operative temperature.

Prototype	Nominal capacity	Nominal voltage	Operative temperature
PYR ₁₄ FSI.LIB	0.8 Ah	1.9 V	20 °C
cl-PEO.LMPB	0.73 Ah	3.4 V	40 °C
PIL.LMPB	0.76 Ah	3.4 V	40 °C

choice. Additionally, because of the intrinsic safety of LFP, the use of this material can also contribute to the safety of the battery.

Considering the overall making of the battery, and specifically the electrode preparation, the use of CMC instead of PVdF as binder appears extremely important since allows the use of aqueous slurry, thus eliminating the use of toxic organic solvents. Moreover, the use of CMC does not cause any electrode performance reduction.

Considering these points, three different cell chemistries were considered within the project:

- 1 Lithium-ion battery containing composite LTO anode, (0.9PYR₁₄FSI–0.1LiTFSI) electrolyte and composite LFP cathode. For both LTO and LFP electrode, CMC was used as the binder (short name: PYR₁₄FSI.LIB).
- 2 Lithium-metal battery containing Li metal anode, cl-PEO–PYR₁₄TFSI–LiTFSI electrolyte separator and composite LFP cathode (short name: cl-PEO.LMPB).
- 3 Lithium-metal polymer battery containing Li metal anode, PIL–PYR₁₄TFSI–LiTFSI electrolyte separator and composite LFP cathode (short name: PIL.LMPB).

Single small cells (few squared centimeter) were assembled and tested for preliminary evaluation [28,30,32]. Based on the promising results, several prototypes were assembled connecting in parallel from 12 to 14 single bipolar cells in order to achieve a capacity ranging from 0.7 to 0.8 Ah. The details relative to the realization of the prototype components (e.g. bipolar cells), the prototypes assembly and testing procedure are reported elsewhere [34]. In Table 4 the nominal capacity and the nominal voltage of each prototype are indicated. The operative temperature used during the tests is also shown in the table.

3.5. ILLIBATT prototypes: performance

The three prototypes were tested under constant current charge–discharge cycling. The PYR₁₄FSI.LIB prototype was tested using a cut-off voltage window of 1–2.5 V, whereas the cl-PEO.LMPB and PIL.LMPB prototypes were tested using a cut-off voltage window of 2–4 V. All three prototypes were tested using current rates ranging from 0.05 C up to 2 C.

Fig. 8 shows the capacity delivered upon cycling and the discharge voltage profile at C-rates ranging from 0.05 C to 2 C for the prototypes PYR₁₄FSI.LIB (a, b) and cl-PEO.LMPB (c, d). As indicated in the figure, the PYR₁₄FSI.LIB prototype delivered 85% of the theoretical capacity at 0.05 C (0.68 Ah), maintaining the same capacity at 0.1 C (0.6 Ah). At 0.2 C the prototype displayed 44% of the theoretical capacity, while at higher rates the capacity decreased more significantly. Very important, these values of capacity were remarkably constant for almost 1000 cycles carried out at 20 °C. The cl-PEO.LMPB prototype delivered nearly the full capacity at 0.05 C (0.70 Ah vs. 0.73 Ah) and a capacity of 0.45 Ah at 0.1 C. At 0.2 C, the prototype displayed 35% of the theoretical discharge capacity (0.25 Ah). Also in the case of cl-PEO.LMPB prototype, it is very

Table 5
ILLIBATT prototypes: results of altitude and thermal cycling tests.

Cell	Altitude test			Thermal cycling		
	Before test	After tests	W90, V90	Before test	After tests	W90, V90
PYR ₁₄ FSI.LIB	1.845 V12.584 g	1.828 V12.585 g	Passed	1.828 V12.585 g	1.780 V12.660 g	Passed
cl-PEO.LMPB	3.449 V11.670 g	3.432 V11.671 g	Passed	3.432 V11.671 g	3.437 V11.678 g	Passed
PIL.LMPB	3.526 V11.815 g	3.431 V11.811 g	Passed	3.431 V11.811 g	3.428 V11.837 g	Passed

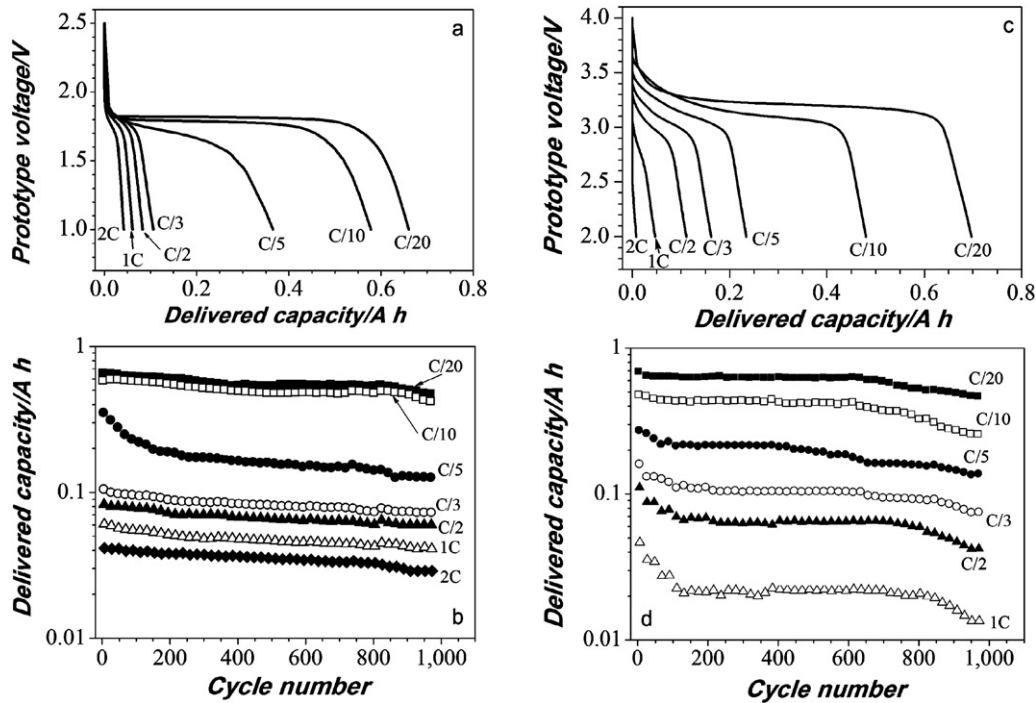


Fig. 8. First discharge voltage profiles (panels a and c) and capacity retention (panels b and d) behaviour at different discharge current rates of: PYR₁₄FSI.LIB prototype at 20 °C (panels a and c); cl-PEO.LMPB prototype at 40 °C (panels c and d).

important to note the remarkable cycling stability (>800 cycles) at low and medium rates.

When the performance of these two prototypes is compared, the PYR₁₄FSI.LIB prototype shows the best electrochemical performance since it displays the highest percentages of delivered capacity and capacity retention upon cycling. This performance was obtained during tests carried out at lower temperature with respect to cl-PEO.LMPB prototype (20 °C vs. 40 °C) at which the conductivity of the ionic liquid is consequentially diminished. However, it is important to note that the high performance shown by the cl-PEO.LMPB prototype clearly indicated this cell chemistry as excellent for the realization of lithium metal polymer batteries. In addition to that, it is also very important to note that the performance of both prototypes matches the target fixed for the ILLIBATT project. As a matter of fact, both prototypes display a high coulombic efficiency during cycling and a loss of capacity lower than 20% with respect to the initial capacity after 500 cycles.

These results indicate that the realization of high performance lithium batteries based on ionic liquid electrolytes is possible. To the best of our knowledge, the performance displayed by the prototypes PYR₁₄FSI.LIB and cl-PEO.LMPB are among the highest ever reported for IL-based batteries. Further improvements are certainly necessary, particularly at high C-rate, but the results of these tests indicated that the cell chemistries identified during the ILLIBATT project are certainly suitable for the realization of batteries with performance approaching that obtained with conventional organic electrolytes.

3.6. ILLIBATT prototypes: safety test

Since the safety improvement is supposed to be one of the main advantages related with the introduction of ILs in lithium battery technology, safety tests were also carried out. These tests have been performed on single bipolar cells based on the cell chemistries selected for the realization of the ILLIBATT prototypes.

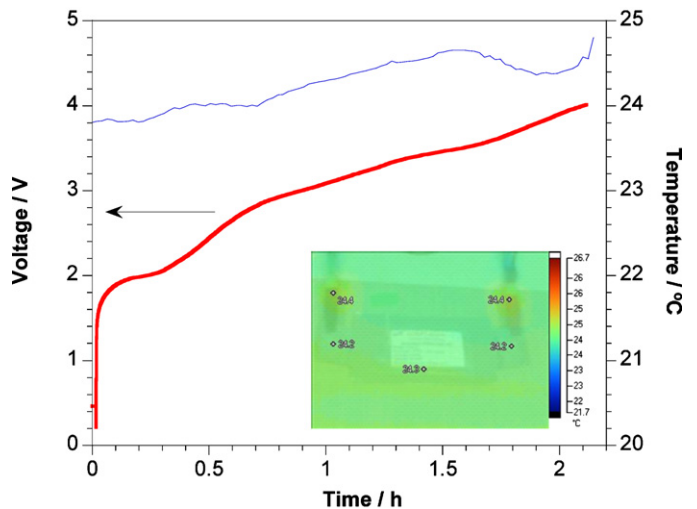


Fig. 9. Voltage and temperature evolution of the PYR₁₄FSI.LIB single cell under overcharge condition. Inset: thermal image of the cell at 4V.

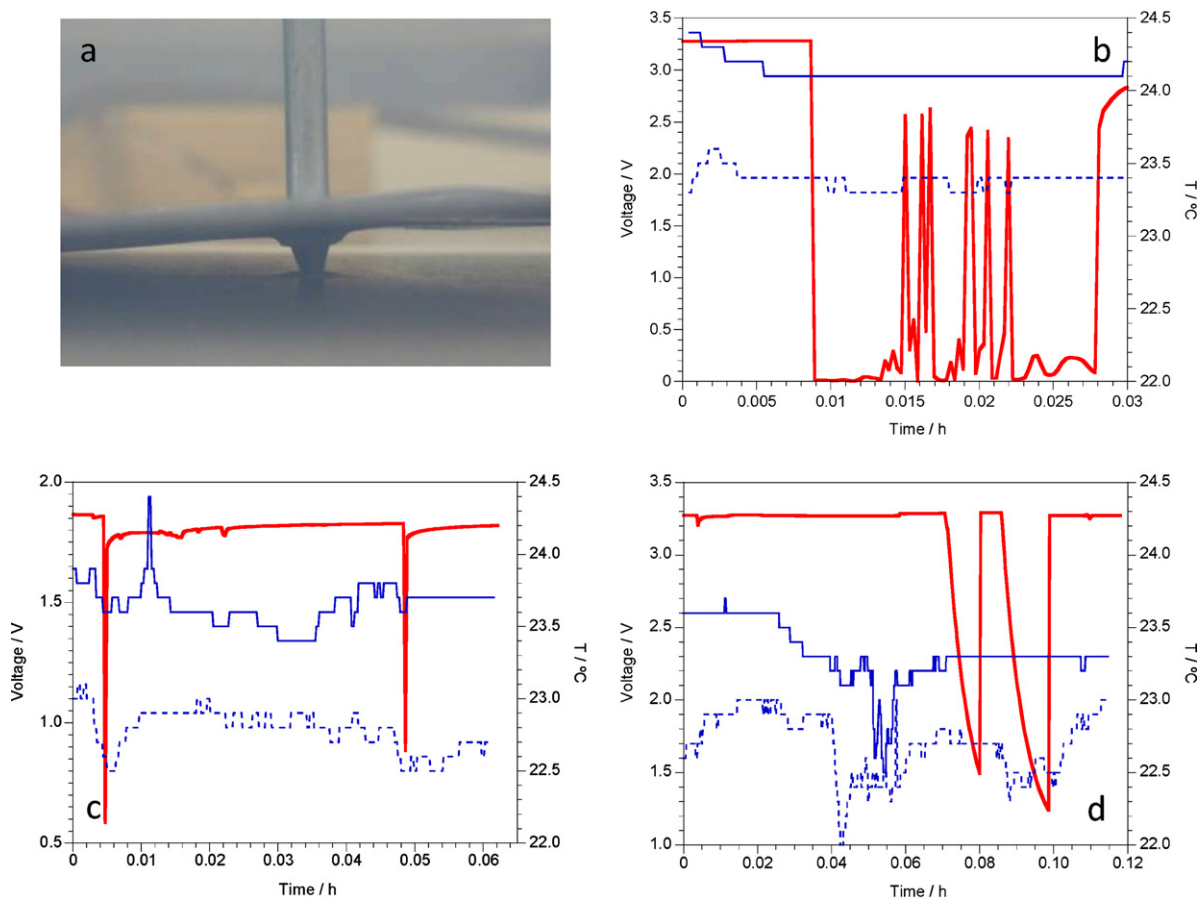


Fig. 10. Results obtained for the nail penetration test: (a) view of nail through a cell, (b) short circuit observed for a graphite/organic electrolyte/LFP cell, (c) behaviour of PYR₁₄FSL.LIB and (d) cl-PEO.LMPB single cells (Thick line: voltage; thin line: cell temperature; dotted line: ambient temperature).

Table 5 summarizes the results obtained during altitude simulation and thermal cycling tests. The altitude tests were carried out under vacuum condition for 12 h, at a pressure of 11.6 kPa, simulating 12 km flight altitude. Prior to be placed under vacuum, the cells (originally discharged, as assembled) were charged under constant current–constant voltage procedure at 0.2 C (12 mA) and 24 °C, to be tested in the charged state (*a priori*, the less “safe” condition). Thermal cycling was also performed. The cells were subjected to a testing protocol consisting on a temperature loop (4 h@75 °C + 2 h@20 °C + 4 h@–20 °C + 2 h@20 °C) repeated 5 times. In this test the cells had to withstand brusque temperature changes (in less than 30 min) in a range simulating different ambient conditions, from high (75 °C) to low (–20 °C) temperatures. As indicated in Table 4, all cells showed no significant weight loss or voltage drop (less than the 0.1% in weight and 90% of voltage indicated in the standard). It is very important to note that these results indicate a noticeable safety improvement due the presence of IL with respect to the conventional organic electrolyte. This improvement is very clear when tests under vacuum condition is considered. As a matter of fact, during these tests cells containing conventional organic electrolyte swell (and therefore may break the sealing and leak) because of the volatility of the organic solvent. To the contrary, no swelling is observed in cells containing ILs [32].

A second series of tests was focused on the behaviour of the cells under overcharge, overdischarge and nail penetration tests. These tests were carried out sequentially using the equipment setup indicated in Section 2. Initially the cells were subjected to overcharge conditions by charging at 0.2 C rate with no upper cut-off voltage limit. For all cells, the temperature increase observed was below

1 °C. As example of the cell behaviour, Fig. 9 shows the results of the test performed with the PYR₁₄FSL.LIB Li-ion cell. During this experiment, the cell was charged applying an intensity of 12 mA starting from the discharged state (as assembled, 0.2 V). The expected voltage plateau at 2 V (1.9 V nominal) can be observed and since no limit is applied, the cell continues charging and the voltage profile rising above the 2.5 V cut-off voltage of this chemistry. Although the electrochemical stability window of the pyrrolidinium ionic liquid electrolyte is wide, above 3 V some degradation of the electrode active materials (further oxidation of LFP to Fe⁴⁺ and/or reduction of Ti in the LTO anode) might take place. Nevertheless, the safety of these inorganic materials is also proved in this test since even though further performance of the cell was diminished, it is still functioning and no safety issues arised. It is important to note that the results shown in Fig. 9 are also representative (only changing nominal voltage) of the data obtained for the lithium metal polymer batteries (cl-PEO.LMPB and PIL.LMPB) for whom the overdischarge can be even more critical due to the presence of lithium metal. After the overcharge test, all cells were overdischarged to near 0 V, again observing less than 1 °C temperature change (results not shown). It is interesting here to note that after the overdischarge tests all three cells could be charged again (albeit only 1/10 of nominal capacity). cl-PEO.LMPB and PIL.LMPB showed a voltage of 3.4–3.3 V, while PYR₁₄FSL.LIB showed a voltage of 1.85 V, prior to the final abuse testing.

Nail penetration tests were also carried out on the cells. As shown in Fig. 10, the nail created punctual short-circuits on the PYR₁₄FSL.LIB and cl-PEO.LMPB cells when punched through them, which resulted in sudden drops of voltage but never reaching 0 V.

For comparative purpose, a similar nail penetration was carried out in a graphite/LFP cell containing conventional organic electrolyte. In this case, as shown in the figure, the nail penetration caused a full short-circuit. For the IL-based cells there was no significant temperature change arising safety concerns. The OCV voltage was recovered immediately after removing the nail from the hole for all ILLIBATT cells, a feature not observed for the conventional cell probably due to major leakage of the electrolyte in this case. The ILLIBATT cells still maintained a quite stable OCV voltage after 24 h of this test, most likely thanks to the polymeric nature of the electrolyte in the LMPB cells and the higher viscosity of the Ionic Liquid (even though there was some leakage) for the Li-ion cell. All in all, the safety tests performed on these single, small scale cells demonstrate and highlight the high tolerance of ionic liquid based lithium battery chemistries under thermal, mechanical and electrical abuse and misuse conditions. These promising safety characteristic should now be validated for real (and large) batteries in which ILs are used as electrolytes or electrolytes components.

4. Conclusions

The results obtained within the European project ILLIBATT indicated that several cell chemistries can be used for the realization of safe and high performance IL-based batteries.

Using *cl*-PEO–PYR₁₄TFSI–LiTFSI and *PIL*–PYR₁₄TFSI–LiTFSI electrolytes in combination with LFP-based cathodes it is possible to realize high performance lithium-metal polymer batteries. Such batteries display high capacity and a remarkable cycling stability. For example, a prototype of 0.7 Ah containing *cl*-PEO–PYR₁₄TFSI–LiTFSI as electrolyte delivers nearly the nominal capacity at 0.05 C and it is stable for more than 1000 cycles carried out at 40 °C.

Using (0.9PYR₁₄FSI–0.1LiTFSI) electrolyte, LTO-based anode and LFP-based cathode it is possible to realize a lithium-ion batteries with high performance, which does not require the use of any volatile organic solvent throughout the electrode making and the battery making. For example, a prototype of 0.8 Ah based on this cell chemistry delivers 85% of the nominal capacity at 0.05 C and it is stable for almost 1000 cycles carried out at 20 °C. In such a system the intrinsic safety of LTO and LFP is further improved by the use of the non-volatile, non flammable electrolyte without any negative effect on the battery performance.

The presence of ionic liquids electrolytes, both solid and liquid, inside the cell chemistries identified during ILLIBATT shows also the ability to improve the battery safety. The safety tests performed on single cells at small scale demonstrate and highlight the high tolerance of ionic liquid based lithium battery chemistries under thermal, mechanical and electrical abuse and misuse conditions. The safety improvement due to the introduction of IL-based electrolytes is very clear when test under vacuum condition are considered. As a matter of fact, during these test cells containing conventional organic electrolyte normally swell (and therefore may break the sealing and leak) because of the volatility of the organic solvent. To the contrary, no swelling is observed in cells containing ILs.

These results indicate that the realization of high performance lithium batteries based on ionic liquids electrolytes is possible. To the best of our knowledge the performance displayed by the ILLIBATT prototypes are among the highest ever reported for IL-based batteries. Further improvements are certainly necessary, particularly at high C-rate, but the results of these test indicated that the cell chemistries identified during ILLIBATT project are certainly suitable for the realization of safer batteries with performance similar to those obtained in conventional organic electrolytes.

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