Collaborative project

FP7-2010-GC-ELECTROCHEMICAL-STORAGE

FINAL PROJECT REPORT

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Project acronym: AMELIE

Project full title: Advanced Fluorinated Materials for High Safety, Energy and Calendar Life Lithium Ion Batteries

Coordinator contact details: Vincenzo Arcella (vincenzo.arcella@solvay.com)
Solvay Specialty Polymers Italy
R&D Centre
V.le Lombardia 20 – 20021 Bollate (MI)
Italy
Tel: +39 02 2909 2209
Fax: +39 02 2909 2152

Project Website address :

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1. General overview of the work

1.1. Context of the project.

One of the main objectives in e-mobility is the increase of the vehicles autonomy.
That improvement is primarily achieved if the specific energy of the batteries is increased. But in parallel to this first objective, a strong focus on safety and cost controlled, improved by recycling of some higher value materials, is mandatory.
The research efforts needed towards the development of such a higher specific energy cell can lean on a basic electro-technical strategy that consists in increasing the voltage of the cell. But with a high voltage cathode material, the development of a stable electrolyte (solvent and salt) is required as well as new separators, stable binders and extended recycling process.
As a base of framework, $LiNi_xMn_{2-x}O_4$ and $LiCoPO_4$ has been considered as promising candidates for high voltage cathode and LiC_6 at the negative electrode. The first step of this project is the selection of the adequate cathode active material.
Then as the weakest link, in a high voltage cell, remains the electrolyte, the main objectives of the AMELIE project is indeed the development of more electrochemically stable components.
The stability of the electrolyte system and safety operating conditions of the battery are the main limitations today for the access to increased energy storage through the increase of the cell voltage.
Over the past years, most of the development efforts have focused either on (inorganic) active materials or on electrodes (cathode and anode).
The project focused on the development of fluorinated organic materials showing the best combination with anode and cathode materials towards high performances and stability.

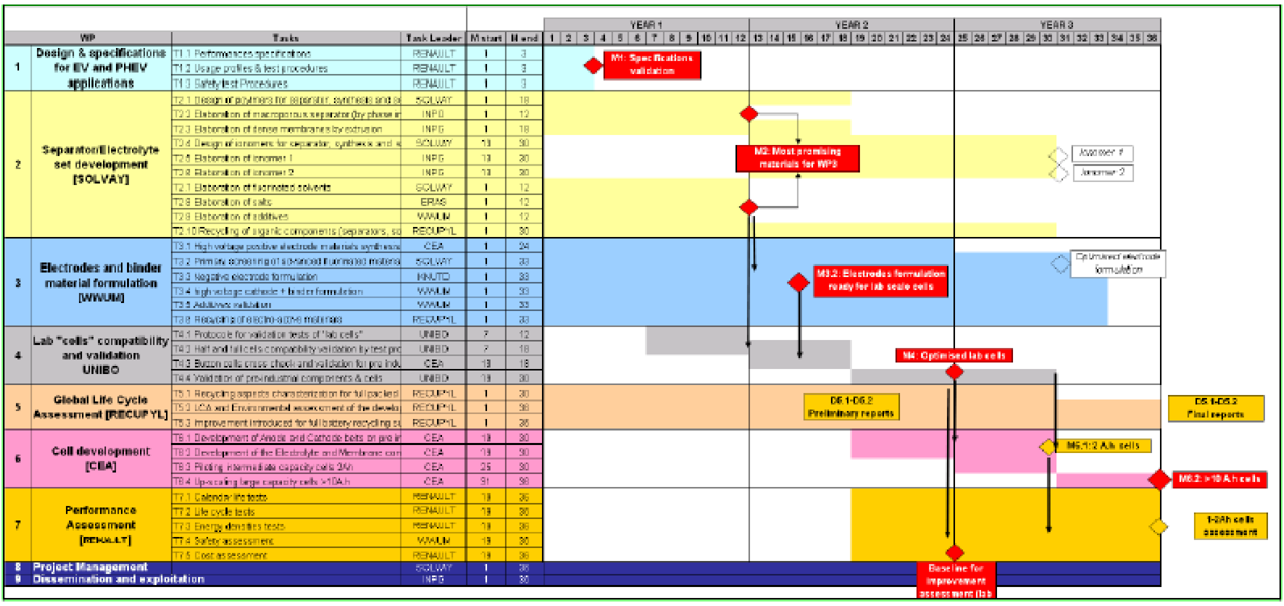
The main base material selected for these components are fluorinated materials.
These fluorinated materials, already known with wider electrochemical window stability, have to operate at high voltage, in safer conditions. This is namely the case of the binder used in the electrodes but especially as well of the Electrolyte/Separator set.
Among others, fluoropolymers are the most appropriate choice in term of thermal and fire resistance, electrochemical stability and electrolytes compatibility. In particular PVDF (Polyvinylidene fluoride) that has been already largely and successfully investigated for liquid and gel electrolytes, offer still room to improvement. In this project, the PVDF backbone is modified with comonomers, to increase the adhesion of binders, increase the ionic conductivity of separators and is combined with reinforcement technique to increase the mechanical properties and reduce the final thickness of the separator (both in dense and porous membranes).
The combinations of fluorinated materials (electrolyte/separator and binders) with new salts or new ionic liquids represent a new orientation to high performances without degradation of the safety operating conditions

The utilization of higher performing “inactive” organic materials (fluoropolymers and fluorinated compounds) used as electrolyte/separator and binders, which are known for their high stability, can be combined with higher voltage cells while allowing safer operation.

These new Fluorinated inactive materials will enable to reduce the amount of the same materials while increasing the energy and power densities of the battery, and consequently decreasing the cost per kWh of the final battery.

As well fluorinated polymers will be combined to active materials at the negative electrode (graphite LiC6) based on aqueous formulations. This brings the project to investigate the advantage of a partial removal of the organic solvents from the production of the electrode.
All the different components are then tested in various combinations to obtain optimised cells of which the performances are tested.
These developed cells are of different types.
After validation of a protocol for Lab cells testing, small validation cells (capacity: 15 mAh) are developed to evaluate in half and full cells the compatibility of the best combination of the new selected anode, cathode and electrolyte.
These cells then serve as a baseline for the further performance assessments cross check and validation for pre-industrial development.
For the second half of the project, the cell will be developed and up-scaled at two pilot level: pre-industrial cells (capacity: 2 Ah) and a prototype cell (capacity 10 Ah) to assess the up-scalability of the components formulations and processes
The final assessment of performances at this last prototype cell level will be performed, looking at calendar life, cycle life, specific energy, safety, cost competitiveness and recycling of end of life batteries.
Recycling, recovery and reuse: a non destructive recycling process is implemented for organic and active components, as well as on the end of life batteries with the target to reach 64% recycling in weight. The design of the components will be done by taking in account the final target of recycling.

The activities and WPs of the project are reported in the following Gantt chart.



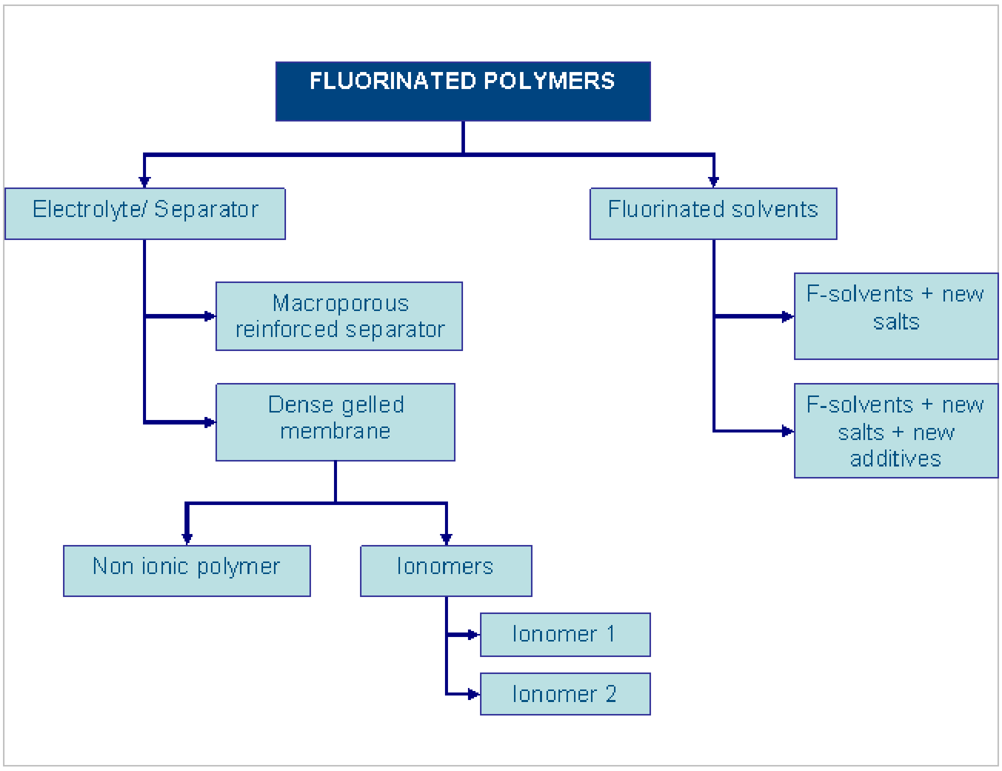
After the definition of the specifications in terms performances and safety in the WP1, the WP2 (Separator/Electrolyte set Material Development) had the ambition to develop electrolyte/polymer sets for EV batteries able to operate in withstand the drastic operating conditions of EV batteries based on a high voltage cathode.
The cornerstones of WP2 were the achievement of:

- **Performance** targets thanks (i) to an optimized compatibility between Fluorinated Chemicals i.e. polymers, salts and solvents and (ii) to efficient SEI.
- **Safety** will result from (i) improved stability in oxidation, (ii) high thermomechanical stability of the set [electrolyte + polymer] and (iii) low flammable components.
- **Low cost** strategy will consist in (i) the use of performing polymers allowing making thinner the electrolyte (ii) and to an extensive reuse of the electrolyte components. Recycling processes will be therefore set-up in parallel of the synthesis of the new materials.
- **Eco-Conception** will allow optimizing recovery & reuse of Fluorinated Materials.

The objective of WP3 is the formulation and scale-up of electrodes active material combined with polymer binders. Optimized electrodes will be provided to WP4 for electrochemical validation.
Briefly, research activitites on active materials are focused on three high voltage cathode materials, namely $LiNi_{0.4}Mn_{1.6}O_4$, $LiCoPO_4$, and Li_2CoPO_4F, and the up-scaling of the synthesis.
In parallel, a preliminary screening of advanced fluorinated materials, which will be subesquently utilized as binding agent for graphite based anodes and the selected high voltage cathode material (Milestone 2 at month 12). Taking advantage of these initial screening processes, electrodes will be prepared, based on the selected active materials and polymers.
These electrodes will be electrochemically investigated, including the electrolyte additives, selected in WP3, in order to determine the most promising electrochemical cell systems, which will be further provided to WP4.
Upon material validation in WP4, the materials and formulations have been transferred to the preparation and optimization of pre-industrial scale electrodes (in WP6, “Cell Development”) and testing of performances of resulting prototypes (in WP7, “Performance Assessment)”.
Finally a new recovery and reuse strategy of the battery materials has also been defined and implemented in WP5.

1.2. Material Development focus

The project aimed to focus on the development of fluorinated organic materials showing the best combination with anode and cathode materials towards high performances and stability.
The development flowchart is described in the following figure:



Starting from the current specifications or data described in other European projects, the specifications of the AMELIE cell, have been then adapted towards EVs and PHEVs. The final AMELIE cell will be prismatic with soft packaging (~ 10Ah Capacity) with agreed specifications on energy/power, cyclability, calendar life and safety.

Technological breakthrough resulting from combination of innovative polymers and liquid electrolytes, adequate combination of solvents and efficient lithium salts with a macroporous or dense polymeric membranes, is supposed to improve not only the performances but also solving safety and recycling issues.

One of the first objectives was the set up the synthesis and up-scaling of the high voltage cathode materials. $LiNi_{0.4}Mn_{1.6}O_4$ has been selected as the most promising cathode material to meet the AMELIE specifications. A study of alternative graphite materials to substitute the one, firstly selected, but no longer available, leading to the choice of SLA 1025, was successfully addressed.

Different VDF copolymers binders have been successfully polymerized and studied as advanced binder materials for graphite based negative electrodes and high voltage cathode materials contributing to the optimization of the electrodes formulations. These newly developed copolymers offer an enhanced cohesion of the electrode particles and improved adhesion to the metallic current collector, leading thereby to an improved electrical contact and electrochemical performance.
The study continued through the investigation of alternative binding agents, enabling the aqueous processing of graphite anodes. Thus PVDF latexes were tested for anode preparation at lab scale, and it was proved that, with the right formulation, it is possible to get electrode with enough

adhesion for battery assembling. This proof of concept still requires further investigation and optimization to be transferred to industrial scale, but it opens the way to the use of stable fluorinated binding materials through a eco-friendly water process.

Other PVDF polymers were selected to target an improved stability and interaction with the electrolyte. The Diffusion Induced Phase separation process was considered as more adapted than the thermally induced phase separation process to prepare macroporous membranes. Dense membranes were produced, at lab level, by solvent casting.
In order to access thinner membranes promising resins have been mechanically reinforced using nanocrystalline cellulose (NCC) as first approach. The NCC route successfully demonstrated an improvement of rigidity of a factor 3 at ambient temperature and a factor 10 at 90°C.
At lab cell scale, the advantage of this type of separator compared to standard commercial Celgard®2400 has been demonstrated. Unfortunately the availability of these films was limited to lab scale samples, with limited surface area, not adequate for pilot-scale prototypes. So it was not possible to implement these membranes in the final prototypes, but just in the 25 mAh small pouch cells.
Although the separator composition still needs optimization, this concept appears to be one of the main outcomes of AMELIE project, paving the way for a future scale-up in view of industrialization.

An interesting class of membranes investigated belong to the ionomer family, polymers containing an ionic group in the chain. The selected membranes were produced combining Solvay know-how in PEM Fuel Cell ionomers & membranes (PFSA) and INPG expertise in chemical modification of ionic functions. By switching the ionic function into Lithium sulfonimide, an increase in conductivity was demonstrated.
Due to the highly innovative content of these membranes to be used in Lithium Batteries, the study was limited to developing synthetic strategy and preliminary characterization, but no test in cell was envisaged.

The use of fluorinated electrolytes is already known to provide advantages to the battery in terms of safety, stability and performances.
Different fluorinated solvents and sulfonamide based Lithium Salts have been synthetized and their electrochemical stability was tested. The respective solubility of the salts in the solvents was tested and the most promising salts were combined with the new solvents, sometimes in binary mixture to tune the ionic conductivity through the intrinsic ions mobility and the final viscosity of the electrolyte. Some interesting trends were observed between their structure and the physic-chemical properties, as conductivity, stability and thermal properties.
Moreover, the screening for electrolyte additives for the LMNO cathode was focused particularly on the further investigation of succinic anhydride, which showed a beneficial effect on the self-discharge of such high voltage cathodes.
The electrolyte composition will still have to be further optimized in order to enable the application of such cathodes in future lithium-ion batteries. So far the different testing using the protocol test on Lab cells have demonstrated the considerable influence of the additivation to the electrolyte.

The second period of the project was aimed to demonstrate at a prototype scale, although representative of the application and using standard up scalable process, that the battery chemistries and materials developed are possible candidates to improve battery energy density.
One of the challenging objectives is in fact the validation of the cycling tests and the safety tests (5 specifications), because this can hardly been done on Lab cells and a different cell geometry and size needs to be available
The work included the preparation of all needed cell components, to assembly prototypes at different sizes: medium size prototypes (~500mAh) and intermediate size prototypes (~2Ah) on pre-industrial tools, and finally full size prototyping (~10Ah).
In addition, a few small pouch cells, 25 mAh size, were produced to evaluate the PVDF-NCC separator developed in WP2. Although these small cells were not produced at pilot equipment, they will allow the electrochemical characterization of the separator in a more reliable cell.

The success in the active materials synthesis up scaling, and in the development of all the electrode formulations, allowed the preparation of negative and positive electrodes on pre-industrial equipment.
Due to difficulties in separator and electrolyte development, specifically to obtain samples in relevant quantities, the strategy was thus modified with the agreement of all partners:

- test three commercial electrolytes, improved by using additives developed in the project as Succinic Anhydride and F1EC;
- use a commercial Celgard® separator.

For the final demonstrator, it was chosen by the consortium to use the electrolyte made of 1M $LiPF_6$ in EC:DMC (1:1) electrolyte, with two additives: 2% SA and 1.6% F1EC, because it gave the best power and ageing performance in the medium cell screening.
Globally almost 100 cells were successfully produced and delivered to the partners for the electrical and abuse tolerance tests, including three final demonstrators, close to 10Ah, providing that AMELIE developed technology to be scalable up to automotive grade large cell format, on the electrode and assembly process basis.

Prototypes were evaluated in terms of battery performances as defined in WP1. Specifically the tests were designed to study calendar and cycle life, energy density, safety assessment and cost analysis.

Unfortunately the results were not completely satisfactory.

Calendar ageing showed significant decrease in cell capacity after one month storage, regardless of electrolytes. This irreversible capacity loss is attributed to the instability of all the three electrolytes tested with regards to the LNMO/Gr technology.
Cycle life, both 2Ah prototypes and 10 Ah demonstrators, showed poor durability. Quick capacity decay is attributed to continuous increase of cell impedance (increase of charge transfer resistance) due to electrolyte instability and decomposition.
Due to the low stability and the capacity fading at the early stages of cell life (from formation step to the last cycle of the refreshment step), the energy density values were negatively affected and

did not reach the target of 200 Wh/Kg. Only considering the capacity measured upon formation step, energy densities are close to the target, 180-190 Wh/kg.
Safety assessment did not show a significant improvement with respect to commercial cells, no effect was observed depending on the used salt. Moreover, the electrolyte decomposition induced by mechanical, electrical and thermal abuse will have to be addressed prior to further the application.
The cost of battery based AMELIE technology was assessed for both PHEV buses and EV applications. Energy storage costs of 176 €/kWh and 323 €/kWh were estimated for volume production of 50,000 EV packs/year and 10,000 PHEV packs/year respectively. Thanks to the lower cost of LMNO and higher voltage, these prices were shown to be much less as compared to the prices estimated using standard "2012 battery technology", namely NMC/Gr (229 €/kWh and 393 €/kWh for same volume production of EV and PHEV pack).

In WP5, the global flow sheet of the LCA for final version of cells was achieved and a new model for LCA related to recycling process was designed.
Thanks to the use of a non-thermal treatment, but a combination of mechanical and chemical steps, it was possible to achieve the Recycling Efficiency of 50% imposed by the EU Directive.

1.1. Conclusions

LNMO/Gr finally appears as a remarkable technology which is able to combine both higher energy density and lower cost compared to the state of art. However, LNMO/Gr still shows modest cyclability and it is hence expected to be improved to benefit from its advantages at Beginning Of Life.
Despite the relevant work and the big amount of scientific data generated at lab scale, these main issues were encountered in the project:

- the production process at lab level still remain challenging;
- the up-scaling of optimized formulations in larger cells is still a high risk, as the positive results obtained at lab cells were not confirmed during battery up-scaling.
- Battery durability and calendar life remain a challenge.

2. Project management during the period

The innovative content of the project, specifically on the development of the electrolyte/separator set pushed these tasks on the challenging side of research where the consortium took advantage of the nice complementarity of expertise of the different partners in polymers, physical chemistry and electrochemistry.
Despite an important amount of scientific data generated, the consortium has been facing some delays both for a separator sample and an important electrolyte sample.
To mitigate the impact of these delays, alternative samples of salts for electrolyte have been tested.
We estimate that the main reason that induced this delay is an excessive innovative content pursuing solutions that lead to unexpected difficulties.

These difficulties reflected in changing approach for scale-up, second important part of the project: the production of electrodes was planned before electrolyte and separator related activities.

INP Grenoble (Covering Tech Mgnt, Scientific tasks in WP2, and Dissemination) who had the management of most of the tasks of WP2 appeared to be short in resources to ensure the administrative aspects of its own tasks in technical management. These limitations in the technical management are probably explaining as well some part of the delays encountered.
Despite its investment of own resources (3 months' salary paid to PhD student Marco Bolloli in 2010 to have available the PhD from the beginning of AMELIE) INP Grenoble, has faced difficulties to follow up the technical and industrial risks and to ensure that the project strategic orientations are implemented at the WP and participant level.
In order to face the lack of resources, the technical manager applied for a six months position as full-time researcher and obtained that position from CNRS. He also obtained, from Grenoble INP an additional discharge of teaching service of 12.5% i.e.24 hours over 196 hours in 2011 and 2012. He has applied for a full time discharge of his teaching activity, and has obtained, from the CNU (Conseil National des Universités) a 1 year full discharge of teaching service from September 2012 (CRCT: Congé pour Recherche et Conversion Thématique) that has been helpful both for the technical management/dissemination, and for the driving of scientific tasks devoted to LEPMI.

One important issue in project management was due to the decision of one partner, CONTINENTAL (TEMIC Automotive Electric Motors GMBH), to leave the project. The decision was officially communicated in November 28th, 2012, and was justified as for internal reorganization of business activities in frame of formation of JV between Continental and SK Innovation, a South Korean company, which will hold a 51% stake of the new company.
The partner has already supported the project in the first part, as in WP1 for the definition and validation of the technical specifications for lithium ion batteries performance requirements towards EVs and PHEVs. However most of the work was planned for the second half of the project.
Another partner, RENAULT, with formal letter of intent dated July 16th, 2013 accepted to take over totally the WP7 leadership and the entire tasks and deliverables previously assigned to Continental.
From an accounting point of view, the remaining funding for CONTINENTAL was made available for RENAULT in counterpart of the new activities and deliverables. This appeared as the best solutions, since Renault has the capabilities and the competences for carrying on the assigned activities, without jeopardizing the final outcome of the project.
Accordingly, the consortium has agreed to terminate the participation of TEMIC Automotive Electric Motors in the AMELIE project effectively from 01/01/2013, and agreed that Renault will take over the activities and tasks which were assigned to TEMIC Automotive Electric Motors.
The Annex I (Description of the Work), including Part B, were subsequently modified changing WP and task assignments.
Another minor modification was the change of SOLVAY SOLEXIS name into SOLVAY SPECIALTY POLYMERS ITALY SPA, without any modification in roles and responsibilities.
Also the legal entity SOLVAY SPECIALTY POLYMERS BELGIUM SA / NV was included to the GA as third party of SOLVAY SPECIALTY POLYMERS ITALY SPA. The employment contract of one of the key persons involved in the project on behalf of the Solvay Group, the Project Manager, has been transferred from SOLVAY SA to SOLVAY SPECIALTY POLYMERS BELGIUM SA / NV as from

01/01/2012. The role of this employee in the AMELIE project has not changed, nor the commitment of the beneficiary SOLVAY SPECIALTY POLYMERS BELGIUM SA / NV.

2.1.Dissemination strategy

The aspects related to the external project communication and the intellectual property issues had to be addressed from the beginning of the project. A great attention has therefore been paid to innovative results that deserved, prior to any public dissemination, to be protected.
As part of dissemination and exploitation strategy of the AMELIE project, a technical workshop between the partners was scheduled in Grenoble on July 4-5, 2013.
This workshop consisted of sessions on fundamental and technological aspects of the Li-ion batteries. It has been organised in the last year of the project in such a way to have available enough experimental data that can be disseminated. Obviously, the new results deserving to be protected were either patented or temporarily withdrawn of the oral & poster presentations.
Several members of the International Advisory Board were invited, and the 5 selected keynote speakers were:
1. Prof. Lorenzo Stievano from Montpellier University 'Negative electrodes materials for Li-ion batteries alternative to graphite.'
2. Dr. Patrick Judeinstein from CEA-Saclay 'Multi-scale NMR: a help to optimize ionic conductivity'
3. Prof. Giovanni Camino from Politecnico di Torino (Member of AMELIE International Advisory Board) 'LCA and recycling issues.'
4. Prof. Daniel Lemordant from Tours University 'Electrolytes design'
5. Prof. Jean-Claude Leprêtre from Grenoble University 'Redox organic polymers as alternatives to current cathodes?'
Lecture 1 was selected to assess the potential of using AMELIE materials with other negative electrodes that could increase energy and/or power densities.
Lecture 2 was focused on physical-chemistry aspects of electrolytes through NMR tool.
Lecture 3 was in relation with LCA and recycling.
Lecture 4 was given by an expert of electrochemical stability of liquid electrolytes.
Lecture 5 dealt with polymeric cathodes that could advantageously replace current inorganic cathodes.
All these keynote lectures were complementary with the oral presentations.
The workshop has gathered about forty participants. Mixing the scientific and technological presentations, it was found very interesting by the whole of the participants and highly educative by the young students (Master, PhD and Post-doc students) that attended the meeting. Four young researchers have delivered an oral presentation, while several other PhD students have presented posters. The friendly atmosphere has favoured direct discussions between on the one hand academic & industrial AMELIE partners and, on the other hand, the students.
A book following the technical workshop event was scheduled, the edition of a proceeding made in Grenoble INP and, later, an electronic version to be uploaded on the AMELIE public website.
Unfortunately at this moment the number of contributions is insufficient, despite the calls promptly sent by Professor M. Duclot from LEPMI. Indeed, papers could not be submitted before the end of the project. Furthermore all the editors of books know that several follow-up letters are indispensable to recover all the contributions.

Additionally, it must be thoroughly checked that this public dissemination does not affect the opportunities to file other patents. Furthermore, it must be checked that these contributions do not reveal, too early, strategic data, even if already patented.

2.2.Final Plan for Use and Dissemination of Foreground

Due to (i) the task organization (ii) the strategic objectives of the project and the patentability of many results, AMELIE was not prone to submit many papers and to deliver many lectures during the project time. Some restrictions still delay some publications and the patentability of 3 inventions is still matter of discussions. Once, overcame these temporary delays, several papers will be submitted, in particular in the field of lithium-ion battery materials e.g. fluorinated polymers & ionomers, fluorinated solvents and subsequent half cells and battery tests.

As much as possible, the contributors will be encouraged to submit publications that really associate the AMELIE partners.