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Advanced Fluorinated Materials for High Safety, Energy and Calendar Life Lithium Ion Batteries

Reporting

Project Information

AMELIE

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Project closed

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31 December 2013

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EU contribution
€ 3 526 000,00

Coordinated by
SOLVAY SPECIALTY POLYMERS ITALY SPA
Italy

Final Report Summary - AMELIE (Advanced Fluorinated Materials for High Safety, Energy and Calendar Life Lithium Ion Batteries)

Executive Summary:
Publishable summary
Project Content and main objectives

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.
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.
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. 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 may 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.

After validation of a protocol for Lab cells testing, small validation cells 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.
In the second half of the project, the cells have 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 has been 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.

Work performed and the main results achieved so far
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.

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. In order to access thinner membranes, prepared by phase inversion, 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 which were investigated belongs 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.

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.
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 including testing of three commercial electrolytes, improved by using additives developed in the project as Succinic Anhydride and F1EC, and by using a commercial Celgard® separator.
For the final demonstrator, it was chosen by the consortium to use the electrolyte made of 1M LiPF6 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, cycle and calendar life did not reached the performance targets, while energy density was negatively affected and was able to be close to the target of 200 Wh/Kg only at Beginning Of Life.
The global flow sheet of the LCA for final version of cells was successfully 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 imposed by the EU Directive.

The final results and their potential impact and use
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, some issues were encountered in the project.
The production processes at lab level still remain challenging. For example interesting products as PVDF reinforced membranes or fluorinated lithium salts were obtained only as lab scale samples, with limited areas and quantities, not adequate for pilot-scale prototypes.
The up-scaling of optimized formulations in larger cells is still a high risk. Positive results obtained at lab cells on electrolyte formulations, were not confirmed during battery up-scaling.
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

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Project Context and Objectives:
One of the main objectives in e-mobility is the increase of the vehicles autonomy.
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Project Results:
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Potential Impact:
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