Development of Novel Solid Materials for High Power Li Polymer Batteries (SOMABAT). Recyclability of Components

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Abstract SOMABAT aims to develop more environmental friendly, safer and better performing high power Li polymer battery by the development of novel breakthrough recyclable solid materials to be used as anode, cathode and solid

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polymer electrolyte, new alternatives to recycle the different components of the battery and life cycle analysis. This challenge is being achieved by using new low-cost synthesis and processing methods in which it is possible to tailor the different properties of the materials. Development of different novel synthetic and recyclable materials based carbon based hybrid materials, novel $LiFePO_4$ and $LiFeMnPO_4$ based nanocomposite cathode with a conductive polymers or carbons, and highly conductive polymer electrolyte membranes based on fluorinated matrices with nanosized particles and others based on a series of polyphosphates and polyphosphonates polymers respond to the very ambitious challenge of adequate energy density, lifetime and safety. An assessment and test of the potential recyclability and revalorisation of the battery components developed and life-cycle assessment of the cell will allow the development of a more environmental friendly Li-polymer battery in which a 50 % weight of the battery will be recyclable and a reduction of the final cost of the battery up to 150 €/kWh is achievable. The consortium is made up of experts in the field and is complementary in terms of R&D expertise and geographic distribution.

Keywords Lithium · Battery · Polymer · Sustainable · Materials · Solid

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1 State of the Art

With economical, infrastructural and technological advancements, the world´s hunger for energy is ever increasing [1]. Finite fossil-fuel resources, nuclear waste and global warming linked to CO_2 emissions necessitate the rapid development of alternative “green” sources of energy. Electricity generated from renewable resources such as solar and wind power offer great potential to meet these future energy demands; however, the output from sources is intermittent while available electricity is required at any time in our daily lives. These crucial energy supply issues, together with the rapid advance and eagerness from the electric vehicle automotive industry (i.e. Electric vehicles and Hybrid electric vehicles) have combined to make the development of radically improved rechargeable batteries a worldwide imperative. Researchers have thus the responsibility for providing the world with better and more efficient batteries.

The science and technology of lithium batteries have dominated the field of advanced power sources and replaced many other batteries in the market, particularly in the areas of communications, computers, electronics, and more power demanding services such as power tools and transportation. The exponential growth in portable electronic devices such as cellular phones and laptop computers during the past decade has created enormous interest in compact, light-weight batteries offering high energy densities. Also, growing environmental concerns around the globe are driving the development of advanced batteries for electric vehicles.

Lithium-ion batteries are appealing for these applications as they provide higher energy density compared to the other rechargeable battery systems such as lead acid, nickel-cadmium, and nickel-metal hydride batteries [2].

Concerning to their use in electric vehicles, Li ion batteries are expected to be one of the most used energy storage devices used for this purpose in the near future. However, in spite of the several advantage of Li ion technology for its use in hybrid and electric vehicles there are still different technological barriers to overcome, such as the performance of the battery, its life, recyclability, cost and safety.

Research on these issues is multidisciplinary and must involve several themes to gather maximized knowledge and critical mass in a research field where step changes are needed.

Concerning *battery materials* the challenge is to find new low cost cathode (nickel and cobalt oxides are expensive and their prices are exploding) and anode materials which allow high energy density and long-life batteries. Additionally, safety problems related to thermal runaway associated to actual commercial electrolytes should also be solved. One interesting alternative for this is the lithium polymer battery (LPB) which uses a solid polymer electrolyte (SPE). The motivation and advantages for using such a polymeric membrane as the electrolyte component in a lithium cell are: (a) Suppression of dendrite growth; (b) Enhanced endurance to varying electrode volume during cycling; (c) Construction of solid-state rechargeable batteries in which the polymer conforms to the volume changes of both electrodes that occur during charge–discharge cycling; (d) Reduced reactivity with liquid electrolyte; (e) Improved safety; (f) Better shape flexibility and manufacturing integrity [3, 4].

Another aspect that will be looked at is the issue of the *recycling of batteries* at the end of their life cycle and the development of technologies to maximize the recovery of materials, in particular for those of high added-value or presenting high environmental impacts.

For existing or near-to-market types of lithium-based batteries, projects dealing with the *comprehension, modelling and management of degradation drivers and processes* with the aim to extend the calendar and operational life of the cells are also essential.

Finally, the environmental *sustainability* of each developed energy storage technology shall be assessed via life-cycle assessment (LCA) studies.

SOMABAT research focuses on overcoming and improvement of different technological barriers of batteries such as the performance, its life, recyclability, cost and safety for their use in EV.

2 Project Description

SOMABAT aims to develop more environmental friendly, safer and better performing high power Li polymer battery by the development of novel breakthrough recyclable solid materials to be used as anode, cathode and solid polymer electrolyte, new alternatives to recycle the different components of the battery and life cycle analysis (see Fig. 1).

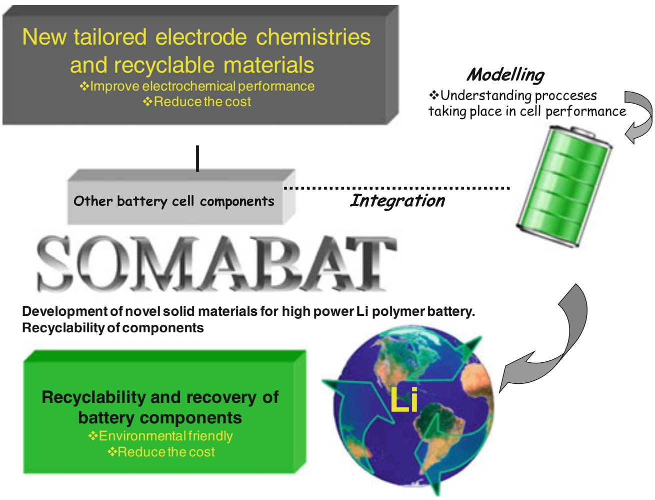

Fig. 1 Schematic representation of SOMABAT project including the main objectives [5]

This challenge is being achieved by using new low-cost synthesis and processing methods in which it is possible to tailor the different properties of the materials. Development of different novel synthetic and recyclable materials based carbon based hybrid materials, novel $LiFePO_4$ and $LiFeMnPO_4$ based nanocomposite cathode with a conductive polymers or carbons, and highly conductive polymer electrolyte membranes based on fluorinated matrices with nanosized particles and others based on a series of polyphosphates and polyphosphonates polymers respond to the very ambitious challenge of adequate energy density, lifetime and safety.

An assessment and test of the potential recyclability and valorization of the battery components developed and LCA of the cell allow the development of a more environmental friendly Li polymer battery in which 50 % weight of the battery will be recyclable.

The general objective of the project is the development of novel breakthrough recyclable solid materials to be used as components (anode, cathode and electrolyte) of a high power and safe Li polymer battery and study and test potential recyclability and sustainability of the battery. The goal is to develop a Li polymer battery with an energy density higher than 220 Wh/kg and a cost lower than 150 €/kWh is the main target.

To achieve the targets novel nanostructured cathode materials based on lithium iron and manganese phosphate will be researched by CIN2 (CSIC-ICN) and UMICORE. The huge advantage of this new material is that it offers maximum energy storage in minimum space, safety and it is environmentally friendly. In addition, anode materials based on synthetic carbon, and other obtained from agricultural wastes will be developed by Université de Liège, Kiev National University of Technologies Design, and ITE. With these materials the energy density will be improved in about 30 % respect to carbon based conventional anodes.

Both electrodes will be much less costly and a lot more reliable than traditional alternatives. Therefore, it will meet the essential requirements for the mass industrial development of electric vehicles.

Moreover, ITE and Institute of Chemistry Timisoara of Romanian Academy will develop new polymeric materials to be used as polymer electrolyte which will reduce outstandingly the safety problems such as leakage, short circuits, overcharge, over-discharge, crush and exposure to fire.

Other strategies which will be followed to reach the ambitious targets are centred on the improvement of materials integration, modelling procedures, and optimizing the management system of the battery. These tasks will be performed by Cegasa International, Virtual Vehicle Competence Center, Lithium Balance, Cleancarb, and Atos.

Expected final results

- Achieve a more environmentally-friendly Li polymer battery in which at least 50 % by average weight of the battery will be recyclable.
- Reduction of the total manufacturing cost of the battery down to 150 €/kW due to recyclability.
- Improvement of the battery safety by the use of solid materials.

3 Project Results up to Now

SOMABAT is a 3 years project which started in January of 2011. In this section, the main results achieved in the project are described divided in the main areas which are under research in the core of the project:

- *Development of synthetic and recyclable material,*
- *Design, development & modelling of a lithium polymer battery,*
- *Recyclability of battery components Sustainability assessment of Li polymer battery.*

3.1 Development of Synthetic and Recyclable Materials

3.1.1 Carbon Anode

In the anode part, the objective is the development of *carbon based hybrid materials composed by graphitisable carbons, novel low-cost synthetic nanostructured carbons and carbon materials obtained using agricultural wastes as precursor as carbon part and metal nanoparticles*, which has the potential to present higher energy density and lower cost than classic carbon anode materials and higher stability and lower environmental impact than lithium metal alloys.

The work has focused on novel carbon/carbon composite material. Such materials were prepared using graphite materials and porous carbon xerogels or carbon material obtained from agricultural waste precursors (i.e. olive stones and orange skin). Composite materials based on different carbon materials have been optimized. It was found that the carbon/carbon composites exhibit high reversible capacity and good cyclability when used as anode materials for rechargeable lithium ion batteries. The graphite based composite with carbon material obtained from agricultural waste precursors with content of 10 wt% exhibits the optimal electrochemical performance with a high reversible capacity over 360 mAh/g. Moreover, the purification of carbon materials in the hydrogen atmosphere at high temperature can further improves the first coulombic efficiency and capacity retention, but decreases the initial capacity of the anode material.

Additionally, the work has dealt with the control of the texture of *carbon xerogels*. In particular, the micropore volume was reduced by addition of secondary carbon precursors either by impregnation or by CVD. In each case, the microporosity was significantly reduced, whereas the mesopore sizes remain unaffected, leaving a good accessibility to the framework. Research on the preparation of ordered mesoporous carbons has allowed identifying some key parameters affecting the structural regularity of the hexagonal mesoporous framework. As can be seen in Fig. 2 introduction of carbon xerogels into the active mass of anode based on

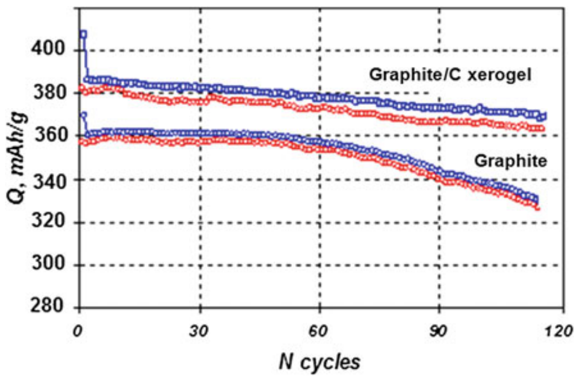

Fig. 2 Specific capacity versus cycle number for anodes based on: graphite SL30; binary mixture

graphite allows to increase a reversible capacity up to 385 mA·h/g per total mass of graphite/carbon content of electrode, and also to improve the stability of characteristics during the cycling.

3.1.2 Polymer Electrolyte

In this case, the objective is the development of safe and highly conductive electrolyte membranes composed fluorinated polymers with nanosized particles and a series of polyphosphates and polyphosphonates.

The effect of several parameters like the effect of amount of different additives such as plasticizers, and lithium salts on the final properties of solid polymer electrolyte has been studied, showing that these two variables affect strongly the final properties of the polymer membranes obtained. After this study the selection of 1st generation polymer membranes was performed. The selected 1st generation polymer membrane presents balanced properties in terms of ionic conductivity, thermal and mechanical properties and was scaled up for integration in 1st generation Li polymer cell. In parallel, the 2nd generation polymer membranes have been under study. The aim of 2nd generation polymer membrane development was to test alternative more stable and environmentally friendly Li salt and plasticizer for their use in polymer membrane composition. The preliminary results show that the alternative plasticizers tested are thermally and electrochemically more stable than traditional carbonates and maintaining the ionic conductivity of the polymer membranes developed.

Additionally, new formulations for polymers and copolymers syntheses with the purpose of improving the electrochemical and mechanical characteristics of the polyphosphate based membranes to fulfil the initial requirements have been studied. The main performed activities were:

Synthesis of phosphate copolyethers from phosphorus oxychloride and polyethylene glycols (PEG 6000, PEG 2000) and membranes based on (co)polyphosphoesters and commercial acrylates, containing lithium trifluoromethanesulfonate by UV curing and their characterisation by FT-IR Spectroscopy, Thermal Analysis

(TG, DSC), EIS, resistance and transference number have been performed. This type of membrane had good conductivity, relatively good mechanical properties but worse stability. New polyphosphoesters based on phosphorus oxychloride, 1,4-butandiol monoacrylate and PEG 2000–4000 were synthesized. Polyphosphoesters–diacrylate-lithium perchlorate composites were obtained by UV curing and characterized by FT-IR spectroscopy and Thermal Analysis. EIS spectroscopy showed good conductivity (3×10^{-5} S/cm) but also low electrochemical stability.

Supplementary work was carried out for searching the best formulation for improving electrochemical and elastic properties required by integration: more sticky membranes to have better adherence to electrodes were developed. Polyphosphates starting from PEG, phosphorus oxychloride and butanediol monoacrylate have been synthesised, from which 90 sticky membranes with dimensions of 86 × 168 mm were obtained. These membranes were sent, in order to develop first generation battery.

After generation cells evaluation, different alternatives were tested by using other polyols instead of PEG-s, namely Polypropylene glycols (for example PPG 1500) in order to obtain polyphosphoesters with improved characteristics such as: crystallinity, conductivity, mechanical properties. Besides, esters of phosphorus derivatives and 1,4-butandiol monoacrylate were obtained, in order to use them as co-monomers or crosslinkers. Membranes obtained by UV-curing or thermal polymerization have been realized. Characterization of these compounds is in progress for the selection of 2nd generation materials.

3.1.3 Cathode

Concerning the design of 1st generation (Gen#1) lithium iron phosphate (LFP) products, the flowsheet was optimized to be able to reach the cost targets of the project. In the same time, performances criteria such as cycle life and power were looked at in order to propose a product suitable for large cells market. Upscaling was done in order to produce large quantities to build scale 1 cells. Products were also sampled to external customers for further market adoption. Then, a high voltage cathode material was successfully developed at lab scale, the benefit of it being to increase the cell voltage and energy density. Substitution of iron by other elements in the LFP structure leads to some inherent loss of power performances. These losses have to be reduced before being able to upscale the 2nd generation (Gen#2) phosphate materials to pilot production.

Additionally, the optimization of two selected synthetic methods for $LiFePO_4$ materials and the corresponding cathodes, namely (i) solvothermal (ii) reflux has been developed, the latter method has been targeted for upscaling. This optimization has included a wide battery of experiments for the fine-tuning of synthesis parameters and a correlation of those parameters with the micro-meso-structure of the $LiFePO_4$ materials obtained. As part of this systematic optimization materials with suitable nanosized particles self-assembled into larger micron-sized aggregates were prepared, a hierarchical structure which provides ideal microstructures for electrode applications. Presently, the work is centered in the characterization of 2nd generation materials and coating of these new materials with carbon and with conducting polymers.

3.2 Design, Development and Modelling of a Lithium Polymer Battery

3.2.1 Integration

The 1st generation design for the SOMABAT Li polymer cells has been performed, with stacked electrode/membrane pouch cell design and large size automotive format, so the scalability of the materials can be proved (see Fig. 3). Since the active area of the electrodes to stack is ~approx. 80 × 160 mm, the slurry formulation and fabrication of the electrodes from the active materials has been developed, while 70 membranes (85 × 168 mm; 50 μm thickness) were prepared required for one cell.

After slurry formulation scale-up and optimisation, several meters of cathode (LFP#1) were prepared. Corresponding quantity of anode using commercial graphite and standard formulation has also been produced for the first proof-of-concept cells assembled. With the available membranes, one cell (expected capacity 2–3.5 Ah) with each selected polymer electrolyte was prepared. This first assembly has revealed swelling issues with polyphosphoester based membranes and difficult handling of fluorinated based samples leading to short-circuit that are being solved for 2nd generation development. Coin cells have been assembled with these materials. In Fig. 4 charge-discharge profile of the one of the 1st generation cell can be seen. Testing results in this format have shown that 1st generation membranes (despite their conductivity being lower than the standard liquid electrolyte) can withstand up to 1 C discharge rate at room temperature with stable cycling for more than 400 cycles.

Fig. 3 The 1st generation prototype cell

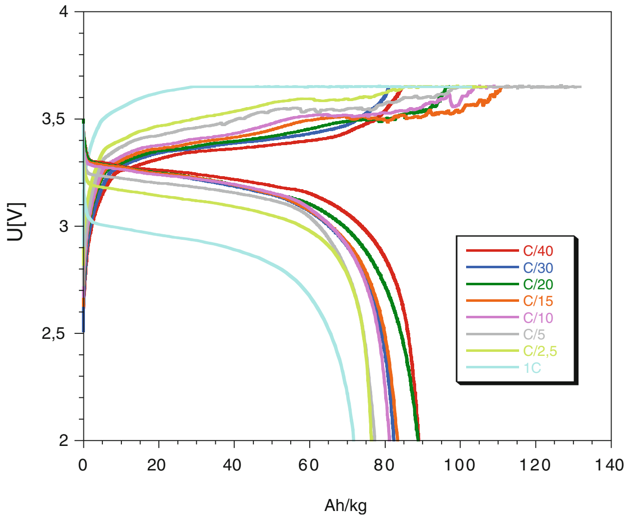

Fig. 4 Charge and discharge profiles of 1st generation cell

Additionally, anode formulation optimisation and scale-up from the C/C composite has been performed. An optimised formulation has been achieved during this period and is ready to be used to complete 1st generation characterisation by assembling smaller area stacked pouch cells.

The concept design of the battery pack with at least 4 cells connected in series has been presented during the workshop at Timisoara in July 2012. Once the generation 2 materials have been developed and tested a second set of pouch cells will be manufactured.

3.2.2 Modelling

In the approach of modelling the SOMABAT battery a multi-scale model of the lithium-polymer battery is proposed. The models will be used to give an insight to the proposed battery module regarding temperature and electrical distribution and to support cell and module optimization. In the attempt of building up a multi-scale model of the lithium-polymer battery with full numerical integration, the following length scales (model levels), are distinguished: device level ($\sim 10^{-1}$ m), electrode level ($\sim 10^{-4}$ m) and particle level ($\sim 10^{-7}$ m). Besides in length scale, they also differ in the time scales of the physical effects of interest. With inputs regarding the geometries of cells and module, the model for the highest level of geometry was implemented. Also, the core set of governing equations of the electrochemical model for the lowest level (particle level) and the interface conditions were defined, the homogenization procedure was set up and implemented in PYTHON. Thereby, the finite element method (FEM) has been chosen on all levels, because of its flexibility. On the top level, the 3D FEM toolbox ELMER is used. The solver, which was coded for ELMER in FORTRAN, was updated and speeded up by some changes in the technical approach to the solution process.

3.2.3 Battery Management System

The environmental testing and firmware development for the *battery management system hardware* that was developed and prototyped during the first year of the project has also been performed. This includes software design, source code development, reviews, validation and testing the system for stability on terms of electromagnetic immunity, vibration robustness and temperature operating range. In Fig. 5 detailed view of CMU diagnostics software is shown.

At the end of the second year prototypes for a battery management system suitable for testing the next generation of SOMABAT battery cells have been completed.

3.3 Recyclability of Battery Components

The recycling work is divided in 3 periods, mainly international comparison of existing recycling processes, investigation of SOMABAT battery materials in viewpoint of recycling procedures, and development of two alternative recycling

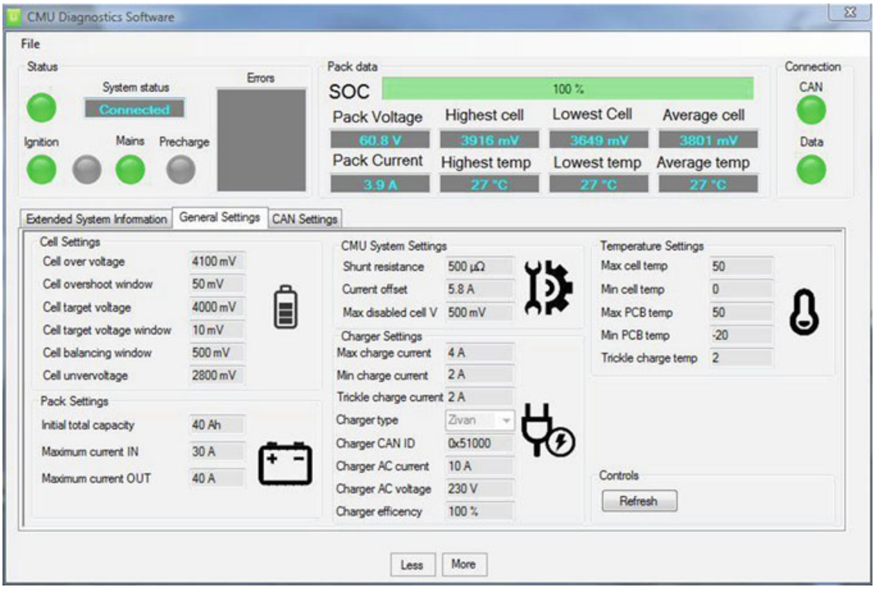

Fig. 5 Detailed view of CMU diagnostics software

processes for this newly developed SOMABAT battery. This development foresees a basic design of hydro- on the one hand, and pyrometallurgical process on the other hand. This process design has to be verified by installing and testing this recycling technique at laboratory scale.

Since beginning of SOMABAT project, there has been activity on the following tasks:

Legislative requirements on transportation, packaging and recycling of end-of-life (EOL) Li-ion Batteries, investigation of theoretically possible recycling routes, data consolidation on existing Li-Ion battery recycling processes (one dedicated, and one non-dedicated recycling facility), evaluation and comparison of these processes in terms of recycling efficiency of recycled materials, compliance with legislative requirements, environmental impact of process, economic performance, flexibility on varying input-materials due to changing Li-ion subtype compositions.

After comparison of technical process performance, the economic features of possible process routes, pilot scale plants as well as industrial implemented plants have been figured out. Summarizing these results, and gathering all detail data of project members on battery components, a specific SOMABAT recycling process to combine economic efficiency with technical optimisation of recovered metals has been designed.

Additionally, a mechanical treatment to achieve the safe and efficient access to active material, physical sorting to separate between metals, oxides and polymers have been developed. The mechanical trials were finalized with success as a separation was done by up to 90 % of each fraction reported. The chemical treatment was made a safe way at room temperature and iron-oxide was recovered from iron based cathodes using dissolution/precipitation shuttle process leading to efficient separation between iron and lithium. The last metal is precipitated as Li_2CO_3. The mechanical and chemical treatment was carried out with closed relation with the recycling efficiency according to EU Directive 066.

The expected mass balance of the cells planned in the SOMABAT Process depends on the route (solvent or water route). The decomposition of this mass balance shows that the polymer has a substantial weight and must be recycled in order to reach 50 % of recycling rate. Without recovery of polymers the recycling rate stays below 50 % but with access to polymers its jump to around 60 %.

3.4 Sustainability Assessment of Lithium Polymer Battery

The sustainability assessment focuses on a complete LCA which analyzes both environmental aspects and impacts of the final Li-polymer battery developed in SOMABAT.

The goal and scope of LCA includes, among other the definition of the functional unit and system boundaries. The functional unit is a key factor for a complete

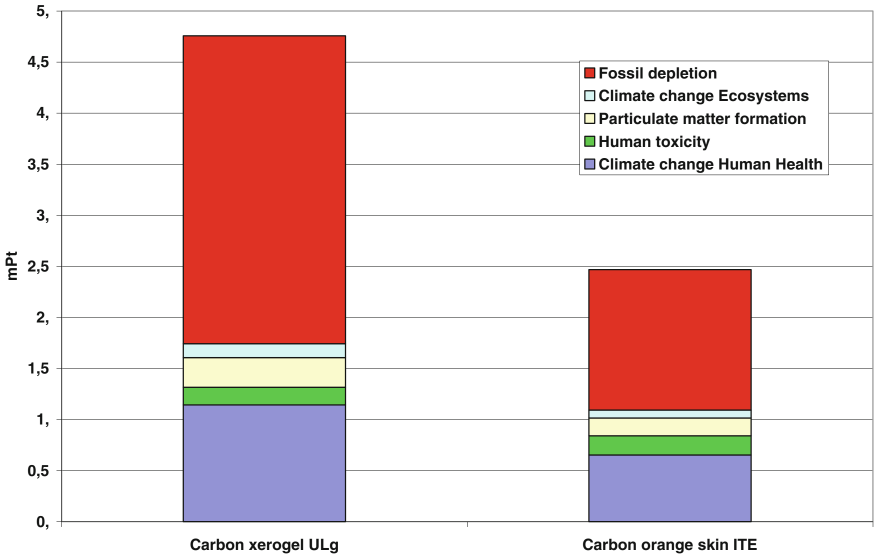

Fig. 6 Comparison of impacts of carbon xerogel and carbon material obtained from orange skin, method: ReCiPe endpoint (H)/World ReCiPe H/H/Single score

evaluation of LCA and, in this case, it is a given amount of energy (30 kWh) accumulated by the battery and then delivered to the powertrain for an electric vehicle capable of sustaining 4,000 charge cycles at 80 % maximum discharge giving at least a 210.000 km operation during the vehicle design life time. System boundaries comprise the entire life cycle of the battery from “cradle to grave”.

During this period, analysis and modelling of several materials were performed. Data were obtained from different partners and preliminary analysis on parts of the battery was carried out. Carbon xerogels obtained by ULg and orange skin carbon from ITE were analysed and compared (see Fig. 6).

The same approach was applied to membranes. Polyphosphonate and PVdF-HFP based membranes were analysed and the comparison was performed.

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