Executive summary:

The main objective of this project is to develop a supercapacitor based energy storage system, capable of storing ten times more energy than the reported State of the Art technology, while keeping the high power density, long life cycle and production cost of currently available supercapacitor systems.

This will lead to a large reduction in the overall cost of the stored kW-h, and as a consequence, a cost-effective improvement of the reliability, efficiency, security and environmental impact of the energy networks, either for stationary or dual-use applications.

The main impact of the energy storage system (ESS), developed in the HESCAP project will be a drastic reduction of the volume and weight for a given energy rate, together with a reduction of the cost of the stored kW-h, in the five applications selected that require short-term power delivery and high duty cycle (between brackets the Industrial Advisory Panel member that is interested in each application):
- SMART GRID application
- Voltage stabilization support (Unbalance control and Harmonics compensation) to the electric smart grids. (IAP: IBERDROLA S.A.)
- Reduction of the variability of photovoltaic (PV) systems and small scale wind turbines in distributed generation systems and micro-grids. (IAP: IBERDROLA S.A, ELYTT)
- Uninterrupted power for critical substation loads. (IAP: , ELYTT, TRAINELEC)
- Railway energy networks, for both stationary (voltage stabilization) and on-board (autonomous traction) power systems. (IAP: TRAINELEC, ELYTT, HILTech)
- Hybrid and full-electric vehicles and their charging networks. (IAP: HILTech, JEMA)
- Safety devices in aviation (IAP: not available yet)

The specifications for every application will be established together with members of an Industrial Advisory Panel (IAP), made up of representatives of industrial companies that are leaders in the energy and transport sector and that have signed an agreement of collaboration with HESCAP project. Moreover, they will provide their expertise to keep the objectives focused on the European energy storage industry and will help in the dissemination of the results of the project.

By the end of the project, a 120 W-h and 10kW (50 kW during 1second with a duty cycle of 10%) HESCAP Energy Storage prototype will be developed. The energy and power of this prototype has been chosen with the aim of demonstrating its performance under the different working conditions established by the addressed applications.

The tests will be performed initially, at lab scale, in the facilities of the coordinator of the project. In addition, it will be tested and validated in the facilities of the IAP members. This will permit the evaluation of the system under real conditions in the five applications foreseen in the project. This evaluation will allow the research team to have a first real approach to the practical use of the new technology to show the advantages of the HESCAP energy storage system for stationary and for dual-use applications.

Project Context and Objectives:

WP1: Coordination and Management
All the tasks for the period from 1st April 2010 to 31st March 2012 were completed as planned. During the first review meeting some information updates were requested by the EC related with WP4 and WP6. Related with the second period of the project (from 1st April 2011 to 30th September 2012) two different technical solutions were presented during the second review meeting in order to overcome the overall technical objectives of the project.

Finally iIn December 2012 the steering committee of the HESCAP project has decided to ask the European Commission to terminate the project the 1st of January 2013 due to it is not possible to achieve at the same time and with the same product all the technical objectives fixed in the Description of Work.

WP2: Design and manufacturing of supercapacitor cells
Three types of materials were evaluated as electrode components: silica coating on carbon-based substrates, metal oxides and activated carbons. All of them were tested with different electroytes aiming at finding the best marriages between electrodes and electrolytes, according to the textural properties of the electrodes and the sizes of the ions in the electrolytes. Best results were found in the case of activated carbons in contact with aqueous gels and with ionic liquids. Particularly promising were the results obtained with some Carbide Derived Carbons (CDC) developed by Skeleton Technologies. For this purpose series of micro- and micro/mesoprous carbide-derived carbon (CDC) materials were synthesised and tested electrochemically. Additionally, the effect of physical activation to the pore size distribution and double-layer capacitance of microporous CDC was investigated. The samples with highest energy density were used to design and optimise the structure of supercapacitor cells for HESCAP prototype.

The best cell configuration was obtained using two CDC electrodes with balanced mass loading and an electrolyte made of a 50% mixture of an Ionic Liquid (PYR14TFSI) and an organic solvent (Acentonitrile). Results showed that 100% of the HESCAP power density objective was reached at 65% of the energy density objective (P = 3 kW/kg at E = 26 Wh/kg) or, in the opposite way, 100% of the HESCAP energy density objective was reached at 17% of the power density objective (E = 40 Wh/kg at P = 0.5 kW/kg).

Ultracapacitor technology initially considered for HESCAP prototype based on the soft packageing design, which indeed is suitable for the demonstration purposes (e.g. for testing electrode materials) and also for certain applications. However, for the long-life high-power supercapacitor modules, especially applying the elevated working voltage of single cells that has been included as a strategy for reaching HESCAP targets, the soft casing is not safe. Recent studies reveal that prismatic, parallelly stacked electrode packages (which also is a case of soft-packaged ultracapacitor cells) suffer significant volumetric changes due to expansion/contraction of high-capacitance electrodes during charging/discharging. The amplitude of 'breathing' is larger, the more layers are stacked in single cell. Very ambitious target parameters of HESCAP cells require the involvement of most-advanced nanoporous electrode materials and, therefore, the 'breathing' effects of ultracapacitor cells must be seriously considered; a strong metal casing is one of the requirements. On these reasons, the testing of materials, considered for HESCAP prototype, was started in strong aluminium test-cells and designing of prismatic-shaped aluminium casing was initiated.

WP3: Sensing technologies

1- Preliminary gas sensor specifications were defined (Task 3.1, deliverable D2): The target gases to detect were defined to be carbon dioxide and hydrogen. Gas sensor specifications were reported in deliverable D2 and updated in deliverable D6. According to the results on gas emission analysis and the suggestion of reviewers, the detection of carbon monoxide was added. Gas sensor will be developed by coating a gas sensitive chemical layer one kind of transducer. According to the gas concentration to detect (typically from 200 to 500 ppm), the quartz crystal microbalances (QCM) have been chosen. Bibliographic studies on chemical coatings sensitive to CO_2, H_2, CO on commercial CO_2, H_2 and CO gas sensors were also done.

2- Sensors testing (Task 3.3): in order to perform gas testing, modifications were done on LETI's gas test bench: dedicated carbon dioxide, carbon monoxide and hydrogen line were added and the software was modified. A Gas testing was performed on few CO_2, H_2 and CO commercial sensors, using LETI's gas test bench. Evaluation of gas sensors performances was done by measuring the gas sensor response for a defined range of concentrations. For each gas, one commercial sensor can be including in the HESCAP prototype.

3- A QCM apparatus (Quartz Crystal Microbalance) was set-up to test chemical coatings under gas flow. Screening of chemical coatings was completed; a large scale of layer was deposited on QCM among: Polymers: polyaniline, polyvinypyrrolidone, poly(4-vinylphenol), Ionic liquids: [C8MIM][NTf2], [C6MIM][NTf2], [C4MIM][PF6], [N4441][NTf2], Organic molecules : phthalocyanine and porphyrins, Silanes: APTES, FDTS, HMDS, EHTES, PFO-U-TMS, Pyralene, Hybrid organic-inorganic materials: SiOCH, Porous silica, Porous silia functionalized

Those different coatings were tested under CO_2, CO and H_2 flow. Several layers have been identified to be very sensitive to CO_2 and H_2, even at low concentrations, but unfortunately no layer was sensitive enough to CO. (Task 3.2).

For each gas, in a first time maximum 2-3 layers have been selected and tested with different thicknesses and concentrations. In a second time, gas tests were performed under a low ranges of concentrations (100-500 ppm for H_2 and 300-1200 ppm for CO_2) in order to confirm our choice. The coating robustness was then evaluated: stability, reproducibility, selectivity (gas mixtures) for each selected layer.

After all this study, it has finally been decided to incorporate one commercial sensor for the detection of CO and two layers have been selected for CO_2 (silica functionalized with HMDS) and H_2 (silica functionalized with EBTMOS).

Related to the physical design of the module, some considerations about where should be installed the gas sensors have been defined in collaboration with WP3 and WP4

Finally, a prototype has been developed: it consist of two QCM (each being sensitive to H_2 gas or CO_2) and CO sensor sensitive commercial. It was transportable and monitoring by a computer.

WP4: Assembling the stack. Testing procedures

As the results of APCT performed investigations have been:

1. Analysis of the results of materials and technologies testing for the stack manufacture (from IMDEA and APCT) was carried out.
2. A comparison of two stack production technologies (from IMDEA + ST and APCT) and their correspondence with the essential requirements to HESCAP technology was carried out.
3. The most probable causes of the difficulties in stack making were identified and possible solutions have been proposed.
4. ACFM technology is proposed to use for the stack manufacture in HESCAP project.
5. Optimization of the stack based on ACFM technology was carried out.
6. Identified key issues for further stack optimization and the conditions necessary for this.

Finally one Ultracapacitor stack for HESCAP prototype has been designed based on the results of electrochemical evaluation of test cells under WP 2 (IMDEA + ST). Energy storage component for HESCAP prototype was proposed which parameters almost reach the targets of the project

WP5: Integration and testing supercapacitor devices
A search for simulation software has been done, particularly for power electronics, mechanical and thermal analysis. CEIT will use mainly PSIM for power electronic simulations, Creo Parametric (ProEngineer) for mechanical analysis and SolidWorks or ANSYS Fluent for thermal issues. However, MATLAB (and SIMULINK) is used as a base for any mathematical analysis. Based on the preliminary data from the HESCAP cells, an ESS model was developed in SIMULINK. It shows the advantages and disadvantages of each technology tested in HESCAP.

A prototype of the DC/DC converted that is needed in order to adequate the supercapacitor array output voltage to the application requirements have been developed. This DC/DC converter is able to work in a wide range of voltages and can work with commutation frequencies up to 100 kHz. In the same line, one high current active voltage equalization system has been developed, build and test by using commercial supercapacitor stacks. This system is based on a modified buck-boost topology.

Several simulations of the ESS system have been developed for two different applications: smart grids and transport. These simulations let's to predict the behaviour of the supercapacitor system embedded directly in the final application. They will be very interesting when the final capacitance and voltage figures are available.

Finally a testing plan for the internal stages of the HESCAP module has been presented. The final prototype is not presented yet, but similar prototype for the DC/DC converter and the voltage balancing circuit have been developed and tested in order to verify the design and testing procedure.

WP6: Ecodesign towards a green ESS
The WP6 involves the environmental analysis of the project which will lead to the ecodesign of the final output, which is the supercapacitor module.

Report D2_WP6 (m6): HESCAP Specifications - Specifications of the HESCAP eco-design requirements (Task 6.1), which involves the specifications of the HESCAP eco-design requirements, was delivered on time. The Environmental Performance and Ecodesign Parameters that have to be followed were laid out. Also the four ecodesign strategies were analyzed.

Report D6_WP6 (m14): HESCAP materials selection - Selection of materials for the HESCAP subsystems (Task 6.1) which deals with the material selection for the HESCAP subsystems has been completed. The subsystems of HESCAP have been analyzed and all the various parts involved have been laid out.

Report D9_WP6 (m18): HESCAP system simulation. Life Cycle Inventory Study -Life Cycle inventory study of the HESCAP subsystem (Task 6.2) is completed. It is based on the Deliverable D6_WP6, a Life Cycle Inventory of all the parts and materials of all the subsystems of HESCAP will be put together

Report D13 (m24): Life Cycle Assessment of the HESCAP subsystems (Task 6.2) has been completed. A complete and accurate identification and quantification of air emissions, water effluents, and other life-cycle outputs is performed for the build-up of life cycle databases.

Report D14 (m28): Selection of materials for the HESCAP system (Task 6.2) is completed with main objective to evaluate the findings of all previous reports, and mainly those of D13_WP6, in order to re-suggest on a new basis the most suitable materials for the needs of putting together a new super-capacitor. A comparative analysis takes place on a component basis and the results have been supported by relevant tables and figures.

Report D18 (m33) (Task 6.2), Environmental Impact of the production processes of the HESCAP system, has been completed. Based on the Life Cycle Assessment, the Material use, the Energy use and the Waste production, in the production of all the units are analyzed. Their environmental Impact is performed and the report includes all the indicative diagrams of the different impacts of the whole production process

Report D20_WP6 (m36): End-of-Life management of the HESCAP system, has been completed. The end of management practices for HESCAP system were investigated and analyzed according the usage, the technological capabilities and the nature of the product itself.

WP7: Results exploitation and dissemination
Dissemination activities have been carried out according to the planning. In the first year of the project the emphasis was made on creating a dedicated webpage for the project and on publishing news and press releases, and giving interviews in general public newsletters, magazines, websites and media to promote awareness about the project. From the second year of project, the focus was placed on making presentations in national or international meetings and publishing articles in specialized research journals. As a result of this effort, 3 papers have been published in peer reviewed journals, 9 oral and poster presentations in scientific conferences have been made, and 2 general presentations about the project have been given.

An initial preliminary Market survey was made along the first six months of the project. It includes an assessment of 5 potential applications for HESCAP supercapacitorsin 3 different sectors. Later, a specific technology survey was initiated on commercial sensors for monitoring gas emission on supercapacitors and batteries.

Informal interviews with companies involved in manufacturing and commercialization of supercapacitors (KONEIKA) and batteries (SAFT, EXIDE) have provided new ideas about the characteristics that would be of interest for their respective markets. Considerable differences have been found, depending on the type of market in which they are competing at present.

With respect to exploitable results, LETI has developed gas sensors for detection of CO2 and H2 based on functionalized microporous silica and CEIT has developed one low cost and high current voltage stabilization system and one new design methodology of high frequency DC/DC converters oriented to low voltage supercapacitor ESS modules.

Finally IMDEA has designed a new electrolyte made of a blend of an Ionic Liquid (PYR14TFSI) and an organic solvent (Acetonitrile) which has been identified as a potentially exploitable result. To make this electrolyte fully useful it is necessary its marriage with activated carbon electrodes pairs, with tailored mass loadings of each electrode.

Project Results:

2 DESCRIPTION OF THE MAIN S&T RESULTS/FOREGROUNDS

2.1 WP2: Design and manufacturing of supercapacitor cells

Objectives

To obtain a new electrochemical capacitor cell with improved specific energy storage capabilities. The most promising cell configurations will be selected, paying attention to their performance, reliability, safety, and cost characteristics. To obtain stacks made of such capacitors. For the selected cell configuration various types of stacks will be prepared and tested. Their performance, reliability, safety and manufacturing cost will be assessed. To supply the necessary stacks to WP6 for building up a module and integrate it in the energy storage system.

Task 2.1: Design criteria and cell specifications. (Months 1-6 (April-September2010))

Progress towards objectives

Preliminary design criteria and cell specifications were delivered according to the planning as part of deliverable D2. The information was not definitive since by the time the report was delivered, there were still many uncertainties regarding the electrode and electrolyte materials to be used. For this reason, the design criteria and specifications were made based on the technology available among partners involved in this Work Package, namely APCT, Skeleton and IMDEA. The document was reviewed and updated when an advanced definition of materials and components was made in February 2012 with the progress of tasks T2.2 and T2.3.

Significant achievements

Materials for electrodes, electrolytes and separators were listed. Two main options were described: (A) Activated carbon electrodes with an aqueous electrolyte in the shape of a gel, and (B) Activated carbon electrodes with an ionic liquid as electrolyte. Current ratings and performance of the reported State of the Art technology were contrasted and a guide of the existing International Standards was included in order to know the different tests methods to be performed for a concrete application.

Task 2.2: Synthesis and characterizations of materials. (Months 3-18 (June 2010- Sep 2011))

Progress towards objectives

In the first period of the project ST performed a series of synthesis experiments with 18 different types of carbides at wide synthesis temperature range to define the range of suitable CDC carbons for HESCAP cells. Later on, the research and development of CDC materials was mainly targeted to improving the effective surface area of carbon materials by means of a physical activation process of 6 types of CDCs, performed with water vapour at 900°C for different times. Results clearly show that the initial pore size distribution of nanoporous carbon has noticeable influence on the depth of physical activation. After synthesizing and testing silica and metal oxide nanoparticles with rather poor results, IMDEA focused its efforts in activated carbons. Up to 4 types of CDC samples from ST, 2 types of activated carbons provided by APCT, and 3 types of commercial activated carbons from other suppliers were characterized and tested aiming at looking for physicochemical properties that could be adjusted to the electrolytes investigated in task 2.3.

Textural properties have been measured together with Thermo-gravimetric Analysis coupled to Mass Spectrometry.

Significant achievements
The concept of effective specific surface that takes into account the specific surface provided by pores bigger than the average diameter of the ions in the electrolyte is a parameter that correlates with the electrode performance better than the total specific surface. Also, the presence of functional groups has strong influence in the behaviour up to the point that it can alter the expected behaviour based on the effective specific surface analysis. Carbons such as PICA, YECA, CDC3 and CDC4 show characteristics that make them good candidates for HESCAP supercapacitors. In addition to this, it has been demonstrated that physical post-treatment of CDC materials promotes a noticeable increase of specific surface and it also reduces the Vpless than1nm / Vpgreater than1nm ratio. This means that physically post-activated materials have a porous structure more open and should facilitate mass transport of ions through their pores. These are, in principle, very good characteristics for supercapacitor electrode materials.

Task 2.3: Research on cell components.(Months 4-21 (July 2010- Dec 2011))
Progress towards objectives
At the end of the first Reporting Period, results got by IMDEA with SiO_2 coated EDLCs in aqueous and organic electrolytes and Pseudocapacitors in aqueous, were far from the HESCAP objectives of energy and power densities. In consequence, new strategies were designed that gave to a remarkable improvement of performances, but still some strong weaknesses were detected: (A) Ionic liquids show a high resistivity at room temperature, and (B) Jellified aqueous electrolytes did not show good stability when the operating voltage was increased over 1.5 volts. So additional work was carried out with the best alternatives, oriented towards reducing the resistivity of the EDLC by mixing ionic liquids and organic solvents, and increasing its cycle life by using asymmetric electrodes with tailored mass loadings. The best cell configuration obtained at IMDEA was made of two CDC electrodes with balanced mass loading and an electrolyte made of a 1:1 mixture of an Ionic Liquid and an organic solvent (Acentonitrile).

Significant achievements
The combination of electrodes with CDC4 and an electrolyte made of mixtures of Ionic Liquid and conventional organic showed that 100% of the HESCAP power density (Ps) objective was reached at 65% of the energy density (Es) objective (Ps = 3 kW/kg at Es = 26 Wh/kg). In the opposite way, 100% of the HESCAP energy density objective was reached at 17% of the power density objective (Es = 40 Wh/kg at Ps = 0.5 kW/kg). Regarding cycle life, after 7000 cycles at 3.0 V, the retention of energy density in the asymmetric configuration was 80% while in the symmetric it was just 50%. In terms of power, the retention of the asymmetric configuration was 95% while it was 80% in the symmetric case. Absolute values of the asymmetric cell after 7000 cycles were Es = 20 Wh/kg at Ps = 0.8 kW/kg.

Task 2.4: Research on cells.(Months 7-21 (October 2010- December 2011))
Progress towards objectives
Skeleton. Test cells with robust aluminum casing were built at ST by using pressure contact as planned for stacks of HESCAP prototypes. In the cells, the following components were varied: (a) Carbon materials (b) Asymmetric electrode pairs (c) Different electrolytes and (d) Different

working voltages. Four different carbons were used: (1) Coconut shell based carbon, (2) microporous - CDC1, (3) nanoporous - CDC5, and (4) microporus carbon with reduced pore resistance - CDC3. The electrolytes were: (1) PYR14TFSI, (2) PYR14TFSI in mixture with ACN (1:1 by volume) and (3) pure ACN with Spiro salt.

APCT-Ukraine. The target of this investigation was searching of electrolytes which meet several requirements namely high values of specific energy and power combining with a low price and safety for customers and environment during all cycles of production, exploitation and recycling of SC. The reference for the investigation was a SC cell based on carbon forms with perfect structure working with a 3M aqueous solution of KOH. The main parameters of this cell were: max. voltage = 1.15–1.25 V; max. energy = 25–28 J; max. power = 6–8 W. Aqueous solutions based on nitrates of Li, Na, K as well as gels were chosen as the subject for investigation. The results obtained for $LiNO_3$ showed a rise of all parameters, particularly of maximum power. The results obtained for $NaNO_3$ showed a rise in the working voltage and maximum power, while maximum energy was similar to the reference.

Significant achievements
Skeleton. Testing results of test cells reveals that HESCAP objective in terms of power density is achievable by using CDC carbon with non-aqueous electrolyte. The target of energy density would be nearly achievable by using nanoporous CDC carbon and supercapacitor metal casing.

APCT-Ukraine. The investigations performed by APCT allowed obtaining some progress from two points of view: to increase the SC technical characteristics and to improve ecological safety without loss in a prime cost. The following technical advantages were identified:
(1) The cell working voltage was increased from 1.2 up to 1.5 V,
(2) The cell maximal power was increased from 6-8 up to 20-28 W, and
(3) Self-discharging current of the SC cell was lowered by 3-5 times.

The following ecological advantages were found:
(1) Aqueous solutions of $LiNO_3$ and $NaNO_3$ salts allow obtaining the gels suitable for the use in SC that improves their safety use,
(2) Application of $NaNO_3$ as an electrolyte decreases hazard class of the compounds used in the SC production,
(3) Electrolytes based on $NaNO_3$ might be considered for their possible recycling as fertilizers.

Task 2.5: Manufacturing of cells.(Months 16-24 (July 2011- March 2012))
Progress towards objectives
Skeleton. Despite soft pouch cells would be certainly better for gravimetric performance, they are not applicable because of safety issues. Very ambitious targets of the project regarding energy and power densities need careful optimization of cell parameters. So far the electrical connections and possible configurations of prismatic aluminum cells for supercapacitor module of HESCAP prototype have been researched. The modeling was made by using real supercapacitor cells of ST, which have current terminals similar to those proposed for HESCAP. However, they differ from the HESCAP cells by the size and composition of electrode materials and electrolyte.

APCT-Ukraine. Based on the SC cell construction grounded on the carbon forms with perfect structure and electrolytes as well as research results from APCT in Task 2.4, the hermetically sealed SC test-samples were designed and manufactured.

Significant achievements

Skeleton. The prismatic capacitor design that is considered for stack of HESCAP prototype is based on the developments of Skeleton Technologies. So far the electrical connections and possible configurations of prismatic aluminum cells for supercapacitor module of HESCAP prototype have been researched. The modeling was made by using real supercapacitor cells of Skeleton Technologies, which have current terminals similar to those proposed for HESCAP cells. However, they differ from the proposed HESCAP cells by the size and composition of electrochemical system (materials and electrolyte).

APCT-Ukraine. The hermetically sealed SC test-samples with electrode size of 50 x 50 mm were manufactured on the basis of carbon forms with perfect structure. The size of electrodes of the samples meets the requirements of the HESCAP project. In the hermetically sealed SC test-samples were used the LiNO3 aqueous solution gel as electrolyte that essentially improves their environmental properties. The SC test-samples created can be transported by all transport types and consequently their independent testing in any place.

2.2 WP3: Sensing technologies

Objectives:

To design the low cost sensors suitable for specifically monitoring the high energy supercapacitor cells and stacks developed in WP2.
To develop a generic gas sensors platform in order to detect several gasses in the supercapacitor which can be produce in the electrolytic cell (safety issues)
To select and test the current, voltage, temperature sensors in order to achieved the optimum and safety performance of the supercapacitor module.

Task 3.1: Specifications and state of the art on target sensors and chemistry. (Months 1-14 (April 2010- May 2011))

Progress towards objectives

This task deals with the definition of gas sensor specifications:
Specifications on the nature of electrolytes were provided by IMDEA and APCT. Aqueous and organic (acetonitrile based and propylene carbonate) electrolytes are intended to be used. A bibliographic study was done in order to define the emitted gases produced under degraded mode by decomposition of these different electrolytes.

This study allowed defining gas composition atmospheres in standard and in degraded mode, according to voltage range. After that, gas emission analyses were performed on supercapacitors stacks prototypes provided by APCT. Both samples were identical supercapacitor in acetonitrile-based electrolytes. One of these stacks was prepared and cycled under standard conditions while the other one was first aged under standard conditions and then kept to simulate degraded conditions.

According to the bibliographic data and to these different results, three gases were chosen for sensing: carbon dioxide, carbon monoxide and hydrogen.

This task deals with the definition of gas sensor specifications:
Based on the target gases to detect, a technology survey was done on the commercial carbon dioxide, carbon monoxide and hydrogen gas sensors. Some

of these sensors have been tested in order to study their potential integration in HESCAP prototype.

Gas sensor developed by CEA-LETI will be constituted of a mechanical transducer on which a gas sensitive chemical coating will be deposited in order to detect target gases.

Significant achievements
Report D2 and D6 on "specifications and state of the art on target sensors and chemistry" was delivered in September 2010.

Three target gases were selected to develop gas sensors: hydrogen, carbon dioxide and carbon monoxide

The update on the nature of the transducer: one mass transducer was chosen according to the supposed gas concentration to detected (QCM).

The bibliographic study was completed on chemical coating sensitive to CO2, CO and H2 and also on commercial gas sensors.

We've been waiting for several months that the batteries that APCT must deliver us.

Task 3.2: Chemical functionalization of commercial transducers.(Months 4-18 (July 2010- September 2011))
Progress towards objectives
This task deals with the functionalization of commercial transducers with various chemical coatings, in order to test their affinity with carbon dioxide and hydrogen.

Three ways of functionalization were used to coat QCM devices with chemical species: drop-coating, spin-coating and Chemical vapour deposition (CVD)

With these methods, deposited thickness ranged between few and several hundred nm.

By setting-up those three deposition procedures, a large variety of chemical compounds have been deposited on QCM devices: organic polymers, Ionic liquids, organic molecules, silanes, parylene, hybrid organic-inorganic materials, porous silica.

Significant achievements
A large panel of materials has been deposited on QCM devices.
All these materials have been characterised : thickness, porosity and morphology

Report D8 was written.
A QCM apparatus was set-up for screening sensitive chemical coatings, in order to develop such gas sensors.

Task 3.3: Sensors testing and characterization (on gas bench) (Months 8-32 (November 2010- November 2012))
Progress towards objectives
GAS TEST BENCH: In order to test the sensitivity of chemical coated QCM devices under carbon dioxide, carbon monoxide and hydrogen, dedicated carbon dioxide, carbon monoxide and hydrogen lines, respectively, were added to LETI's gas test bench.

COMMERCIAL GAS SENSORS: Gas testing was performed on few CO_2, H_2 and CO commercial gas sensors, using LETI's gas test bench. Each commercial gas sensor was set-up in a closed-chamber, in which various concentrations of target gases were inserted. Evaluation of gas sensors performances was done by measuring the gas sensor response for a defined range of concentrations.

CHEMICAL LAYERS developed by CEA-LETI
Carbon monoxide:
Chemical layers sensitive to carbon monoxide: no chemical layer shows an affinity to carbon monoxide. For safety reasons, the concentration of the pressurised gas cylinder is equal to 50 ppm which is very low to develop a gas sensor prototype.

Hydrogen:
Few chemical layers show a significant affinity to hydrogen and may be used to coat QCM devices in order to develop H_2 gravimetric gas sensors : PVP for example.

Carbon dioxide:
Some chemical layers show a significant affinity to carbon dioxide and may be used to coat QCM devices in order to develop CO_2 gravimetric gas sensors:silanes PFO-U-TMS for example

Significant achievements
A methodology was set-up, including modification of LETI gas test bench and set-up of a QCM apparatus for screening sensitive chemical coatings, in order to develop such gas sensors.

Gas testing of commercially available gas sensors was realised, sensors that could be integrated into HESCAP prototype were identified. One commercial sensor has been chosen for the detection of CO (alphasense). This last one will be used in HESCAP prototype.

Several chemical layers were deposited on QCM devices and tested under gas exposition. Screening of these chemical layers allows identifying interesting three chemical coatings for each gas that are sensitive to carbon dioxide and hydrogen.

The final choice is on the following layers: microporous silica + HMDS for carbone dioxide and microporous silica + EBTMOS for H_2.

Task 3.4: Physical sensors selection and testing.(Months 19-32 (October 2011- November 2012))
Progress towards objectives
The physical sensor should be selected when the stacks will be well defined. Until then, the preliminary selected voltage and current sensors series are LV25 and HASXXX from LEM technologies

Significant achievements
Preliminary test have been started with the current and voltage sensors oriented to the equalization voltage systems.
*Please fill in the below questions taking into account all the task of the WP

2.3 WP4: Assembling the stack. Testing procedures

To assemble the stacks using the materials and technologies developed under WP2
To test the stacks using the correct methodology and to compare test results with other technologies available on the market
To apply test results for the cases study in order to find the market applications for the HESCAP system
To develop the optimal stack design and basic module concept for WP5
To address cost optimization and manufacturability issues during the stack design development

Task 4.1: Developing testing methodology.(Months 4-12 (July 2010- March 2011))

Progress towards objectives

A very simplified methodology for cross-checking characterization of cells and stacks using simple galvanostatic charge-discharge tests and complex impedance measurements, both at controlled temperatures.

APCT has developed methodology for assembling the supercapacitor stacks and optimized technological process so that to maintain similar characteristics of the stacks when being connected in series. In order to carry out the corresponding tests and develop testing methodologies, a series of supercapacitor cells and stacks have been assembled.

On the basis of International Standard IEC 62576 (Electric double-layer capacitors for use in hybrid electric vehicles – Test methods for electric characteristics. Edition 1.0, 2009-08) and FreedomCAR Ultracapacitor Test Manual (DOE/NE-ID-11173, 2004) APCT has defined Testing Methodologies best fitting to the specified needs and objectives, which will be used throughout the Project. The following parameters will be measured for characterization of the designed stacks: Capacitance, internal resistance, maximum current, maximum energy stored, maximum power, leakage current, self discharge, Life time, Cycling life, Safety Test. In the last category safety testing methodology have been elaborated following recommendations from the international standards manuals (USABC Abuse Test Procedure Manual).

Finally Cycle-life tests have been conducted in order to determine the supercapacitor device performance degradation over certain number of charging/discharging cycles. The experiments have been intentionally conducted at the increased voltage 3,5 – 1,75 V (compared to the rated voltage of 2,7 V). The current was 40 A.

Significant achievements

Overall, significant achievements by APCT over the period under report can be summarized as follows:
Optimized specifications for the stack components and optimized stack design have been developed.

Standard testing methodologies have been formulated.

Excel-based program "Parameter estimation" for evaluating specific parameters of the stacks has been developed. This program will be used throughout the Project for the material selection and data treatment.

The experimental procedure applied in task T2.3 to the characterization of single carbon electrodes and metal oxide electrodes has proven to be adequate for a preliminary evaluation of specific capacitances and to get a qualitative indication of their kinetics by applying various scan rates. Results from this method have to be checked with two-electrode characterization methods such as galvanostatic charge-discharge cycles.

Task 4.2: Assembling the stacks.(Months 13-32 (April 2011- November 2012))

Progress towards objectives

For the design of the original stack a single electrode was chosen with a size of 50x150 mm. This will allow to implement a current of 9.75 A from one electrode at a density of 130 mA/cm 2. It allows to realize a peak current of 100 A by using 11 electrodes. Based on the test results for the first stacks capacitance, maximum voltage and internal resistance was planned to optimize the size of the base electrode. Related with the stack appearance was decided to designing of high-impact polystyrene case. This case material combines: mechanical strength, compatibility with all water-based electrolytes for stack, ease of manufacturing handmade stacks with arbitrary form and size,easy seal in. Due to the freedom capability about the selection of the stack output electrodes (terminals), APCT decided to use the material SSM304, recommended by IMDEA (4.2.). Input control of materials made ARST and showed satisfactory mechanical and electrical properties of the material SSM304 for it. Nickel rolled products was used for manufacturing of stack output electrodes (terminals) also.

Chemicals and Materials for assembling of stacks was selected during WP2 by IMDEA and supplemented by APCT. In April 2012 APCT was ready to manufacturing near 30 stacks per month with a total energy of 30 W-h at condition given necessary materials.

Four different electrolyte compositions were prepared for these test stacks:
CMC – proportion 1g of CMC+14ml of Water + 5% $NaNO_3$ salt with respect to CMC content
$NaNO_3$ gel
KOH gel
PYR14TESI electrolyte

As one other option for HESCAP prototype, ST investigated the supercapacitor cells and stacks based on the hard aluminium casing. The semi-wound electrode assemblies were used for designing of stacks of HESCAP prototype.

ST carried out theoretical modelling of ultracapacitor stack based on aluminium-packaged prismatic cells with dimensions of 55*75*120mm (W*H*L). The aluminium prismatic corpuses as one option for the HESCAP ultracapacitors were proposed to use in safety and long-life reasons. Modelling was carried out with considering the target energy 120Wh and power 10kW of HESCAP Module. According to theoretical estimations, the impact of aluminium casing to the total weight of the cell #4 is less than 20%.

Significant achievements

1. The initial dimensions for the electrode stack were selected. The chosen size of the electrode must provide requirements to peak current prototype of the HESCAP module.
2. High-impact polystyrene case for testing the stack with electrodes 50x150 mm was designed.
3. Laboratory technological process of electrode making (from IMDEA and APCT) is adapted to fabrication of 50x150 mm electrode.

4. Water-based electrolytes (CMC, $NaNO_3$ gel, KOH gel) and ionic liquid (PYR14TESI) was prepared and adapted for use in the stack;
5. 41 stacks with different configurations were produced on basis of four electrolytes.
6. 17 stacks (on basis of 4 electrolytes) were sent for testing in IMDEA facilities
7. Theoretical modelling carried out by ST for prismatic aluminium cells predicts that the HESCAP targets are achievable with nanoporous asymmetrically configured carbon electrodes and with the spiro-type electrolyte (it has smaller cation than other commercially available electrolytes) at increased working voltage.

Task 4.3: Testing the stacks. (Months 13-32 (April 2011- November 2012))
Progress towards objectives
Electrochemical characterization of 3 full size cell samples manufactured by APCT for cross checking with their own results was carried out by IMDEA.

Simple and fast test procedure was defined by IMDEA (Task 4.1). At the measurements performed in APCT for the stacks with different configuration, this procedure had the next features:
Peak operating voltage is determined at constant charge current 0.5 mA/cm2 for gel electrolyte and 0.8 mA/cm2 for Ionic liquid. The total duration of one measurement is from 2.5 to 3.0 hours.
Capacitance is determined at constant current discharge: from 0.6 V to 0.5 V for gel electrolyte and from 1.8 V to 1.5 V for Ionic liquid. Series of measurements for each stack was carried out at different amperage (1.3; 2.6; 5.0; 10.0; 20.0; 50.0 mA/cm2. Total duration of one series measurement is from 6 to 7 hours.
Internal resistance is determined at switching on/off at electrical load with resistance 1, 10 or 100 O.

Based on results of WP2 the ultracapacitor cells of approximately 25F developed in Task T4.2 as one alternative to the APCT proposed technology were assembled and tested by ST in wide temperature and current ranges.
Significant achievements

As the results of APCT investigations the following achievements have been obtained:
1. The stacks on both activated carbon powders from different sources and on carbon forms with perfect structure. The size of electrodes of these samples meets the requirements of the HESCAP project.
2. The stacks with the use of the aqueous solutions of alkali, salts, gels and Ionic liquid PYR14TESI;
3. Working voltage of the stacks depends on the electrolyte nature and is in the range from 1.2 to 3.0 V;
4. The stacks electrical capacity depends on the nature of activated carbon, content and concentration of electrolyte and is in the range from 13 to 630 F.

As the results of ST investigations the following achievement has been obtained: It was shown that spiro type salts are advantageous for highly nanoporous carbon electrodes and give a possibility to use more effectively the surface of carbon electrodes in nanopores. The latter is very important regarding achieving of the HESCAP targets.

Task 4.4: Final Optimization of the stacks. (Months 25-32 (April 2012- November 2012))

Progress towards objectives

One analysis in order to detect problems in the integration of new materials proposed by IMDEA, ST and APCT in the manufacturing process of stacks have been done. In this line, different materials have been analysed in order to find their advantages and disadvantages like for example: stainless steel mess for the preparation of current collectors. In this particular case for example this study demonstrated that it will be necessary to find other materials for SC with aqueous electrolyte like for example nickel grids obtained by galvanic deposition. In this line other subsystems have been studied: separators, powder of activated carbons, etc.

Speaking about the preparation method, in order to obtain reproducible results for the mass deposited material the deposition of the AU on the collector has been proposed.

The analysis process developed by APCT has demonstrated that the ACFM in the manufacture of stacks has better performance compared with the materials presented and recommended by IMDEA if the energy density is not one priority. Nevertheless some possible opportunities to increase the energy density of this kind of devices can be explored in future opportunities like for example to improve the carbon matrix in order to achieve its maximum theoretical limit of 68 wh/kg. Other SC components that could be optimized shall be: the material for the collector, the separator, etc.

In a parallel work and Based on the characteristics of prismatic aluminium packaged ultracapacitor cells the general characteristics of 120Wh module were calculated by ST. Selected characteristics are shown in the following table.

	#1	#2	#3	#4	#5
Single cells in HESCAP pcs	15	21	15	12	11
Maximum working Voltage V	48	67.2	48	38.4	37.4
Internal resistance m?	7.1	11.32	7.1	3.7	3.4
Maximum power, Pmax kW	81	99.7	81	100	103
HESCAP Module Weight* kg	10.9	14.4	10.9	8.2	7.5
HESCAP Module Volume L	7.5	10.5	7.5	6	5.5

*Does not include connections and package of HESCAP prototype.

Significant achievements

As the results of APCT performed investigations have been:

1. Analysis of the results of materials and technologies testing for the stack manufacture (from IMDEA and APCT) was carried out.
2. A comparison of two stack production technologies (from IMDEA + ST and APCT) and their correspondence with the essential requirements to HESCAP technology was carried out.
3. The most probable causes of the difficulties in stack making were identified and possible solutions have been proposed.
4. ACFM technology is proposed to use for the stack manufacture in HESCAP project.
5. Optimization of the stack based on ACFM technology was carried out.
6. Identified key issues for further stack optimization and the conditions necessary for this

Finally one Ultracapacitor stack for HESCAP prototype has been designed based on the results of electrochemical evaluation of test cells under WP 2 (IMDEA + ST). Energy storage component for HESCAP prototype was proposed which parameters almost reach the targets of the project

2.4 WP5: Integration and testing supercapacitor devices
To design and develop the energy storage system prototype.
To develop connectivity and integration strategies to configure modular Energy Storage Systems, attending to end-user specifications from IAP members.
To develop a supercapacitor module through the integration of the different subsystems and its energy management unit will be implemented.
To integrate and test the HESCAP energy storage system.
Task 5.1: End-user specifications and ESS system modeling.(Months 1-18 (April 2010- September 2011))

Progress towards objectives

In the following the progress towards objectives in this task are summarised:
A first pre-configuration of the HESCAP module has been defined in collaboration with the companies that form part of the IAP group. This pre-configuration fix the maximum and minimum values of some physical properties like the output voltage, the available energy that shall be stored and the power capability of the module.
All the sub-modules that shall be designed in order to overcome the objectives of the HESCAP project have been defined. Each sub-module have been studied in a preliminary stage. This sub-modules are:
Communications and Control Unit

Energy Management Unit

DC/DC converter
Voltage Balancing System
A simulation model has been designed in order to study different configurations of serial and parallel stacks in order to prepare a tool able to be used in the design of the HESCAP module. This simulation tool has been programmed in "Matlab/Simulink" and some possible topologies for the HESCAP module have been defined by using the information about the cells and the stacks obtained from WP2 and WP4.

Principal electronics general-purpose applications and power electronics specific simulation environments have been evaluated and a Fault tolerant philosophy has been introduced in the model in order to increase the final reliability of the system. Several solutions have been studied. These solutions imply the introduction of additional electronic systems into the module.

Significant achievements
One pre-configuration of the HESCAP module has been defined taking into account all the subsystems that will be integrated: SC stacks, energy management unit, Voltage Balancing System, etc.
The simulation software able to be used in order to study different physical configurations of SC stacks has been developed.
Task 5.2: Connectivity and integration strategies.(Months 12-18 (March 2011- September 2011))

Progress towards objectives
During the first month of this Task some work about the integration of gas sensors in the HESCAP module has been made in collaboration with CEA-Leti and APCT.

In order to integrate the HESCAP module in real applications, a smart-grid and a transport example have been studied. In the first scenario the objective of the SC module shall be to compensate the harmonic currents generated by non-linear loads and power electronic devices. In the second scenario the simulation model developed in T5.1 has been integrated into the ADVISOR software for Advanced Vehicle Energy Analysis.

A search for simulation software has been done, particularly for power electronics, mechanical and thermal analysis. CEIT will use mainly PSIM for power electronic simulations, Creo Parametric (ProEngineer) for mechanical analysis and SolidWorks or ANSYS Fluent for thermal issues. However, MATLAB (and SIMULINK) is used as a base for any mathematical analysis. Based on the preliminary data from the HESCAP cells, an ESS model was developed in SIMULINK. It shows the advantages and disadvantages of each technology tested in HESCAP

Significant achievements
One study of the best oriented software simulation products has been prepared. One ESS based on supercapacitor modules has been developed. Two different application scenarios have been studied in order to demonstrate that the HESCAP electrical simulation model is able to be integrated into other computational systems.

Task 5.3: Supercapacitor module design.(Months 12-24 (March 2011- March 2012))
Progress towards objectives
In order to study and to prepare a future HESCAP stacks production phase, APCT has calculated the possible configurations of HESCAP module with optimized technology stack for optimal current, power, energy and design. This work, similar to the pre-configuration that was made in T5.1 by CEIT, takes into account more real configuration parameters that APCT has generated as Background during the last years.

One preliminary DC/DC converter design and the voltage balancing system were presented.

For the DC/DC converter two alternatives were proposed: a half-bridge and a series resonant converter.

For the voltage balancing system, a buck-boost was tested in several commercial supercapacitors. The target prize that have been fixed is 9 EUROS/equalization unit for a total production of 1000 units. Final device present a final prize of 4.5 EUROS/equalization unit for a total production bigger than 100000 units.
The control and communication unit will be design around a DSP from Motorola, the DSP56F8037V. It has two analog outputs, eight analog inputs, two serial communication units, two SPI, one I2C and more than 30 digital input/output pins. So it can fulfill the requirements for the communication with external devices by using the serial communication units and also with the sub-stages with the digital and analog input/outputs.

Significant achievements
One more realistic configuration of HESCAP module has been developed by APCT taking into account their supercapacitor stacks production experience.

Preliminary designs of the DC/DC power converter and the voltage balancing system were presented in a simulation way.

Task 5.4: ESS energy management. (Months 19-30 (October 2011- September 2012))

Progress towards objectives

This task has been postponed due to the lack that we are experienced in the final definition of the HESCAP stack's figures.

Significant achievements

One supercapacitor ESS based on commercial stacks have been developed in order to test the ESS energy management estrategies developed during the project.

Task 5.5: Prototyping and Testing.(Months 25-42 (April 2012- December 2012))

Progress towards objectives

CEA-LETI:

The gas sensor prototype has been designed to be transportable and can be easily used. The prototype is a sealed-box in which one there are two QCM devices for hydrogen and carbon dioxide and one commercial sensor for CO detection. A microfluidic channel transports the gas mixture on the three components. The prototype is independent and runs on batteries. QCM signal is recorded by a computer which is connected to the prototype by Wi-Fi or via USB.

Several tests will be done on this prototype. In a first step, the test will be performed with only one gas in order to check if there is any interaction. After that, QCM and sensors have been tested under a mixture of the three gases: hydrogen, carbon dioxide and carbon monoxide. Different criteria such as stability, repeatability and reproducibility of the measurements have been tested in November.

ST

ST has studied the performance of 25V supercapacitor module comprising prismatic cells, which were considered in WP 2 and WP 4 as one of the options for HESCAP energy storage unit. The module was built of 9 supercapacitors (500F, 2.85V) connected in series and equipped with the active cell voltage balancing system to avoid overvoltage of the individual cells.

CEIT

A testing plan for the several stages of the HESCAP module has been presented: DC/DC converter testing procedure, Voltage balancing circuit testing procedure , voltage balancing circuit attached to the main control testing procedure, DC/DC converter attached to the main control testing procedure, communication unit attached to a computer testing procedure, gas sensor communication and internal stack test.

One supercapacitor test bench has been implemented able to discharge the supercapacitor stack array (125V, 120F) at a maximum current of 1600A: It consist of a high power DC/DC converter system that delivers an output voltage range from 400 to 600V.

Significant achievements

A prototype was developed in order to detect CO_2, H_2 and CO. The software is developed under Labview and manages the data acquisition/transition and the possible post-treatment. This device has been tested in laboratory conditions showing a performance in line with the technical specifications that were fixed during the development stage.

Several working-tests have been performed and delivered for the supercapacitor test bench developed in tasks T5.3 and T5.5. The results have demonstrated that all the simulation models that have been presented works correctly.

2.5 WP6: Ecodesign towards a green ESS

Table 5. Work Progress and Achievements of Work Package 6 (WP6)

Objectives

To identify optimal materials to be used for the HESCAP system.
To identify real production costs of the HESCAP system.
To calculate the environmental impacts of the HESCAP system.
To examine all alternatives for the end-of-life management of the high energy supercapacitor ESS and identify the optimal.

Task 6.1: Materials selection.(Months 4-14 (July 2010- May 2011))

Progress towards objectives

All objectives of WP6 have been met. The last deliverable D20 which was due the 1st of April has been completed taking into consideration all the material that has been used. Data about materials selected to build cell components have been provided to NTUA by IMDEA according to specification documents.

Significant achievements

A complete environmental analysis of all the materials used has been performed. The comparison of material using the life cycle assessment leads to the most ecological choice of material from the designer for the supercapacitor.

Task 6.2: Production process.(Months 7-33 (October 2011- December 2013))

Progress towards objectives

Requested from NTUA, IMDEA has issued a document describing the mass balance of the main synthetic methods used for metal oxide preparation. The document includes a qualitative and quantitative description of the raw materials, physicochemical treatments, products, and residues generated in each synthetic method. The document issued includes information related to the sol-gel procedures for the synthesis of Base-Hydrolyzed Silica (SiO_2), of Bohemite ($AlOOH$), Manganese Dioxide (MnO_2), Titanium Dioxide (TiO_2), and Nickel Oxide (NiO). For each case the information provided covers: list and quantities of chemical reagents, description of the experimental procedure, list and quantities of products, list and quantities of residues and/or effluents, and quantities required per electrode or per cell.

Related with the gas sensor development, CEA-LETI determined that gas sensor should be localized inside each sub-module, the final product will be easy to use and will be independent. The prototype is design to be in a sealed-box of reasonable size so that it can be placed and moved anywhere. In addition, this module does not require the use of consumables.

Related with the NTUA this is the description of the work done taken into account deliverables:
Report D6_WP6 (m14): HESCAP materials selection - Selection of materials for the HESCAP subsystems (Task 6.1) which deals with the material selection for the HESCAP subsystems has been completed. The subsystems of

HESCAP have been analyzed and all the various parts involved have been laid out.
Report D9_WP6 (m18): HESCAP system simulation. Life Cycle Inventory Study -Life Cycle inventory study of the HESCAP subsystem (Task 6.2) is completed. It is based on the Deliverable D6_WP6, a Life Cycle Inventory of all the parts and materials of all the subsystems of HESCAP will be put together
Report D13 (m24): Life Cycle Assessment of the HESCAP subsystems (Task 6.2) has been completed. A complete and accurate identification and quantification of air emissions, water effluents, and other life-cycle outputs is performed for the build-up of life cycle databases. The emissions analysis is extended to the production of the primary energy carriers. This enables the formation of a complete picture for the life cycle of all the supercapacitors' components described in the study. In order to obtain concrete results from this study, the specific working tools used are the Eco-Indicator '95 and Eco-Indicator '99 as being reliable and have been widely applied within LCA community. A process that relates inventory information with relevant concerns about natural resource usage and potential effects of environmental loadings is attempted. Any product or service needs to be represented as a system in the inventory analysis methodology.
Report D14_WP6 (m28): HESCAP materials selection - Selection of materials for the HESCAP subsystems has been completed.
The environmental profile of capacitors is of crucial importance, especially when considering manufacturing and release of innovative super-capacitors. HESCAP project research team has undertaken the responsibility of implementing life cycle analysis environmental tool in order to satisfy the need of providing an environmentally-sound proposal for this new capacitor.
Hitherto, reports D6, D9 and D13 have been referred to the usable material alternatives for super-capacitor's subsystems manufacturing. For each one of these categories of components, and for the purposes of the current research, the materials that constitute them have been determined by IMDEA ENERGIA and Skeleton Tech.

The main objective of present report (D14_WP6) is to evaluate the findings of all previous reports, and mainly those of D13_WP6, in order to re-suggest on a new basis the most suitable materials for the needs of putting together a new super-capacitor. A comparative analysis takes place on a component basis and the results have been supported by relevant tables and figures. In order to obtain concrete results from this study, specific LCA tools have been used, namely Eco-Indicator '95 and Eco-Indicator '99. Both of them are considered reliable and widely applied within LCA community. A process that relates inventory information with relevant concerns about natural resource usage and potential effects of environmental loadings is attempted with EI'99.
Report D18_WP6 (m33): Environmental Impact of the production processes of the HESCAP system has been completed.

Life Cycle Assessment for the proposed super-capacitor has to be referred to all elements and processes that take part in the production of HESCAP system.

Reports D13 and D14 have been referred to the usable material alternatives for super-capacitor's subsystems manufacturing. For each one of these categories of components, and for the purposes of the current research, the materials that constitute them have been determined by IMDEA ENERGIA and Skeleton Tech.

The main objective of present report (D18_WP6) is to evaluate the aggregate environmental Impact of production, material use, energy use and waste production of all units of the HESCAP system. After performance of Impact, a report will be produced with all the indicative diagrams of the different impacts of the whole production process.

As we have underlined in previous reports, in order to obtain concrete results from this study, specific LCA tools have been used, namely Eco-Indicator '95 and Eco-Indicator '99. Both of them are considered reliable and widely applied within LCA community. A process that relates inventory information with relevant concerns about natural resource usage and potential effects of environmental loadings is attempted with EI'99.

The most important component of the HESCAP prototype is a high-energy-density electrode material – nanoporous CDC, which despite of its excellent electrochemical characteristics commonly is considered as the costly and low-yield material. ST has created an economically effective CDC production model with minimized consumption of waste and by-products. The model describes a closed circle of connected sub-processes: A) production of metal carbide, HESCAP Deliverable D.15 Due date: 30/11/2012 FP7 ENERGY Contract No.214405 1 April 2010 – 30 September 2013 Page 90 of 133 B) production of CDC and metal chloride, and C) production of metal oxide.

ST has also carried out the cost analysis of circular CDC production process, which shows that price of CDC is well competitive with commercially available activated carbons.

Significant achievements
A simple design for prototype is realised and can be easily integrated in each sub-module. The cost of production of this module will soon be felt. For example, a request for a purchase price of a lot of QCM (over 100 units) was started.

Based on the Life Cycle Assessment, the Material use, the Energy use and the Waste production, in the production of all the units are analyzed. Their environmental Impact is performed and all the indicative diagrams of the different impacts of the whole production process are shown.

Task 6.3: End of Life Management.(Months 18-36 (September 2011- March 2013))
Progress towards objectives
Report D20_WP6 (m36): End-of-Life management of the HESCAP system, has been completed. The end of management practices for HESCAP system were investigated and analyzed according the usage, the technological capabilities and the nature of the product itself.

Best management practices dictate that the waste is processed in the most environmentally desirable method. Environmentally desirable method means that none of the waste will be handled in such a way as to contaminate the environment.

The waste management options that can be possibly used:
1.Reuse of some of the HESCAP subsystems.
2. Reuse of components, or disassembled items.
3. Recycling equipment or components for material recovery.
4. Recycling of components for energy recovery.

5. Disposal of material resources via incineration
6. Disposal of material resources via land filling

According to the nature of materials after usage and residues there have been implemented various methods of waste management in order to be consistent with best environmental practices, e.g. avoid environmental pollution

Significant achievements
An analysis of the end of life management of all the material that are used in the HESCAP.

2.6 WP7: Results exploitation and dissemination
Objectives
This work package will study the result exploitation and business model that are appropriate for the proposed system. It will also coordinate the publications and patents resulting from the project. Additionally, it will study the business possibilities of the different subsystems of the HESCAP system.

Task 7.1: Dissemination. (Months 1-42 (April 2010- September 2013))
Progress towards objectives
According to the planning a Webpage fully dedicated to the HESCAP project was implemented after 3 months of project. Additionally, a project leaflet has been issued in order to promote a wider dissemination of the project objectives, structure and partnership.

Initial dissemination activities were essentially focused on publishing news and press releases, and giving interviews in general public newsletters, magazines, websites and media, particularly at the beginning of the project, to create awareness about the technology in general and the project in particular. Details can be found in sections 3.3.1 and 3.3.2 of this report. Although presentations in national or international meetings were initiated in the first year of the project, but this activity was consolidated mostly in the second year. Details can be found in sections 3.3.2 of this report.

During the time corresponding to the second periodic report partners have been able to start the publication of articles in specialized research journals. Details can be found in section 3.3.2 of this report. Finally HESCAP partners have presented the project in different speeches and presentations.

Significant achievements
Dissemination activities have been carried out according to the planning. In the first year of the project the emphasis was made on creating a dedicated webpage for the project and on publishing news and press releases, and giving interviews in general public newsletters, magazines, websites and media to promote awareness about the project. From the second year of project, the focus was placed on making presentations in national or international meetings and publishing articles in specialized research journals. As a result of this effort, 3 papers have been published in peer reviewed journals, 9 oral and poster presentations in scientific conferences have been made, and 2 general presentations about the project have been given.

Task 7.2: Technology and Market survey. (Months 1-42 (April 2010- September 2013))

Progress towards objectives
The work in this task started with an initial market survey that was based on the assessment of 5 potential applications in 3 different sectors: industrial, transportation and consumer electronics. Despite this was not at all a comprehensive assessment, and that the Market size estimations for supercapacitors vary considerably depending on the sources. The applications evaluated in the survey cover 33% of the estimated potential market in 2014-2015. However, it must be highlighted that this figure could be as low as 11% in the pessimistic case or as high as 50% in the optimistic.

Additionally, related to the gas sensors devices, CEA-LETI initiated a specific technology survey on commercial sensors for monitoring gas emission on supercapacitors and batteries.

Those are just preliminary market surveys so further analysis efforts are required to identify and assess new application cases and to evaluate the competitiveness of the HESCAP technology versus its competitors, its weaknesses and strengths as well as the opportunities and threats that can be found in the different markets. With this aim IMDEA maintained informal contacts with companies involved in manufacturing and commercialization of supercapacitors or batteries (Koneika, SAFT, Exide) to explore the potential use of high-energy density supercapacitors.

The main conclusions are that:
- Koneika as a company that produces and sells very robust supercapacitors based on KOH aqueous solutions is essentially interested in applications that require high-power and extremely long cycle life. Such interest is mostly motivated by the technical limitations of their technology, so if a new technology able to provide higher energy densities would be available new applications would be addressed. Their main restriction is that they would not accept an increase in energy density if they have to pay the price of significant reductions in their power density and cycle life specifications of their products, because in their opinion they are a major competitive advantage against batteries.
- The nickel battery business of SAFT and the lead-acid battery business of EXIDE are mostly driven by prices, because reliability and safety are not a problem. Their potential interest in high energy density HESCAP supercapacitors would depend mostly on providing very competitive costs. Higher investment costs could be acceptable if the cycle life is long enough to reduce replacement costs significantly.
- The lithium-ion business of SAFT is totally different. In this case safety and reliability are big issues while price, although being important, is not so critical. The energy density of these devices is so high compared to supercapacitors that the only possible niche for them will be in the business of power batteries, if their cycle life could be extended far away from the usual values in power batteries.

APCT has evaluated the performance of the low cost solution that they have proposed as a technical solution by making a exhaustive comparison with other market solutions from Panasonic, Maxwell Technologies, Ness Cap and Wima. This analysis shows that all these manufactures have comparable technical results but they have not made significant advantages in cost/power. A direct cross study between HESCAP device and BCAP3000-P270-K04 (Maxwell) shows that HESCAP device has several advantages with only one exception: weight/volume factor that requires further improvements.

Finally, as a consequence of this study it is clear that the development of the HESCAP project will lead to a very cost-effective energy storage system suitable for short term delivery applications both in stationary and dual-use applications, as noted in [4]. Following table shows the application areas the where HESCAP plan be oriented.

Market segment
Critical parameters HESCAP
project plan APCT SC-Opt
(ACFM technology)
Micro grid 10k W-h =E=100k W-h Yes Yes
Solar and wind systems in distributed generation systems 0,5 W-h = E = 500 W-h NO Yes
Full Electrical Vehicle (FEV) 50 W-h = E = 800 W-h Yes NO
UPS 3 W-h = E = 30 W-h Yes Yes
Application in everyday life 0,01 W-h = E = 0,5 W-h NO Yes
Significant achievements

Deliverable D3 was generated as a result of the activities carried out within this Task 7.2 along the first six months of the project. It includes an assessment of 5 potential applications for HESCAP supercapacitors and the analysis of their corresponding markets.

Related to the gas sensors devices, a specific technology survey was initiated on commercial sensors for monitoring gas emission on supercapacitors and batteries.

Informal interviews with companies involved in manufacturing and commercialization of supercapacitors (KONEIKA) and batteries (SAFT, EXIDE) have provided new ideas about the type of characteristics that would be of interest for their respective markets. Considerable differences have been found, depending on the type of market in which they are competing at present. No particular interest has been found in moving their businesses towards new market niches, but they would be interested in technologies that could replace the current ones providing better performance.

Task 7.3: Exploitation. (Months 1-42 (April 2010- September 2013))
Progress towards objectives
LETI has developed gas sensors for detection of CO_2 and H_2 based on functionalized microporous silica. LETI has been also working on detection of gas (CO_2 and H_2) with functionalized QCM. This process of functionalized microporous silica can be used for detection of CO_2 or H_2 for healthcare application or environment detection for a large variety of micro sensors.

IMDEA has designed a new electrolyte made of a blend of an Ionic Liquid (PYR14TFSI) and an organic solvent (Acetonitrile), which has been identified as a potentially exploitable result. To make this electrolyte fully useful it is necessary its marriage with activated carbon electrodes pairs, with tailored mass loadings of each electrode.

CEIT has designed one low cost, high current active voltage equalization system for supercapacitors able to be used also with different kind of commercial supercapacitors. On the other hand CEIT has developed one design methodology of high frequency DC/DC converter able to work with a wide range of input/output voltages.

Significant achievements
During the execution of the project different exploitable results have been identified for CEA-LETI, IMEDA and CEIT. These exploitable results are presented in the IPR Final report that has been included in this report as one Annex.

Potential Impact:

3 POTENTIAL IMPACT AND MAIN DISSEMINATION ACTIVITIES AND EXPLOTATION OF RESULTS

3.1 SOCIO ECONOMIC IMPACT

According to most of the market surveys reviewed, the market of supercapacitors is still very limited. However if all the targets of the HESCAP were fulfilled a significant increase in the spectrum of applications would have occurred. Together with this, a major market projection could have been expected. Specific capacity increases and cost reductions in the order of the HESCAP objectives would have made supercapacitors to become an advantageous alternative to some battery technologies such as lead-acid.

Unfortunately the project has not reached all the objectives in one single technology, but some of them were close to be attained with the design that included electrodes made of customized Carbide Derived Carbons and an electrolyte made of a mixture of an ionic liquid and acetonitrile. This configuration provided energy densities reasonably similar to lead-acid batteries with larger power densities. Best HESCAP results are around 30-40 Wh/kg at 0.5-2.0 kW/kg, while average values for lead-acid batteries are 30-40 Wh/kg at less than 0.05 kW/kg.

In addition to this, although the cycle life of HESCAP supercapacitors has not been fully evaluated, life over 5,000 cycles has been demonstrated. This is not enough for HESCAP expectations, but it is much longer than the usual 500-800 cycles of lead-acid batteries.

Taking into account different market segments that have been analyzed Table 7 shows that the combination of both technologies developed by the HESCAP consortium, one oriented to the high energy density (HESCAP project plan) and the other oriented to the low cost (APCT-SC-Opt) can cover all the addressed applications.

Nevertheless, the problem arises from the fact that the expected HESCAP costs in the first technological approach (high energy density) per kWh, and even per kW, are considerably higher than those from lead-acid batteries .If this problem can be solved in the future, there would be new opportunities for supercapacitors as substitutes of lead-acid batteries in many applications, particularly those with higher value added where the cost will not be the only driver.

In the case of just substitution of batteries by supercapacitors the socio-economic impact will not be very significant because the total market will not grow, eventually. The real impact will take place only if the development of the new technology will promote the use of energy storage devices in new applications. In that case, the demand will increase and so will do the market associated to manufacturing those devices and installing them in energy storage systems.

3.2 THE WIDER SOCIETAL IMPLICATION OF THE PROJECT

In general, the potential market of supercapacitors is estimated from their application as devices that will be used for storage purposes in small capacity and medium power applications, both stationary and mobile. Stationary applications are mostly oriented to use supercapacitors to compensate transient phenomena in electrical grids. For example, frequency regulation, reactive power compensation and bridging power supply in grids where power quality and reliability is required. Mobile applications are mainly associated to complementary storage systems for kinetic energy recovery, particularly regenerative braking, and for cranking of engines.

In principle, medium capacity storage is not among the potential applications of supercapacitors, but if all the HESCAP objectives are fulfilled the situation will be quite different, provided that their specific energy will be similar to that of lead-acid batteries with a much higher specific power and longer cycle life.

As stated in the previous section, if the cost limitation is overcome HESCAP-type supercapacitors could enter in new market niches: specifically in Distributed Energy Storage Systems located next to the consumption sites, and in distributed remote generation systems located next to the generation sites that make use of renewable generation technologies such as photovoltaic or small windmills. In these applications the new supercapacitors could be useful not only as complementary units in the storage system, but as the main storage element with a robustness and cycle life far beyond the limits of current batteries.

3.3 MAIN DISSEMINATION ACTIVITIES
This information has been electronically submitted to the WEB repository information.

3.4 EXPLOTATION OF RESULTS
A general strategy for exploitation of these results has been established in three steps:
Identification of the exploitable result
Protection of the IPR associated to the result
Definition of a specific exploitation plan for each result

3.4.1 Identification of the exploitable result
During the last three years five possible exploitable results have been detected. These exploitable results are the following:
Ultracapacitor Stack design features, including quantitative information (size of details, specifications, etc.) Owner party: APCT
One model based on Excel-based program "parameter estimation" able to estimate some parameters like: electrode thickness, single electrode pair thickness, number of electrodes, electrode mass, collector thickness, number of double side collectors, number of one side collectors, etc. It also calculates the estimated mass of all the subsystems that are necessary in order to build one stack: electrode, collector, leads, separator and electrolyte.

Multigas sensor module (H_2, CO, CO_2) Owner party: CEA_LETI
The multigas sensor module consists of a multi-sensors fluidic chamber mounted with a wireless data acquisition module powered by a 15V battery giving to the device autonomy of 12 hours. The fluidic chamber is designed and optimized to guaranty an efficient fluidic repartition on each sensor to assure the suitable response of sensors: 2 QCM and a CO sensor by AlphaSense. The counter is a 4-channel, bidirectional digital input module NI CompactDAQ wifi chassis. The device has two operating modes: in laboratory mode gas can be pushed into the fluidic chamber, in the outdoor mode, a pump and a flow rate control module has to be added.

High current supercapacitor voltage equalization system. Owner party: CEIT

One high current, low cost supercapacitor voltage equalization system has been developed in order to assure that the module can work with its maximum operative voltage value. This exploitable foreground includes the power electronic hardware oriented to make the energy compensation (microprocessor, low cost buck/boost converter, high frequency coils, analog filters, etc.), the embedded software needed in order to make the primary control of each equalization device and the error control. Finally it includes also the communication channel and protocol that is necessary in order to identify which device is not working properly.

100 kW DC-DC resonant converter (Vin 50V, Vout 420V). Owner party: CEIT
In some applications, depending on the number of supercapacitor stacks, the output voltage of the supercapacitor module can be very low (typically in transport applications). In these situations it is necessary to connect in series one DC/DC converter able to increase the voltage up to the level that is required by the addressed application. When the voltage is very low, it is possible to use as power semiconductor the MOSFET technology. This technology can work with a very high commutation frequency. When the DC/DC converter works at high frequency the power density is very high (lower volume and weight). The addressed exploitable Foreground consists in one DC/DC high frequency modular converter. It includes the specific design methodology developed for this topology, the embedded primary control software and the power electronic hardware of the converter. As an evaluation example one DC/DC converter that uses this technology has been built and tested. (Vin 50V, Vout 420V, 100 kHz, 100 kW).

100 kW DC-DC bidirectional boost converter (Vin 300V, Vout 700V, 15 kHz, 100 kW). Owner party: CEIT
When the volume is not a hard restriction, it is possible to build supercapacitor modules with a high operating output voltage. On the other hand if the nominal voltage of the addressed application is very high (higher than 600 VDC or 400 VAC) it is not possible to use the MOSTEF technology and more traditional IGBT semiconductors shall be used. These semiconductors can't work with commutation frequencies higher than 20 kHz. The addressed exploitable Foreground consists in one DC/DC medium frequency modular converter based on a full bidirectional back/boost converter. It includes the specific design methodology developed for this topology, the embedded primary control software and the power electronic hardware of the converter. As an evaluation example one DC/DC converter that uses this technology has been built and tested. (Vin 300V, Vout 700V, 15 kHz, 100 kW).

Use of mixtures of an Ionic Liquid. Owner party: IMDEA
A new electrolyte made of a blend of an Ionic Liquid (PYR14TFSI) and an organic solvent (Acetonitrile) has been identified as a potentially exploitable result. To make this electrolyte fully useful it is necessary its marriage with activated carbon electrodes pairs, with tailored mass loadings of each electrode.

3.4.2 Protection of the IPR associated to the result

Throughout the project, the IPR Office of the project has identified the foreground generated in the project. Annex A.1 presents the final report of the IPR Office where the ownership of the generated foreground is identified. Annex A.2 summarizes he publications declared as foreground by each partner of the consortium.

3.4.3 Definition of a specific explotation plan for each result

This section presents the explotation intentions and strategy of the HESCAP partners according to the rules established by the IPR the ownership of some exploitable results. The objective is to incentive some actions from partners and launch possible commercial initiatitives.

CEIT is a non-profit research centre whose core mission is to serve the industrial sector by carrying out R&D projects. Therefore, CEIT will exploit the knowledge gathered within HESCAP in the Power Electronics area by means of research and development projects with the local industry. This will ensure that this knowledge is transferred to the industrial sector.

In this line, all the subsystems that have been developed within HESCAP project will be installed in one Smart Grid laboratory in June 2013 in the framework of the "iSARE Microred Gipuzkoa" project. This project, that is supported by the Basque Country FEDER operative program 2007-2013, the Gipuzkoa Provincial Government and the Ministry of Economy and Competitiveness of Spain will developed with the local industry one Smart Grid laboratory, that as a prototype will serve as a platform for evaluating new products and equipment for companies in the territory to validate their own generation, loading, storage and renewable and clean energy distribution systems. iSARE will include electromechanical systems (transformers, high and middle voltage protections), storage systems (batteries, flywheels and supercapacitors) and an interoperable communication infrastructure. One member of the iSARE consortium has been member of the IAP of the HESCAP project.

Te integration of the HESCAP prototypes (one supercapacitor module system with a total capacitance of 30 Farads and a available energy of 220 wh, the high current voltage equalization system, the intermediate DC/DC converter) will allow in a first stage to test the HESCAP technology in a real environmental condition and will allow also to introduce different improvements and to maintain alive the technology.

On the other hand, the foreground produced during the HESCAP project has started to be applied directly to another research project called "Irizar Electric Bus" (IEB) with a completely different application scope.

Throughout the project, CEIT has published non confidential results of the HESCAP project and participated in scientific and technical forums, and will keep doing this after the end of the project.

IMDEA ENERGIA. The scientific programme of IMDEA Energy Institute has been outlined for contributing to the future establishment of a sustainable energy system. The Institute foster the development of renewable energies that have none or minimal environmental impact. The legal structure of IMDEA Energy Institute is a Foundation and the activities developed by the Institute are financed through the resources associated to public and private funds including revenues stemming from the industrial sector.

In this line, HESCAP Project has become for IMDEA a source of other projects in the field of supercapacitors for different applications. The experience acquired, the foreground generated and some of the lessons learned in the project have been used to apply for other research and development projects.

Successful cases in IMDEA have been:

ADECAR (2011-2014) – Spanish programme INNPACTO for applied research. Supercapacitors for water deionization.
CAPSETA (2012-2014) – Spanish national program for fundamental research. Metal oxides and sulphides for pseudocapcitors.
RENAISSANCE (2012-2016) – International Training Network on innovative polyelectrolytes for energy and environment (call FP7-PEOPLE-2011-ITN, contract FP7-289347).
SUPERLION (2013-2015) – Spanish national program for fundamental research. Supercapcitors using ionic liquids as non-conventional electrolytes..

In the same line as CEIT, IMDEA as a research centre will continue with different dissemination activities in both scientific and technical forums in order to guarantee the explotation of the HESCAP results.

ST and APCT have been working in the field of the Supercapacitor technology during the last years and they have demonstrated their experience with both, the products that they have in the market and also with their active scientific activity in conferences and scientific publications. In this line, both companies will apply all the knowledge generated during the HESCAP project in their respective product lines. Despite not all the objectives of the HESCAP project have been solved, some possible working paths have been discarded as a consequence of the HESCAP project.

In this line, the low cost technology proposed by APCT (ACFM technology) has started to be developed in order to increase the overall efficiency of some photovoltaic generation systems by applying the Electrical Energy Take-Off System (EETOS)

Also, APCT has started to apply this technology in the Hybrid Electric Vehicle segment by the construction of one Capacitor-Accumulator System (CAS) for start engine and one Voltage stabilizer for electronic ignition.

4 USE AND DISSEMINATION FOREGROUND

4.1 SECTION A- PLAN FOR DISSEMINATION

The dissemination plan that was described in the DoW document is summarized in the next Table where four of the five key elements for a dissemination plan are included with the exception of the Messages, which had to be customized for each specific case.

Phase I was aimed to create awareness about the project, its objectives and challenges. It was therefore oriented to a very general audience including not only experts in the subject but also general public with interest and curiosity about energy storage technologies and applications. As planned, most of this dissemination effort was made during the 1st year of the project. Details of the activities carried out are listed in table (or template) A2. Awareness about the project and the activities of partners in this field has also been promoted by the presence of IMDEA and CEIT (as member of IK4 alliance) in the Joint Programme in Energy Storage of the European Energy Research Alliance (EERA). For example HESCAP has been included in the Project mapping created by the JP to evaluate the state of the art of research on supercapacitors in Europe.

Phase II was planned to inform the specialized community about the scientific and technological results of the project. Although these activities started a bit earlier than planned, the major part of them was performed during the second and third year of the project. Details of the activities carried out are listed in table (or template) A1.A total of 3 articles have been published and 9 oral and poster presentations in international conferences have been made by 4 of the 6 partners involved in the project.

According to the Journal citation Reports the Impact factor of the journals where HESCAP-related papers have been published are:
Energy and Environmental Science. Impact factor 2011= 9.610 (3rd of 81 in Energy and Fuels, 3rd of 133 in Chemical Engineering, 1st of 205 in Environmental Sciences)
Electrochimica Acta. Impact factor 2011= 3.832 (7th of 27 in Electrochemistry)
RSC Advances. Impact Factor 2011= not available yet.
For this year, at least two additional papers are expected to be published on HESCAP results in journals such as Electrochimica Acta, Carbon,Journal of Power Sources…

Phase III was designed to offer the outcomes of the project (technology, products or services) to potential customers. Unfortunately it has not started yet because the project has not reached the point of having a technology, a product or a service with enough degree of development for this type of pre-commercial dissemination. It is not discarded that during 2013 some of the partners could undertake activities within this phase (Anything from Skeleton here?). For example, IMDEA aims to participate in an international brokerage event at the GENERA 2013 fair in Madrid, where stakeholders of the energy sector meet to show and offer their technological portfolio.

List of Websites:
http://www.hescap.eu/