Composite Structural Power Storage for Hybrid Vehicles

Reporting

Project Information

STORAGE

Grant agreement ID: 234236

Funded under
FP7-TRANSPORT

Overall budget
€ 3 396 348,60

EU contribution
€ 2 510 412

Closed project

Start date
1 January 2010

End date
30 June 2013

Coordinated by
IMPERIAL COLLEGE OF SCIENCE TECHNOLOGY AND MEDICINE

United Kingdom

This project is featured in...

RESEARCH*EU MAGAZINE
Nothing gets lost: the power of biomass

NO. 34, JULY 2014
Final Report Summary - STORAGE (Composite Structural Power Storage for Hybrid Vehicles)

Executive Summary:

The need to develop greener, safer and more competitive road transport has been recognised as a critical societal and commercial importance for Europe. To increase range, and to reduce the weight of the energy storage, lighter vehicles must be made. In this context STORAGE aimed for the development of unique lightweight electric power storage materials for highly efficient and attractive future electric vehicles. Conventional design maximises the efficiency of the individual subcomponents, but an alternative is to utilise multifunctional materials that simultaneously perform more than one function. The focus of STORAGE was structural power materials which could store electrical energy whilst meeting the demands of mechanical loading. Although STORAGE strove to achieve mechanical and electrical performances comparable to existing structural materials and electrical devices respectively, the goal was to demonstrate an overall weight saving of 15% as compared to the combined mass of conventional materials and devices currently used in hybrid cars.

The programme consisted of six technical work packages. The initial research had been split into two parallel paths; Reinforcement Development and Grafting (WP2), and Multifunctional Resin Development (WP3). The former culminated in the development of several different reinforcements/electrodes including optimised activated carbon fibres, CNT grafted and CNT sized fibres and carbon aerogel (CAG) coated carbon fibres. All the resulting reinforcements showed significant enhancements in their electro-chemical performance with several fold increase as compared to the raw carbon fabric. In addition, fibre level structural batteries were demonstrated which have the potential to revolutionise the micro-battery field. In parallel, advances in stiff separators (compared to the traditional material used in actual supercapacitors or battery systems) were also achieved. Regarding the matrix development, a bicontinuous morphology had been achieved and characterised using a mixture of the existing fully formulated epoxy resins and liquid electrolyte (IL+LiTFSI). A resin formulation containing 50 wt.% of MTM57 and 50 wt.% of ionic liquid and Li salt was used for composite production. Finally, structural electrostatic capacitors were demonstrated and the effect of constituents investigated.

Selected constituents were taken forward into WP4 (Composite Manufacture) and subsequently studied in WP5 (Composite Characterisation). The former identified and partially addressed issues such as short-
circuiting of the carbon layers and the out-life and shipping issues. WP5 characterised the critical electrical and mechanical properties of the multifunctional materials, as well as addressing crashworthiness. This workpackage achieved an understanding of the relationships between these properties and the microstructure and fracture processes in these materials. It was shown that there was a critical balance between the optimum microstructures for mechanical and electrical performance; rigid, solid structures for mechanical performance, whilst porous and non-tortuous structures for ionic conductivity.

In parallel with the material development, key engineering and operational issues were addressed in WP6 (Systems), beginning with the identification of a multifunctional design approach, and investigating how to package, integrate and connect the structural power composites within a vehicle structure. These studies demonstrated how lightning strike protection material could improve power density and how machining under controlled conditions would affect the electrical properties. Application of the materials developed in this project would require justification in terms of cost and weight benefits, which were both modelled and analysed. The legal and practical ownership issues were studied which considered factors including safety, driving range, charging and maintenance.

Finally, the project culminated in three demonstrators in WP7 (Technology Demonstrator Development), a small scale radio controlled car with a structural supercapacitor roof, a plenum cover with commercial Lithium-ion batteries which has been driven on the Volvo prototype car in Gothenburg for over a year, and a trunk lid with supercapacitor laminates. Although there is still work to do on the electrical and mechanical performance of these multifunctional materials, they have demonstrated that they offer great potential. In STORAGE, incorporation of multifunctional materials and components in vehicle systems led to huge weight savings (64% for the plenum cover and 60% for the trunk lid).

Project Context and Objectives:

1. Summary Description of Project Context and Objectives

1.1. Background

Weight is a premium; any material which does not contribute to load-carrying capacity is structurally parasitic. Conventional design attempts to maximise the efficiency of the individual subcomponents. A different approach is to create novel multifunctional materials that simultaneously perform more than one function, thus offering significant savings in mass and volume, or performance benefits. Such structural power materials were the focus of the STORAGE programme, the final results of which are reported here. The versatility of polymer composites means that they provide an ideal opportunity to develop novel multifunctional materials which can store the electrical energy required to power systems, whilst meeting the demands of mechanical loading. Carbon fibre composites are attractive as they are commonly used as both electrodes and high performance reinforcements but usually the forms of carbon are different. Previous work has demonstrated such multifunctional materials can be synthesised at a laboratory level, and the technology is ready to be taken up by industry. The overall aim of this research programme was to show these materials imbue at least a 15% improvement in efficiency over the performance of conventional materials and devices.
The need to develop greener, safer and more competitive road transport has been recognised as a critical societal and commercial importance for Europe. To assist the EC the European Road Transport Research Advisory Council has been preparing a strategy document to guide research for the step changes needed. As a result of this work, the electrification approach to urban mobility and transport has been highlighted as the most urgent research area. For a successful introduction of electric vehicles lightweight technology is identified as key. For city cars the energy consumption is inversely proportional to the weight of the vehicle. To increase range, and to reduce the weight of the energy storage, lighter vehicles must be made. In this context the STORAGE aimed for the development of unique lightweight electric power storage materials for highly efficient and attractive future electric vehicles.

1.2. Overview of the Programme

The programme consisted of six technical work packages. During the early stages of the research the nature of the material had been conducive to parallel development of the constituents of the composite; the reinforcing and matrix phases. Therefore, the initial research had been split into two parallel paths; Reinforcement Development and Grafting (WP2), and Multifunctional Resin Development (WP3). Following this, the constituents were brought together in WP4 (Composite Manufacture) and WP5 (Composite Characterisation). WP6 (Systems) addressed application of these new materials and the research culminated in WP7 (Technology Demonstrator Development).

Work Package 2 (Reinforcement Development and Grafting) had been split into three sub-Tasks; Carbon fibre activation and grafting (WP2.1) Separator layer development (WP2.2) and Anode development (WP2.3). WP2.1 had focussed on increasing the surface area (and thus electrical properties) of the carbon fibres without compromising their mechanical properties. The onward strategy had been to make use of carbon fibres grafted with CNTs to provide the required combination of reinforcement and high surface area. The CVD synthesis of the hairy fibres was scaled up by NCYL using their existing expertise. Commercially available and bespoke woven carbon fibre cloths have been used and NCYL have also used their own non-woven carbon fibre cloth. Both types of carbon fibre cloths had been sent to ICL for surface activation, and growth of carbon nanotubes on carbon fibres were compared with activated and non-activated carbon fibre cloths. Characterisation of the hairy fibres had drawn heavily on electron microscopy, Raman spectroscopy, surface area, wetting and electrokinetic measurements.

Development of thin but stiff separator layers was undertaken in WP2.2 to allow efficient ion migration in batteries and supercapacitors, and it was anticipated that this Work Package would entail minimal resources. Separator layers, with minimal thickness and fibre brooming but maximum mechanical properties were identified and used.

Finally, WP2.3 had focussed on the development of metallic anodes lamina which can be used in structural batteries and hybrid capacitors. ICL had developed carbon aerogel and metal oxide whereas SICOMP had focussed on battery ½-electrodes. The development of metal oxide electrodes had built on the work previously published at ICL which utilised the deposition of a manganese complex followed by conversion to manganese oxy-hydroxide.

Work Package 3 (Multifunctional Resin Development) was split into two sub-tasks; WP3.1 (Structural
Electrolyte Development) and WP3.2 (Structural Dielectric Development for Capacitors). Given the similarities in the requirements for the electrolytes in all but the dielectric capacitor devices, the generic development of the electrolytic resins had been undertaken in WP3.1 building on the existing expertise of the partners and exploiting a two-phase polymer system that forms a self-assembled bi-continuous microstructure. The activities had focused on mesoporous and bicontinuous matrices with good interface forming characteristics, optimised for both mechanical performance and electrical transfer, and generation of the electrolyte phase by in situ polymerisation. Characterisation of the bicontinuous structure been undertaken using electron microscopy with the ionic conductivity determined by impedance spectroscopy. For WP3.2 existing polymer matrices offered good dielectric properties and required limited development for structural capacitors. The focus had been on minimising porosity and fibre cross-over during fabrication, to thus maximise the breakdown voltage of these matrices.

Work Package 4 (Composite Manufacture) brought together the constituents developed in WP2 and WP3 to produce the electrical power devices. The task was split into device specific sub-tasks; Capacitor Concepts (WP4.2) Battery Concepts (WP4.3) Supercapacitor Concepts (WP4.4) and Hybrid Capacitor Concepts (WP4.5) but with an additional sub-task (WP4.1) which had focused on Composite Processing. Although there are two potential processing routes for these materials; either via a prepregging route or a resin infusion route, the former was quickly chosen as preferable. This entailed prepregging the modified fibres from WP2 in the resins developed in WP3. Consequently WP4.1 characterised parameters such wetting, viscosity and permeability as well as the cure kinetics for the developed matrix resin. The electrodes were woven from the modified fibres with a thin, insulating veil of woven glass fibres and a microstructured bicontinuous matrix.

Following fabrication of the devices, both the Electrical Properties (WP5.1) and Mechanical Properties (WP5.2) were characterised in Work Package 5 (Composite Characterisation). WP5.1 entailed measuring the capacitance, charging/discharging and current leakage characteristics using methods such as impedance spectroscopy and cyclic voltammetry, as well as direct charge/discharge cycles. The energy and power densities achievable with the system were determined with the target to increase these to that of conventional batteries, capacitors and supercapacitors. Test cells were examined for their capacity and charge/discharge rates under a variety of conditions to determine their respective power and energy densities. The performance of the cells utilizing electro-chemical impedance spectroscopy was also done to understand the dynamics of charge discharge and slow processes such as self-discharge, electrolyte decay, and morphological changes (electrolyte creep, etc). An important aspect which was also characterised was the equivalent series resistance of the supercapacitors and the need to decrease this parameter as much as possible in order to improve specific power. Repeated cycling of the cells was used to assess stability of the material.

WP5.2 aimed to achieve a viable engineering material by addressing the key mechanical properties which drive composite selection. It was anticipated that the composite stiffness parallel to the fibres would be good, but transverse stiffnesses (E22), compression strength (Xc) and toughness (GIC), which are influenced by the modified matrix, had been expected to have exhibited reduced properties. However, this trend was countered by the introduction of the CNT reinforcement and the nanostructured matrix; CNTs greatly assist stress transfer across the fibre/matrix interface. Finally, durability of the composite was addressed, since both temperature and moisture content influence the mechanical and electrical
performance; hybrid laminate design will at least allow a degree of control over durability and damage tolerance. Following manufacture, the microstructure and fracture mechanisms were assessed by optical and electron microscopy. The key properties were characterised using standard tests.

It was recognised that a critical aspect of automotive structural design is that of crashworthiness; in fact, one industrial partner in this programme (Volvo) has a considerably strong reputation in this field. This issue was of particular importance for structural power materials, since under crash conditions, the material should not undergo thermal runaway, sparking or initiate a fire. Consequently, in WP5.3 (Crashworthiness), impact tests (both for electrical storage devices and load-bearing materials) were conducted of both uncharged and charged laminates, using thermal imaging to characterise any rapid temperature changes in the laminates during failure.

As mentioned in the previous Section, to provide an overall benefit, the multifunctional materials developed in STORAGE did not need to have achieved the mechanical and electrical properties of existing structural materials and storage devices respectively, but to demonstrate an overall weight saving in comparison to existing structural materials and devices. Therefore, WP5 culminated in WP5.4 (Ranking of Devices), in which all the configurations were ranked. The target was to replace existing materials and storage devices used in automotive applications. The structural materials taken as a baseline was woven fibre reinforced engineering plastics, which typically have a Young’s Modulus (E11) of 20GPa, shear stiffness (G12) of 5GPa, compression strength (Xc) of 250MPa, and peel (GIC) and shear (GIIC) toughnesses of 500J/m² and 1000J/m² respectively. The multifunctional material would replace devices with specific energy and power density of 5Wh/kg and 1.3W/kg respectively.

Work Package 6 (Systems) entailed five sub-tasks; Concept Design (WP6.1) Power Management and Connectivity (WP6.2) Packaging (WP6.3) Cost and Benefits Modelling and Analysis (WP6.4) and Ownership Issues (WP6.5). WP6.1 focused on the laminate design whilst WP6.4 addressed modelling of the costs incurred and benefits accrued (such as weight and volume savings) by replacing existing components (both power sources and structures) with the new multifunctional materials. WP6.2 and WP6.3 addressed issues regarding connecting the multifunctional material to the component electrical systems and issues such as finishing (machining and painting). Finally, WP6.5 considered the through-life and ownership issues such as inspection, repair and disposal.

The programme culminated in Work Package 7 (Technology Demonstrator Development) in which the technology demonstrator components were produced. This entailed four sub-tasks; Design (WP7.1) Manufacture (WP7.2) Testing (WP7.3) and Assessment (WP7.4). The focus was production of real components; such as replacement of a trunk lid and plenum cover. The function of these components was to protect the interior of the car or engine from physical damage, whilst being as light and cheap as possible. These products were simple to process (essentially thin relatively flat laminates) and the structural requirements were not overly demanding. SICOMP and ETC undertook tests, supported by Volvo, to demonstrate the technology. This entailed demonstration of the structural battery, capacitor and supercapacitor components capabilities at system level needed for the short and long term electrical performance and degradation of the component over the temperature range –30 ºC to 50 ºC.

1.3. Objectives of STORAGE
The focus of the research in STORAGE were materials which simultaneously carry mechanical loads whilst storing electrical energy; note that this target is distinct from a volume saving material, such as a flexible or shaped battery. Although the latter still provides space optimisation within a component, it is still mechanically parasitic and not truly multifunctional. Since the laminated architecture of fibre composites mirrors the configuration of many current electrical storage devices, they offer an exciting opportunity to develop structural energy storage materials. The potential applications are numerous and diverse; essentially any load-bearing component in a system which requires electrical energy. The research programme spanned forty-two months, and met the following objectives;

Objective A: Through using material selection methodologies and cost-benefit analyses, provide guidance for the technical requirements of structural power materials and formulate an implementation plan for using them in current and future hybrid car applications.

Objective B: Develop constituents (reinforcements and matrices) that, when combined, form a composite material for structural power storage.

Objective C: Demonstrate the capabilities of these multifunctional materials through the manufacture and testing (mechanical and electrical) of laminates, and show that they offer at least a 15% improvement over the performance of discrete materials and devices.

Objective D: Address the system issues associated with structural power sources such as power management, packaging and connectivity.

Objective E: Ultimately, through the production and testing of the materials within demonstrator components on a benchtest, to assess the improvements these materials would imbue upon a hybrid car.

The overall goal of this research was to develop demonstrators that show a practical level of performance. To imbue a benefit, the multifunctional material was not required to match the performance of the monofunctional materials which it replaced; the sum of the material efficiencies for each of these functions only needs to exceed unity. Therefore, although STORAGE strove to achieve mechanical and electrical performances comparable to existing structural materials and electrical devices, the goal was, for a given level of performance, to demonstrate an overall weight saving of 15% as compared to the combined mass of conventional materials and devices currently used in hybrid cars. To demonstrate this, the goal was to store the energy associated with decelerating a 1000 kg car from 50 to 20 km/hr over 5 seconds (as might be encountered during urban driving). Using these performance values and the above example, we would then require a supercapacitor of about 2.5 kg mass to store all of the deceleration energy. The challenges included optimisation of multiple, often interdependent properties. Conception, design and implementation required interdisciplinary coordination and cooperation.

Project Results:

2. WP2 Reinforcement Development (Nanocyl)
2.1. WP 2.1 Carbon fibre activation and grafting

2.1.1. Introduction

Carbon fibre activation and grafting (WP2.1) was a sub-task focused on increasing the surface area (and thus electrical properties) of the carbon fibre fabrics without compromising their mechanical properties. Two parallel approaches were followed to allow efficient and homogeneous deposition of CNTs over carbon fabrics: either post-deposition of CNTs using a sizing solution or direct in-situ growth of CNTs over a catalyst pre-coated fabric.

2.1.2. Main work performed, key findings and highlights of research

Following preliminary trials, two kinds of woven carbon fabrics (T300 and HTA types) and a non-woven were provided by Cytec. The T300 woven carbon fabric performed best, both in terms of specific surface area and capacitance after modification.

A first modification to carbon fabrics was activation using KOH as a reactant to modify the fibre surface. Chemical approaches to activation were preferred over physical ones as they were less prone to deteriorate mechanical properties of the carbon fibres. Moreover, the use of chemical agents as activators allows better yields with higher homogeneity along with controllable pore size distributions. Consequently, this KOH-activation treatment led to promising results in terms of specific surfaces but also for the resulting capacitances. Regarding scale-up, some problems of inhomogeneity during the activation treatment occurred. A significant increase in electrochemical activity was obtained without any degradation in the mechanical properties of the carbon fibres, suggesting the potential application of KOH-activated carbon fabrics as electrodes in the multifunctional structural supercapacitors. However, although this approach was promising, the batch nature of the activation meant it was difficult to scale up within the STORAGE programme.

As carbon nanotube grafting was also under consideration to enhance the specific surface area of the raw materials, two different methods of modification had been investigated: direct in-situ growth of carbon nanotubes over the fabric surface and impregnation with CNT-containing sizing solutions. After optimization of the CNT-synthesis process over carbon fabrics, reproducible CNT deposit on T300 cloth was achieved with control over the CNT yield. The successful growth of carbon nanotubes on the surface of carbon fabrics fibres was realized by catalytic decomposition of gaseous precursors at a moderate temperature. The coverage of the fabric fibres by carbon nanofilaments was found to be dependent on the interactions between the precursor catalytic phase and the surface of the fibres. Finally, an optimum loading of carbon nanotubes was found to be close to 10 wt.% to ensure homogeneous covering of the fibres, high generation of specific surface area and excellent electro-chemical performance without detrimental effects on the further processability of these CNT-grafted fabrics.

On the other hand, modification of different carbon fabrics with carbon nanotube-containing solutions was successfully performed and yielded homogeneous coverage of carbon fibres by a thin layer of CNTs enhancing specific surface area. Trials on different types of deposition methods concluded that successive impregnations followed by a thermal treatment were the best process to improve electrochemical
performance of the modified carbon fabrics. Impregnation with an aqueous dispersion of CNTs reached almost the same characteristics in terms of specific surface area and capacitance that CNT-grafted fabrics obtained by in-situ growth. The direct outcomes of the initial study were to settle CNT-grafting procedures with, on one side, a protocol for the use of a CNT-containing solution and, on the other side, fixed parameters for the in-situ growth of homogeneous and reproducible layer of CNTs. Consequently, two potential configurations of CNT-enhanced fabrics were identified to take forward to the later work packages:

- CNT-growth modified fabric: Obtained by direct in-situ growth of CNTs by catalytic decomposition of gaseous reactants over a catalytic precursor (mixture of metallic salts) at quite moderate temperature (750 °C).
- CNT-sized modified fabric: Post-deposition of CNTs via an aqueous dispersion of nanotubes followed by a thermal treatment at rather low temperature (400 to 450 °C) to decompose the surfactants used to disperse and stabilize the water dispersion.

Results from the mechanical properties of modified fabrics showed that the KOH chemical activation procedure had not affected the tensile strength or the tensile modulus of the fibres. On the other hand, single fibre pull-out tests with an epoxy system have demonstrated that CNTs grown on carbon fibres were further acting as anchoring points within the matrix, leading to reinforcement of the interface.

By iterating the growth of CNTs using different synthesis parameters, an optimized set of values were determined and further production of CNT-enhanced T300 fabrics was carried-out: These parameters were used to produce the panels for the STORAGE project.

An alternative route to the direct synthesis of carbon nanotubes on carbon fabrics was the sizing of these fabrics with solutions containing CNTs. Such a method allows the use of an aqueous dispersion of CNTs and can be easily scaled-up without requiring particularly specialised processing equipment. The other advantage of the sizing method is that it does not alter the mechanical properties of the carbon fibres as they remained undamaged during the impregnation. However, the non-reactivity between the carbon fibres and the CNTs may also lead to phenomena such as debonding or delamination.

Up-scaling of the sizing process of carbon fabrics with a carbon nanotube-containing solution was successfully performed and yielded a homogeneous coverage of the carbon fibres by a thin layer of CNTs, thus enhancing their specific surface area. Several attempts had been conducted to reproduce the process at a higher scale to treat fabrics of larger dimensions. In particular the emphasis was set on the precise and reproducible deposition of aqueous dispersion over all the fabrics. For the samples prepared for STORAGE this impregnation step was still done manually but its transformation into an automatic system is quite straightforward and could be easily implemented. After drying at 120 °C, the coated fabric was once again sized with a second layer of carbon nanotube solution. This two-step deposition had proven to be more efficient than the deposition of a single and thicker layer of CNTs. The sizing process was completed by a final heat treatment at 400 °C which allows complete drying of the fabric and decomposition of the surfactants used in the Aquacyl modified formulation.

Aside from the work of up-scaling the CNT-grafting processes from lab-scale to pilot-scale, a cost study
was also performed in order to determine the impact of CNT deposition on the price of the final laminates. A detailed overview of the cost components with some assumptions, and forecasts for higher productivities are presented in Deliverable D2.4 “Scale-up of carbon nanotube-grafted carbon fabrics for structural power applications”.

2.2. WP2.2 Separator Layer Development

2.2.1. Introduction

Development of thin but stiff separator layers was undertaken in WP2.2 to allow efficient ion migration in batteries and supercapacitors. Initially it was anticipated that this work package would entail minimal resources. Separator layers with minimal thickness and fibre spreading but maximum mechanical properties were identified and used, but problems of short-circuiting were encountered.

2.2.2. Main work performed, key findings and highlights of research

Given the prerequisites, different types of woven fabrics have been tested (filter paper, glass fabrics and PP membranes) to act as separator membranes. In particular, preliminary trials making use of filter paper were used as a reference for determination of the capacitance. First glass fabrics provided by Cytec (E-Glass) were characterized using optical microscopy and showed that the gaps between fibre tows could allow carbon fibres to poke through, thus leading to a short circuit in the final composite.

In parallel, PP membranes (acquired from Celgard) exhibited rather good capacitances but suffered from severe delamination issues during mechanical testing. Ultimately, woven glass fabrics were found to be a good compromise between the mechanical properties and electrical performance. In particular, denser glass fabrics usually used for galvanic protection were quite promising as they would prevent the short-circuiting concern in the final composite architecture.

Among all tested materials, woven glass fibre fabrics seemed to have been the most suitable alternative to use as a dielectric layer in capacitor/supercapacitor systems. Two woven glass fabrics were finally selected amongst the tested materials: woven glass fabric “842.0200.01” (Tissa) and woven glass fabric “Style 120” (Cytec). Another potential material issue which impacted on the choice of separator was voidage.

2.3. WP2.3 Anode Development

2.3.1. Introduction

WP2.3 focused on the development of metallic anodes lamina which could be used in structural batteries and hybrid capacitors. ICL had developed hybrid electrodes based on metal oxide and conducting polymer electrodes whereas SICOMP had been working on battery ½-electrodes.

2.3.2. Main work performed, key findings and highlights of research
The work at SICOMP was aimed at finding suitable carbon fibres to use in structural battery systems. The principle was to use the graphitic structure of the fibres to intercalate lithium ions to build up energy-storing devices based on lithium-ion batteries technology. This study focused on polyacrylonitrile (PAN)-based fibres (supplied by two different manufacturers: Toho Tenax and Toray). PAN-based fibres have been shown in an earlier study to have a suitable performance for use in multifunctional applications.

Two different routes for manufacturing structural composite batteries were tested, one at lamina level and one at the fibre level. The lamina level manufacturing route was fairly straightforward and involved stacking of cathode lamina/separator/fibres followed by an infusion of the stack by an ion-conducting polymer matrix. On the other hand, the fibre type batteries manufacturing was much more complicated and so far only functioning half cells have been manufactured.

ICL developed a new type of structural hybrid supercapacitors from structural fibre composite laminates. A crucial requirement was the development of structural electrode materials that possess good electrochemical performance whilst under mechanical load. The strategy was to embed structural carbon fibres into a continuous network of carbon aerogel (CAG) to form a porous layer. This hierarchical structure of CAG-modified carbon fabrics could offer a high electrochemical surface area to facilitate a capacitive double-layer of charge whilst providing a mechanical reinforcing effect of the matrix-related properties. The unique porous structure of CAGs could also act as a 3D scaffold for the deposition of metal oxide, leading to a hybrid electrode composite which offers pseudocapacitances resulting from Faradaic redox reactions of metal oxides.

A new hierarchical structure had been created by embedding the T300 carbon fabrics into CAG based on a resorcinol/formaldehyde mixture. This newly developed CAG/carbon fibre structure was further used to investigate hybrid systems with pseudocapacitive effects: MnO2 nanoparticles were successfully coated over the CAG-modified fabrics using a simple electroless deposition. Consequently, significant improvements in both specific surface area and specific capacitance were evident due to a Faradaic redox reaction of the metal oxide coating. Further details of CAG composite properties (infused with a structural or multifunctional matrix), are presented in Section 5.

2.4. Summary of WP2 (Reinforcement Development)

WP2 was centred on the development of reinforcing materials for novel structural power composites. In particular the focus was the creation and/or modification of existing materials to improve their intrinsic properties and thus tailor them to act as both reinforcements and electrode media. Consequently, successful grafting of carbon nanotubes (CNTs) to carbon fabrics was achieved using two different processes, namely direct impregnation and in-situ growth. The most promising development was carbon aerogel coating of carbon fibres, which led to huge improvements in surface area (and thus capacitance) but also enhancements in mechanical properties. All the resulting reinforcements showed significant enhancements in their electro-chemical performance with several fold increase compared to the raw carbon fabric. In a parallel approach, advances in stiff separators (compared to the traditional material used in actual supercapacitors or battery systems) were also completed and opened a broad new field of applications for structural power composites. Further incorporation of these boosted materials was also accomplished and yield to the formation of innovative supercapacitors and batteries systems. Even if not
at the level of current systems, very promising and encouraging results were achieved for structural batteries and hybrid systems.

3. WP3 Multifunctional Resin Development (Imperial College)

3.1. WP3.1 and WP3.3 Structural Electrolyte Development

3.1.1. Introduction

The structural electrolyte development was carried out in two approaches; development of multifunctional polymer electrolyte with a bicontinuous structure for supercapacitors (WP3.1.1) and thermoplastic polymer matrices with different degrees of saturation for electrolytes for structural batteries and hybrids (WP3.1.2). For the former (WP3.1.1) initially three different strategies were discussed and developed. Those included modification of the existing fully formulated epoxy resins (1), synthesis of block copolymers via RAFT polymerisation (2) and statistical copolymerisation (3). However the later stages of the research concentrated on strategy (1) and strategies (2) and (3) were abandoned.

For the first strategy, three fully formulated commercially available high performance epoxy resins (MVR444, VTM266 and MTM57) provided by Cytec were used, which differ in resin type, cure rate and viscosity. These epoxy resins were formulated with an additional electrolyte, which was selected to be an ionic liquid doped with a lithium salt (EMIM-TFSI+LiTFSI). To form a bicontinuous structure, epoxy resin was dissolved in the ionic liquid based electrolyte and expected to precipitate during curing and form continuous network where ionic liquid based electrolyte would form a second phase.

3.1.2. Main work performed

Using different epoxies it was possible to manufacture structural electrolytes with a wide spectra of morphology and properties. It was found that MVR444 and VTM266 resulted in the structural electrolytes with bicontinuous structures where the dimensions of the structural features were significantly affected by the composition of the formulation. The addition of an ionic liquid based electrolyte to MTM57 resulted in a more complicated structure, which comprised of a continuous polymer phase, formed by a part of the epoxy which was poorly soluble in the ionic liquid based electrolyte, surrounded by the globular nodules, formed by a soluble part of the epoxy. The morphology and dimensions of the microstructural features in the structural electrolytes had a significant effect on their properties. The effects of the composition on curing behaviour, processability, structure and properties of the cured structural electrolyte, including ionic conductivity, mechanical and thermo-mechanical properties, were characterised.

Based on extensive studies of viscosity, curing kinetic, ionic conductivity, mechanical and thermal properties of formulations with different compositions, based on MVR444, VTM266 and MTM57, a multifunctional formulation with MTM57 to ionic liquid ratio 50:50 wt.% and LiTFSI concentration 2.3 mol/l (2.3_50/MTM57) was recommended for further studies and composite manufacture. This chosen formulation showed increased ionic conductivity with a minimal effect on curing and processing associated with the addition of ionic liquid based electrolyte (EMIM-TFSI+LiTFSI) as compared to neat MTM57. However, this formulation exhibited the lowest mechanical performance amongst the studied formulations.
To achieve improvements in the mechanical performance, it was essential to find a way to tune the morphology of the structural electrolytes based on 50/MTM57 by reducing the phase separation prior to curing or increasing curing rate. Therefore, it was decided to change the curing temperature or tune the composition of the MTM57 based formulations by varying the lithium salt content, resin content and addition of an organic solvent with a high dielectric constant.

The increase in the curing temperature from 100°C to 140°C did not affect the morphology of the resulting structural electrolytes. However, decreasing the curing temperature to 80°C resulted in the formation of heterogeneous samples. The lithium salt was essential for obtaining homogeneous samples. In the absence of LiTFSI, homogeneous samples were obtained only when no less than 70 wt.% MTM57 was used. In the latter case, despite a high Young’s modulus (2.29 GPa) and strength (115.5 MPa), the ionic conductivity of this sample was too low (0.62 x 10⁻⁷ mS/cm) to consider this formulation in further studies or applications. Increasing the LiTFSI concentration for both 50 and 55 wt.% epoxy resin content led to a decrease in ionic conductivity but improvement in mechanical performance. However, ionic conductivity was significantly more affected by the composition of the structural electrolytes as compared to the mechanical performance. The observed behaviour could be interpreted by changes in the morphology; with increase in LiTFSI concentration, the microstructure became finer, and both the continuous polymer phase and the spherical nodules phases became smaller and more uniform.

Decreasing the LiTFSI concentration in parallel with an increase in the epoxy content, from 50 wt.% to 55 wt.%, led to a doubling of the ionic conductivity from 0.43 mS/cm to 0.9 mS/cm and a 30% increase in the Young’s modulus from 0.23 GPa to 0.25 GPa. It is important to note that homogeneous samples based on 55/MTM57 with different LiTFSI concentrations had higher ionic conductivity as compared to homogeneous samples with different LiTFSI concentrations based on 50/MTM57. A sharp drop in the ionic conductivity to below 10⁻⁹ mS/cm was observed when the LiTFSI concentration was increased from 2 mol/l to 2.3 mol/l without the same order of magnitude increase in the Young’s modulus.

Substitution of EMIM-TFSI with the respective amount of propylene carbonate (PC) had a significant impact on morphology and properties of the resulting structural electrolytes. It should be noted that the morphology of 2.3M_50/MTM57 containing 1% PC resembled the morphology of 4.6M_50/MTM57 more closely than that of 2.3M_50/MTM57. An increase in the PC concentration led to an increase in the solubility of MTM57 resulting in the formation of a rubber-like material (gel) when more than 1 wt.% PC was used. As gels do not possess permanent porosity, there were no pores to be seen after electrolyte extraction. However, significant improvements in the mechanical properties were achieved via substitution of 1 wt.% of EMIM-TFSI for PC in the 2.3_50MTM57 formulation. This substitution of EMIM-TFSI promoted a four-fold increase in the Young’s modulus from 0.23 GPa to 0.9 GPa with the ionic conductivity reduced by less than three times from 0.43 mS/cm to 0.15 mS/cm.

The resin formulation of 50 wt.% of MTM57, 50 wt.% of ionic liquid and 2.3M lithium salt, 50/MTM57 was chosen for further studies and composite manufacture in WP4 and WP5 on the grounds of providing the best compromise of ionic conductivity, viscosity and curing kinetics. Morphology studies showed
differences between formulations based on MTM57 and other two resins MVR444 and VTM266. To answer the question as to whether the morphology was responsible for the poor mechanical performance of MTM57 based formulations, it was considered to be important to find a formulation for MTM57 that exhibited a bicontinuous morphology, similar to that identified for MVR444 formulations.

To achieve changes in morphology of MTM57/50 it was important to reduce phase separation prior curing. That is why it was decided to tune the composition of the MTM57 based formulations by varying lithium salt content, resin content and an addition of the organic solvent. Studies on the improvement of the structural electrolytes did not lead to a systematic simultaneous significant increase in the mechanical properties and ionic conductivity. Nevertheless, structural electrolytes with a wide range of properties were obtained, and in some cases, a net improvement of both parameters was observed over the original 50/MTM57 formulation reported in Deliverable D3.2.

For WP3.1.2 electro-polymerisation and characterisation of copolymers from monofunctional and difunctional methacrylate monomers for structural batteries and hybrid capacitors was performed. The monomer systems studied were the highly lithium ion conductive monomer methoxy polyethylene glycol (550) monomethacrylate, CD552, from Sartomer and the stiffer, less conductive, tetraethylene glycol dimethacrylate, SR209 also from Sartomer. These monomers were co-polymerised to produce a solid polymer electrolyte material. Studies on multifunctionality of synthesised copolymers showed that all copolymers provided some multifunctional benefits as their performance in ion conductivity and stiffness was above the linear fit of the performance of the pure SR209 and CD552 polymers. A battery cell has been assembled using fibres coated with SR550.

3.2. WP3.2 Structural Dielectric Development for Capacitors

3.2.1. Introduction

Early in the project a series of structural capacitors made from carbon fibre reinforced polymer electrodes were manufactured and evaluated.

3.2.2. Main work performed

The structural capacitors were made from carbon fibre epoxy pre-preg woven lamina as electrodes separated by a dielectric material. The dielectric materials employed in this study were three different surface weights papers and three different polymer films (PA, PET and PC), as well as plasma treated PA- and PET-films. Modification was done to study effect of surface treatment of the polymer dielectric films on structural performance. The surface of the films was plasma treated in nitrogen for 15 seconds. The electric properties of the capacitors involved measurements of dynamic capacitance and losses. It was found that capacitor made using the 80 g/m² paper had the highest capacitance among other studied capacitors. For the polymer film dielectrics, thickness was the main variable that controlled capacitance. As a result the capacitor made using PET film had the highest capacitance amongst the polymer films used. Dielectric breakdown voltage (dielectric strength) of the capacitors was measured by applying a voltage until failure was evident as a large drop in voltage. The dielectric strength of the polymer film capacitors was at least one order of magnitude higher than that for capacitors with paper dielectric
separators. A significant improvement in interlaminar shear strength (ILSS) was found when plasma treated dielectrics were used in capacitors. A visual inspection of the fractured specimens showed that all specimens fractured at the midplane, i.e. at the dielectric. Multifunctional efficiency of the developed structural capacitors was evaluated on the basis of achieved energy density and ILSS, specific normalized tearing force, as well as in-plane stiffness. All capacitors with a polymer film dielectric separator indicate the potential for high multifunctional efficiency.

PET film showed an interesting potential for further work, and it is readily available in many different thicknesses. DuPont Mylar A was the film chosen for study due to availability in different thicknesses and good electrical properties. Nevertheless, further research is needed to identify best choice of polymer film thickness and surface treatment.

3.3. Summary of WP3 (Multifunctional Matrix Development)

Formation of a bicontinuous morphology had been achieved using a mixture of the existing fully formulated epoxy resins and liquid electrolyte (IL+LiTFSI). The effect of the composition of liquid electrolyte (IL+LiTFSI) on the properties of epoxy based uncured formulations, such as the curing kinetic, viscosity, dielectric properties, as well as cured formulations properties, morphology, ionic conductivity, mechanical and thermal behaviour, have been studied. A resin formulation containing 50 wt.% of MTM57 and 50 wt.% of ionic liquid and Li salt was recommended for composite production. Further optimisation of this formulation via varying the composition of the structural electrolyte led to formation of the structural electrolytes with improved both mechanical and ion conductive properties.

Regarding synthesis of block copolymers via RAFT polymerisation and conventional free radical / statistical copolymerisation, both strategies are more innovative and will allow ultimately a more precise control over phase separation and bicontinuous network formation. So far it has been demonstrated that the prepolymer synthesis is feasible for both strategies and remains a longer term goal to evaluate such a matrix.

The characterisation of the multifunctional performance of the co-polymers made from different mixtures of SR209/CD552 was performed and their multifunctional performance was studied, followed by the electrocoating of the carbon fibres. Characterisation of the coating in a parametric study is being continued.

A series of structural capacitors made from carbon fibre reinforced polymer electrodes have been manufactured and evaluated for their mechanical, electric and multifunctional performance using different dielectric materials. Capacitors manufactured using 50µm PET film were the most promising regarding capacitance and mechanical performance.

4. WP4 Composite Manufacture (Cytec)

4.1. WP4.1 Composite Processing

4.1.1. Introduction
WP4.1 assessed the potential issues and collated the knowledge developed from practical experience in synthesising and fabricating components from these unusual materials. This culminated in a summary of the requirements for the manufacture of structural electrical storage devices as developed within STORAGE. It was intended that the devices developed would be manufactured using conventional composite processing methods of lamination of prepreg onto a tool to form the shape followed by consolidation under pressure and curing of the matrix resin through the application of heat. The components of interest to this project were generally thin-skinned with only one moulded surface.

4.1.2. Main work performed, key findings and highlights of research

The basic materials that had been selected for STORAGE were based around high-strength carbon fibres in woven form (as developed in WP2) and multifunctional epoxy resins (as developed in WP3). An early difficulty encountered during matrix development was the acceleration of the matrix cure upon the addition of ionic liquids, in particular this was very apparent for the liquid infusion resin MVR444 which then cured rapidly at room temperature and became unprocessable.

The impact of the ionic liquid on the curing of MTM57 and VTM266 was much lower and these systems were usable although the ionic liquid had a large impact on the outlife of the resin, reducing it from several days to a few hours. It was also observed that the prepreg had issues being frozen which rendered the prepreg unshippable meaning that the final laminates had to be made ‘at source’; i.e. the prepreg process and resulting lamination/curing needed to all be done at Cytec. This behaviour had a significant impact on Work Package 7.

Significant short-circuiting problems were encountered with the satin-weave based devices, so the decision was made to remanufacture all of the devices using twill weave fabrics which had been found to be less susceptible to short-circuiting across the separator layers.

The final manufacture of the laminates used in WP7 entailed the following stages. Firstly the electrical contact between the electrodes and the carbon fibre electrodes was achieved using an aerospace lightning-strike protection mesh (LSP) covering most of the area of the electrode. Before any processing took place the mesh was cut to the required size which is the same shape as the electrodes but with a 2 cm reduction on each side to avoid any bridging and short-circuiting of the device. Corrosion had been identified as a potential issue with this construction so the LSP panels were treated with a corrosion-resistant paint.

The prepreg was produced in discreet panels of the correct size rather than the usual industrial process of continuous production. Before the start of prepreg production the reinforcement was cut to size, this was for both the glass separator layers and for the carbon electrodes, the glass separators being larger than the carbon electrodes to avoid edge short-circuiting. Prepreg production commenced with the resin filming, this was carried out in two main stages, firstly the base resin system was mixed with the ionic liquid using a speed mixer to ensure good blending. Prepreg production was performed using Cytec’s California Graphite film coater and prepreg line. The first stage was to make a resin film which was made by drawing the resin through a tightly-controlled aperture on backing paper. The thickness of the resin film was
adjusted to give the correct resin content for the prepreg, this was determined by cutting out a section of backing paper and measuring the areal weight. The width of the resin film was controlled by the size of the reservoir and was set to be wider than the width of the glass fabric panels to ensure full coating of the fabric while trying to minimize the wastage rate of the resin. Once the correct resin thickness was being produced the pre-cut fabric panels were manually placed on the resin film. After placement of the fabric a polymer backing film was fed automatically onto the upper surface and the material was then drawn between rollers to partially impregnate the fabric and wound onto a roll.

4.2. WP4.2 Capacitor Concepts

4.2.1. Introduction

Firstly considering structural capacitors; the outer carbon fibre prepreg layers must be electrically insulated to avoid the electric shock hazard when touching the charged laminate. These layers sandwich a polymer film (DuPont Mylar A), which may require preforming for doubly curved surfaces. A copper mesh or flat cable was used for the connections, whilst an outer layer of glass fibre prepreg was used for safety insulation. A number of issues had been identified, such as methods for internal connections, adhesion and prevention of delamination, exit of connectors and edge trimming effects.

4.2.2. Main work performed, key findings and highlights of research

The structural capacitors had been demonstrated at SICOMP and the results of this work are reported in Section 5.

4.3. WP4.3 Battery Concepts

4.3.1. Introduction

Two approaches were investigated towards the manufacture of structural batteries: stacked laminated batteries and coated fibre batteries. The laminate needed to be shielded from air to avoid premature degradation due to moisture intake affecting the behaviour of the modified matrix resin. The positive and negative electrodes needed to be isolated from each other at all times to avoid short-circuiting.

Laminated batteries used the individual layers of the laminate as the electrodes with the carbon fibres forming the anodes and the cathodes being produced by the inclusion of Aluminium foil within the structure. The electrolyte was a modified epoxy resin which forms the matrix of the composite in the region of the structural battery; this was the route that SICOMP were pursuing, using the same matrix as ICL’s supercapacitors but including Li ions. The key issue that had been identified was keeping the moisture out; a requirement is to determine as to whether this is feasible with a prepreg route.

Fibre batteries were manufactured on a much smaller scale than laminate batteries with the fibres themselves forming the anodes with the rest of the battery structure relying on fibre coatings. Two approaches were investigated for the construction of fibre batteries using different cathode designs, firstly with a doped matrix cathode and secondly with an oxide coating cathode.
4.3.2. Main work performed, key findings and highlights of research

The two structural battery concepts were investigated by SICOMP and ETC. However, the laminated batteries ran into difficulties associated with short circuiting. The results of the fibre level batteries are reported in Section 5.

4.4. WP4.4 Supercapacitor Concepts

4.4.1. Introduction

The basic architecture of a single cell of a structural supercapacitor was two CF layers which sandwiched a GF layer, all embedded within a structural electrolyte. This was then extended to a multicell configuration.

It was desirable to reduce the insulating glass fibre layers down to a single ply it will help to reduce the weight and thickness. Each supercapacitor (CF/GF2/CF) was about 1 mm thick and it was desirable to reduce this thickness; however, the initial glass layers were too open to prevent shorting between the carbon layers, and therefore glass fabrics with a higher areal weight had to be employed.

4.4.2. Main work performed, key findings and highlights of research

The structural supercapacitors had been demonstrated at ICL, using the materials developed by Cytec and Nanocyl. The results of this work are reported in Section 5.

4.5. WP4.5 Hybrid capacitor Concepts

4.5.1. Introduction

The original intention was to combine laminated structural batteries (Section 4.3) with structural supercapacitors (Section 4.4). However, since the laminated batteries were not developed to the extent that they could be made robust enough to cope with processing, this was abandoned. Consequently, an alternative configuration (CAG based pseudocapacitance) was pursued in the hybrid device role.

4.5.2. Main work performed, key findings and highlights of research

The development of the electrodes is described in Section 2.3 and the results of this study are reported in Section 5.

4.6. Summary of WP4 (Composite Manufacture)

The developments carried out in this Work Package enabled the structural storage devices to be manufactured by the partners but the manufacturing was not without issues and there are still a number of issues to be overcome, in particular the short-circuiting of the carbon layers and the out-life and shipping
issues that were encountered with the modified resins.

5. WP5 Composite Characterisation (BAM)

5.1. WP5.1 Electrical Properties

5.1.1. Introduction

The aim of WP 5.1 was the electrical characterisation of the three different types of structural energy storage devices developed in STORAGE: capacitors, supercapacitors and batteries. A particular challenge was the low power densities of these materials, which resulted in difficulties when trying to use standard electrical test methods.

5.1.2. Main work performed, key findings and highlights of research

A detailed test plan was issued (Deliverable D5.1) which outlined the procedures for cutting, labelling, instrumenting, electrical and mechanical testing of the different Devices.

INASCO measured the effect of moisture and temperature on the electric properties of the multifunctional materials developed within STORAGE using impedance spectroscopy. The DiAMon monitoring system, a fully developed and manufactured system from INASCO was used for this purpose. Volvo had defined the environmental conditions to simulate real weather extremes and the results of this are reported in WP7. For an exterior component this entailed (i) Exposure for 2000h in 38 °C and 96%RH. This is equal to the load of about three years of use in a Malaysian climate; (ii) in a humidity test road salt (+water) sprayed four times during each day. The latter entails a repeated cycle of 25°C 95%RH (18h) followed by 50°C 70%RH for 6h with salt spraying. Tests have been conducted in a climate chamber, where all laminates were enclosed after setting the temperature and humidity. Dielectric measurements were taken at different time intervals, applying current at sensor electrodes (if a sensor has been embedded) and at copper electrodes (placed at the edge of top and bottom CF layer).

Three different electrochemical techniques (cyclic voltammetry, chronoamperometry and impedance spectroscopy) were employed to test various properties of the composite materials. Cyclic voltammetry measurements were made between a potential range of ±0.1 V. Due to the very low power density associated with these materials a scan rate of 0.01 mV/s was used to obtain the cyclic voltammetry plots. Cyclic voltammetry allows the capacitance of structural power devices to be determined, which can then be used to calculate the energy density. For a typical chronoamperometry measurement the potential is stepped from 0V to 1V for 4000 seconds followed by another step in potential from 1V back to 0V for a further 4000 seconds. Extended times for charging and discharging devices were required due to the high series resistance through the electrolyte. The capacitance CSP, resistances RS and RP were determined by fitting the transient response to a fitting function which was derived from the Randall circuit.

Test cells were examined for their capacity and charge/discharge rates under a variety of conditions to determine their respective energy and power densities. The performance of the cells was also done to understand the dynamics of charge discharge and slow processes such as self-discharge, electrolyte
decay, and morphological changes (electrolyte creep, etc). An important aspect which was also characterised utilising electro-chemical impedance spectroscopy was the equivalent series resistance of the supercapacitors and the need to decrease this parameter as much as possible to improve specific power. Repeated cycling of the cells was used to assess stability of the material. In terms of energy density, Device D performed the best with a value of 1.39 mWh/kg and was followed by Devices B, E and C. In terms of power density, Device D had the highest value of 4.3 mW/kg followed by Devices B, E and H. Device B was the most reliable device and did not suffer from any short circuiting issues. It was envisaged that reinforcements modified with CNTs would show improved performance due to an increase in the electrode surface area. However, this was not reflected in the results.

5.2. WP5.2 Mechanical Properties

5.2.1. Introduction

The aim of WP5.2 was the mechanical characterisation of the structural energy storage devices developed in StorAGE. The mechanical characterisation included the following test methods, details of which are given in Deliverable D5.1. In addition, micromechanical test where also undertaken; pull-out tests to determine the interfacial shear strength (IFSS) and DMTA (-40°C to 160°C) to characterise the dynamic performance.

5.2.2. Main work performed, key findings and highlights of research

An encouraging observation was that once the effect of fibre volume fraction (vf) had been accounted for, the normalised moduli of the composites were relatively insensitive to the matrix. Under relatively modest loading the softer matrix would not disadvantage the mechanical performance of the material. However, for matrix dominated properties, as anticipated there was a significant drop in performance.

Following mechanical testing, some failed samples were characterised using fractography to understand the composite microstructure. In particular, the glass fibre/carbon fibre ply interface delamination surfaces of the ±45° in-plane shear specimens were exposed to characterise of the matrix morphology, and relate it to that observed in the bulk matrix studies. Overall, in all multifunctional devices examined there was a high degree of heterogeneity in the matrix morphology. In particular, the ionic liquid constituent tended to be dominant at the fibres, whilst in the interstitial sites the structural epoxy dominated. The following observations were based on general trends. Unfortunately, it was apparent that the multifunctional baseline (Device B) had a high degree of voidage at the ply interface, leading to a smooth exposed surface. However, the sites which did exhibit bonding had a porous structure. It should be noted that these pores are not voids, but would have contained ionic liquid. The pores varied in size, from 1 to 10 microns, and did not appear to have been interconnected. The bonding between the fibres and matrix was fairly heterogeneous, with large regions with no mechanical bond (but good ionic conductivity). However, in some regions sheathing of the fibres by the structural component of the matrix was identified. Here it was apparent that there was no direct contact between the glass fibres and the ionic liquid (i.e. pores). Such a morphology would insulate the active electrode (fibres) from the electrolyte if it had developed at the carbon fibres, but perhaps would be preferential at the glass fibre separator.
The addition of CNTs to the fibres (Devices C, D and E) led to enhanced wetting of the matrix to the fibres during fabrication. Firstly consider the carbon fibres with grafted CNTs, with a lithium salt concentration of 2.3 mol/l (Device C). The morphology of the matrix was akin to that of Device B, with a porous structure throughout the matrix. However, in some sites beads of structural matrix were apparent. These were sites at which there had been a higher concentration of the ionic liquid, leading to the structural epoxy having formed isolated beads. Clearly such sites would have poor structural performance, but superior ionic conductivity. Finally, the bonding between the carbon fibres and the matrix was akin to that of the baseline multifunctional, with pores adjacent to the carbon fibres which would facilitate good ionic access.

Next consider the influence of increasing the concentration of the lithium salt to 4.6 mol/l on the composite morphology. The matrix morphology differed from that of the lower lithium salt concentration. In this instance, the matrix was much more heterogeneous, with large ‘islands’ (up to 200 microns in size) containing agglomerations of the bead-like structures. These islands are within a ‘sea’ of structural polymer with very fine pores (order of 1 micron in size). Similarly, the wetting of the carbon fibres by the matrix was more heterogeneous, with large regions dominated by ionic liquid, whilst other areas in which structural epoxy/fibre bonding was present.

Finally, the influence of CNT sizing rather than CNT grafting was characterized by examination of Device E. There were subtle differences in the microstructure. In particular, in some regions close to the fibres the structural matrix had formed an almost skeletal microstructure, with large pores next to the fibres. Interestingly, away from these sites the structural phase was more dominant, with only small, localized pores present.

5.3. WP5.3 Crashworthiness

5.3.1. Introduction

In WP5.3 standard impact and crush tests (both for electrical storage devices and load-bearing materials) were conducted for both uncharged and charged laminates, using thermal imaging to characterise any rapid temperature changes in the laminates during failure. This aspect is critical for automotive structures, since under crash conditions, the material should not undergo sparking or initiate a fire.

5.3.2. Main work performed, key findings and highlights of research

This study involved penetration testing of the STORAGE materials with the aim to understand what happens to the electrical energy originally stored in the charged material during an impact. The multifunctional composite laminate was connected in parallel to a conventional supercapacitor and both devices were charged to store electrical energy. Akin to the nail penetration test standard, a 3 mm diameter steel nail was driven through the laminate, and both the nail and laminate were electrically isolated. As well as measuring the voltage across and the current through the material, the surface temperature of the material was also measured using a thermal imaging camera and any evidence of sparks or combustion were be observed using a high speed camera. The structural power materials used to manufacture the Volvo multifunctional boot lid demonstrator had a benign response to the nail penetration test and to overcharging to 5 V. Most of the energy originally stored in the laminate went to local heating with a 29 °C temperature rise under the worst case conditions tested in this study in which
500 J of energy were stored.

5.4. WP5.4 Ranking of Devices

5.4.1. Introduction

The ranking of the supercapacitor devices were made by comparing the mechanical key properties, such as compression and shear properties, with the electrical key property being power density.

5.4.2. Main work performed, key findings and highlights of research

As was expected, the presence of ionic liquid led to a reduction in the matrix dominated properties (XC), but the fibre dominated properties (EC) seemed unaffected by the introduction of the electrical constituent in the matrix. This was encouraging since stiffness would probably be the most important factor for engineering design. Such an observation will mean a system could be optimized for electrical performance without compromising on mechanical performance.

5.5. Summary of WP5 (Composite Characterisation)

The aim of this work was to characterise critical electrical and mechanical properties of the multifunctional materials, and understand the relationships between these properties and the microstructure and fracture processes in these materials. However, critical to evaluating the mechanical performance was the balance with the electrical properties. This balance led to conflicting microstructures; rigid, solid structures for mechanical performance, whilst porous and non-tortuous structures for ionic conductivity. In summary, WP5 provided an insight into the influence of the different constituents (reinforcements and multifunctional matrices) on the composite electrical and mechanical properties, microstructures and fracture processes. Both the reinforcement type and the matrix formulation had a strong influence on the microstructure. Consequently, understanding how the microstructure influenced the resulting electrical and mechanical properties directed future material refinement and optimisation.

6. WP6 Systems (SICOMP)

6.1. WP6.1 Hybrid Laminate Design

6.1.1. Introduction

In this work package laminate design had been performed, such as how these materials could be used in conjunction with conventional lamina to produce hybrid laminates. The work was led by ICL in collaboration with ETC and SICOMP, and culminated in Deliverable D6.3 “Report on the conceptual design of structural power source materials”.

6.1.2. Main work performed, key findings and highlights of research

A procedure for multi-objective optimisation proposed by Ashby was suggested as an appropriate method
to aid decision making in the materials selection process for structural power source materials where there are a range of solutions, with varying electrical and mechanical performance, for a single problem. The design methodologies outlined within this work package demonstrated the capability to generate a range of possible material configurations suitable for a given design scenario and to subsequently decide the optimum solution based on external factors; cost was used as a particular example. It was therefore proposed that these procedures be employed in the design and assessment of the final demonstrators in WP7.

6.2. WP6.2 Power Management and Connectivity

6.2.1. Introduction

WP6.2 addressed issues regarding connecting the multifunctional material to the component electrical systems. The work in WP6.2 was conducted in concert with work in WP6.3 “Packaging” and the two work packages had completed by the issuing of the Deliverable 6.4 “Report on the connectivity and packaging issues of structural power source materials”. This study highlighted several different approaches to developing an efficient current collector system for structural power devices.

6.2.2. Main work performed, key findings and highlights of research

Lightning strike protection material has been identified as a suitable material for the use as electrical connections. Coating copper mesh with a corrosion resistant ink has been shown to prevent corrosion of the underlying metal and improve the long term stability of the current collector. It has also been shown through various electrochemical measurements that the capacitance can be improved over the current copper tape system that is employed. A reduction in the equivalent series resistance has also been observed in systems utilising LSP by reducing the in-plane resistance through carbon fibre electrodes.

Commercial products (flat cables connectors) have been used to manufacture prototype battery/capacitor connectors. Connectors were moulded into a carbon fibre prepreg (MTM 57 composites from Cytec) together with a copper mesh while a PTFE tape was used to protect the power implants from the epoxy. The effects of heat, pressure, and time on the processing technique were studied and trimming of the cured composite was also investigated. Optimization of the composite processing was pursued toward maximising the mechanical performance. Successful incorporation of flat cable implants into prepreg composite systems was completed allowing further manufacturing of structural composites. The issue of trimming was also considered and this was resolved by making use of a sacrificial connector and then connecting a new one in its place. For further implementation in commercialized structural composites, it is expected that dummy male connectors made of low friction materials such as Teflon® will be used instead, reducing the use of additional protective layers.

6.3. WP6.3 Packaging and Integration

6.3.1. Introduction

In engineering applications it is often necessary to machine laminates including drilling holes for assembly
purposes. The susceptibility of the energy storage laminates to machining was addressed along with the integration of the materials into the final demonstrator in WP6.3.

6.3.2. Main work performed, key findings and highlights of research

Capacitances of the Device B based on chronoamperometry tests were largely insensitive to drilling. The inherent variability was greater than any trend resulting from drilling alone for one sample while the capacitance increased slightly with number of holes for the second sample beyond the inherent variability. Both capacitance and resistance were affected more by ambient conditions. This study concluded that drilling did not negatively affect the capacitance and hence the multifunctional capability. During integration of the supercapacitor in the final demonstrator, some issues regarding the supercapacitor slabs were found shortly before the manufacture of the trunk lid requiring an extra step to ensure that the slabs would not be damaged by the final manufacture. The two working slabs were covered with an extra layer of NIP3075PE from Skultuna flexible. This is a laminate of PP/Aluminium/PET that effectively protects from moisture and oxygen. The edges were sealed with 3M Scotch double sided tape with pressure sensitive adhesive. The single cells were covered with the same layer of NIP3075PE with the addition of a layer of thin Mylar film in between each cell to insulate them from each other.

6.4. WP6.4 Cost and Benefits Modelling and Analysis

6.4.1. Introduction

In this work package assessment of benefits with the new material replacing traditional components was performed, such as how these materials could be used in conjunction with conventional laminate to produce hybrid laminates. The work has been led by ICL was performed in collaboration with ETC and SICOMP. The work culminated in the issuing of the Deliverable D6.1 “Report on the cost/benefits analysis associated with structural power source materials”.

6.4.2. Main work performed, key findings and highlights of research

Weight and volume savings from replacement of existing components (both power sources and structures) was analysed. If the battery material contributes structurally to the overall system, the total system mass, MSYS, can be less than the sum of the individual masses, MS + MB. By this approach, although the structural and electrical performances of the multifunctional battery may be significantly below those of the monofunctional materials, overall system mass savings are possible because the battery performs multiple functions simultaneously.

Performance gains of the multifunctional systems, with respect to system mass were measured by the efficiency index I, defined below, and the requirement for multifunctionality to be more mass efficient than conventional monofunctional devices is that I exceeds unity. Both the structure and the batteries of the conventional system has unity mass. In reality there will also be benefits from reducing the need for joining separate systems, but on the other hand possible disadvantages and issues arising from the need to incorporate a multifunctional material with unconventional processing routes and material properties.
It is possible to add a cost calculation based on the costs for a conventional separated system and a multifunctional system. One proposed approach is based on the respective masses for the same performance of separated and multifunctional system × cost per unit mass. These should be the same types of structure as used in the mass analysis. Taking CS to be the cost per kg for a conventional structure, CB to be the cost per kg for a conventional battery and CM to be the cost per kg for a multifunctional material, the cost for a multifunctional system can be calculated by \( CM = (CS + CB) \frac{[1 + (1 - \Omega_{Sbatt})]}{\Omega_{Ebat}} \).

6.5. WP6.5 Ownership Issues

6.5.1. Introduction

The investigation of ownership centred around two main issues, the legal ownership issues and the practical ownership issues. In the first part, the focus was on the disposal issues of the composite structural power storage materials only, even if other legal issues may exist. The second part dealt with practical issues which affect both manufacturers and users, such as safety, performance in critical conditions, driving range, charging and maintenance. In addition, a summary of the advantages and drawbacks of structural energy storage materials was presented.

6.5.2. Main work performed, key findings and highlights of research

Based on the societal needs expressed in several research report (ERTRAC Road Transport Scenario 2030+ “Road to Implementation”, 2009; European Aeronautics: a vision for 2020, 2001) and on directives from the European Commission concerning vehicle manufacturing and end-of-life (Directive 2006/66/EC of the European Parliament and of the Council, 2006; Directive 2000/53/EC of the European Parliament and of the Council on end-of-life vehicles, 2000), the ownership issues of the use of composite structural power storage materials in electric vehicles were investigated. Clear distinctions have been made to separate the "legal" ownership issues and in-service ownership issues. In the first part, the focus was on the disposal issues of the composite structural power storage materials, the separation process of the different materials, the re-use options and some cost estimation. The second part dealt with practical issues which affected both the manufacturers and the user, such as the safety, the driving range, the charging and the maintenance.

6.6. Summary of WP6 (Systems)

Key engineering and operational issues were addressed, beginning with the identification of a multifunctional design approach, and investigating how to package, integrate and connect the structural power composites within a vehicle structure. These studies demonstrated how lightning strike protection material could improve power density and how machining under controlled conditions would affect the electrical properties. Application of the materials developed in this project would require justification in terms of cost and weight benefits, which were both modelled and analysed. Finally, the legal and practical ownership issues were studied which considered factors including safety, driving range, charging and maintenance.
7. WP7 Demonstrator Development (SICOMP)

7.1. WP7.1 Demonstrator Design

7.1.1. Introduction

To visualize and demonstrate the STORAGE materials, technology demonstrators were designed. Such demonstrators are vital since they provide a focus for the research, and give a vision for future industrial implementation. The chosen types of demonstrators are listed below and are reported in Deliverable D7.1:

- A small scale demonstrator, based on a radio controlled Volvo XC60 model car.
- An adapted plenum cover from a full size Volvo S80. This demonstrator utilised off the shelf lithium ion batteries. The demonstrator functioned as a system demonstrator as to how a multifunctional part may interact in a car system.
- The final demonstrator was a trunk lid for a Volvo S80 incorporating the structural supercapacitor materials developed by ICL and Cytec.

7.1.2. Main work performed, key findings and highlights of research

The chosen basis for the small scale demonstrator was a radio controlled XC60 model car (1:14 scale Volvo approved merchandise). The roof was most suitable component to interchange for a multifunctional laminate since it was reasonably flat and the largest visual surface on the car. Consequently the roof on a model car was measured and used to reverse engineer a CAD model. The Device B supercapacitor material was chosen to use in this demonstrator. The laminate was designed as a double supercapacitor in series employing a stacking sequence [CF/GF/GF/CF/GF/GF/CF].

The second demonstrator (plenum cover) was chosen as the first larger demonstrator of a multifunctional component. The goal of the component was to replace the standard plenum cover, start/stop battery and provide an additional feature of a rally bar. The production part is made from injection moulded plastic. The plenum cover was chosen because it was fairly large and flat part, which therefore made possible to fit the lithium-ion battery cells within this area to provide a multifunctional component.

The structural part of the plenum cover comes from the rally bar function; this is a stiffening rod connected to the front spring towers to provide torsion stiffness to the car, improving the cars handling on the road. The chosen design was to make the outer skins from a CF weave and the rally bar part from a UD fibre covered foam core. Battery placement was based upon geometrical constraints, stemming from the use of an existing part. The batteries were connected in series to achieve total voltage of 13.2V (3.3V per battery). The use of four battery cells stems from the need to replace the 12V needed for the car’s star/stop function.

Material and manufacturing route chosen for the plenum cover were prepregs; 2x2 Twill HS (3K) 0°/90° configuration, MTM57/CF3200-42% RW, and UD MTM57/T700S (12k)-200-40% RW, both supplied by Cytec. The twill weave were chosen for the outer skin parts of the plenum cover and the UD was chosen for the beam parts to give the needed stiffness in the transverse direction of the plenum cover. The beam
The lithium ion batteries chosen for the plenum cover were four EIG 7Ah battery cells with a nominal voltage of 3.3V supplied by ETC. A finite element simulation of the plenum cover was performed in order to ensure that the final component would withstand the loads it will be subjected to simultaneously as it protects the lithium ion battery cells from excessive strains. The main results were that the initial stiffness was 1770 N/mm which fulfils the requirement provided by Volvo (1500 N/mm). This was achieved with single ply skins, one ply on each side of the batteries, and a four layer thickness of UD pre-preg surrounding the foam core beam. The estimated weight reduction for the complete system was between 57-64%.

Regarding the final demonstrator, this used a Volvo S80 (model year 2011) boot lid to demonstrate use of a multifunctional (MF) composite material in a representative automotive component. This part was chosen due to being visible, interchangeable and has stiffness demands suitable for the materials developed in the project. It also provides space internally for thicker laminates and additional wiring. The original part is made of pressed steel sheet (predominantly 0.9mm thick) and comprised a two part outer skin joined above the licence plate ‘scoop-out’. Total weight of the painted steel part was around 13kg.

The demonstrator boot lid was based on a CFRP skin with MF material integrated to serve both as structural reinforcement and electrical power source for lighting the boot space. It was decided to use a simplified geometry of the rear surface which now omits the license plate ‘scoop-out’. The complex inner would not be replicated in the MF demonstrator boot lid but a simplified stiffening system replaced the inner. This enabled mounting on a prototype car whilst maintaining the opening/closing function. An open composite tool based on the simplified geometry has been made by SICOMP. An original steel boot lid was 3D scanned and the geometry modified via CAE. The skin part was laid up in the mould and cured out-of-autoclave. The chosen material system was MTM57/CF3200 2x2 twill weave prepreg, identical to the material system used for the plenum cover. A final ply thickness of 0.26-0.28mm was achieved in the plenum cover although a nominal thickness of 0.3mm has been used here for analysis purposes. FEA showed that a nominal skin thickness of 1.8mm should be sufficient to resist typical operational handling loads. An outer skin of four plies (1.2mm) would be laid up and pre-cured in the mould. Pre-made MF laminates and a foam mask would then be bonded to the skin while in the mould and covered by two additional plies of MTM57/CF3200 (0.6mm). A stiffening structure will be added to the skin and the full assembly post cured before removal from the mould.

Prototype MF laminates produced during the project typically consist of two 0.1mm thick glass fibre separator plies sandwiched between single plies 0.3mm thick woven T300 carbon fabric oriented at ±45° giving a nominal cell thickness of 0.8mm. It was decided to pre-fabricate laminate cells of 200x300mm size. These would be double cells comprising of lightning strike protection (LSP) expanded copper mesh (t=0.05mm) on the surfaces for current collection. Structurally, each unit would consist of three carbon plies and four glass plies. A unit (two cells) should be able to charge/discharge to at least 3V which is the minimum required for white LEDs which will be used for lighting the boot space. Units would be stacked three-fold through the thickness with 0.1mm glass isolators between units and on the surfaces of each slab. This results in a total nominal thickness of 4.6mm. Six slabs will be placed with 20mm gaps which will be filled by a foam mask. Hence a total of thirty six cells would be incorporated into the design. All double cells (eighteen) would be pre-fabricated and electrically tested prior to being assembled into slabs. The three double cells would be parallel coupled within a stack which would have two terminals penetrating...
through the outer glass insulating ply. Thus a total of twelve terminal points will have to penetrate through the two inner skin plies. A scaled down version of the L-shaped connectors used on the plenum cover were be used for this purpose. The six slabs would be parallel connected with conventional wiring on the inner boot lid surface; a whole slab could easily be disconnected if a fault had developed.

The simplified stiffening structure consisted of a foam core bonded to the inner skin. Four plies of MTM57/CF3200 fabric will be draped over the core thus forming omega sections with a nominal wall thickness of 1.2mm. The profile height was 10mm at the hinge points and 12mm at the bottom lip with a 100mm fillet radius at the transition from the horizontal top part to the vertical rear part. These dimensions were transferred in rough form from the original steel boot lid. Apart from providing general stiffness to the boot lid, the stiffeners form fixing points for hinges and a lock catch.

An FE model was set up based on the CAD generated skin and the simplified stiffener structure added in Simulia Abaqus/CAE. The omega stiffener foot was omitted from the model which consisted of 6684 second order shell elements which conform well to complex curved geometry. The mesh consisted predominantly of quads and some triangular elements where necessary. Three load cases were analysed where a 100N nominal point load was applied in various ways: 1) Bending, where a central load was applied to the bottom lip. This resulted in less than 1mm maximum deflection. 2) Indentation, where a load was applied to the central upper skin. The predicted indentation was here around 1.4mm. 3) Torsion, where a couple was applied. This generated deflections in the order of 12mm which were considered to be the critical design case in terms of stiffness. Strength has not been considered in detail as stresses generally were below 100MPa.

The torsion load case was repeated with the skin alone to illustrate how important the stiffener structure was. A significant stiffness increase was achieved by adding the stiffeners and a further 33% increase by adding the MF slabs. This stiffening effect was mainly due to increased spacing between the continuous skin plies. In other words, the MF slab stiffness was not highly critical in this case. The composite boot lid with MF capability was about three times more compliant in torsion than the original steel part. This was thought be acceptable, given that the boot lid would not be subjected to a normal service life. The mass was less than half of the steel part which in principle could be utilised for additional electrical storage capacity but this will not be explored in the demonstrator for cost reasons. On a practical note, the hinge opening force would most likely need tuning to the reduced boot lid mass on the demonstrator vehicle.

The discrete stack design was not optimal from a structural perspective but it did, however, mitigate the risks associated with a fault developing because individual stacks could be disconnected from the system. It also allowed testing of double cells before assembly and finally different device types can be mixed. A mix of MF Device types was proposed where three slabs of Device B and one slab of Device C, D and E respectively. This should not affect any of the manufacturing, structural or electrical assumptions in a negative way. Each cell then had a capacitance of 759mF which gives 854mJ per cell at 1.5V. Hence 36 cells can store 30.7J or 8.51mWh. As an example, an Osram Duris E3 white LED requires between 2.8V-3.2V and emits 7lm at 20mA. This results in 8.5 minutes of burn time if all the stored energy could be utilised. Subject to the actual discharge characteristics, perhaps half of the energy could be utilised. Given that it would be desirable to have more than one LED (7lm), the burn time would be reduced to a couple of minutes. This may, however, be extended somewhat if a voltage booster was employed (also known as a
‘Joule thief’), although these typically have an efficiency of around 80%. For comparison, the existing lighting arrangement consists of two 5W festoon bulbs with a total light output of 90lm (at much higher power). Yet it should be possible to demonstrate the electrical storage function of the boot lid with the chosen number of cells.

Double cells were proposed since it was necessary to supply white LEDs with at least 3V. Here a double cell implies two cells coupled in series which can lead to over voltage in one of the cells. Some form of balancing is commonly needed to prevent this. The simplest form is dissipative balancing with simple resistors but this not very efficient as up to 20% loss of stored energy can be expected. Switched balancing is better as the loss is reduced to less than 10%. In the boot lid demonstrator it would, however, add significant complexity to the laminate manufacture and assembly. While a double-cell appeared to be working in the small scale demonstrator, it is strongly recommended that a prototype double cell was tested prior to manufacture of all the cells for the boot lid demonstrator and the need for voltage balancing established.

7.2. WP7.2 Demonstrator Manufacture

7.2.1. Introduction

Following the design of the technology demonstrators, they were manufactured, the results of which are reported in Deliverable D7.2.

7.2.2. Main work performed, key findings and highlights of research

The laminate for the RC car was fabricated as described in Section 7.1.2. The laminate was cut to size using a diamond saw and the edges were sanded to final finish. The roof laminate was connected electrically by gluing the copper wire cables to the upper and lower surface of the laminate with a conductive epoxy adhesive (Circuit Works conductive epoxy supplied by ELFA, Sweden). The roof was attached to the car with hot glue to ensure easy disassembly if needed. The car was internally wired with a female mono tele mini connector and a push button to close the circuit. The RC controller was made into a charger using the internal 9V battery directly connected to a cable with a male mini tele mono plug as the connector for the car.

The plenum cover was made in three versions. The first version was a non-functional mock up to validate the heat compensation of the mould and the plenum cover geometry in a physical car. The second and third versions were based on the lessons learned on the previous versions. The geometry around the spring tower connections were altered somewhat to produce less differences in height between the different surfaces and hence less complicated geometry to drape. The first version was made with as large pieces of weave as possible to have as few visible seams as possible. However the resulting laminate proved to have poor surface finish in some of the radii (resin pockets and air bubbles). Furthermore, there was some print-through of the batteries through the skin.

The second version was made by pre-curing the first layer before laminating the rest in an attempt to improve the surface properties of the laminate. This was a calculated risk since the thermal shrinkage of
the mould made this approach difficult; some wrinkling of the procured skin had developed. The resulting surface finish was still poor due to the small radii in some corners, hence this approach was not used for the final version. Off-the-shelf batteries were used for this version but proved difficult to position correctly and in the end the positive connector of the battery pack short circuited to the pre-preg skins making this version impossible to mount in a car. The second version showed an improvement on the finish compared to the first one but still there were some print-through from the batteries and some resin pockets and air bubbles at the small radii.

The final version was made using strips of prepreg in all small radii with approximately 10mm overlap to the larger flatter parts. This may not be the best choice from a structural point of view but for this particular case the skins have a more aesthetic function, hence any loss in stiffness and strength can be accepted for better surface finish. Also two layers of prepreg were placed under the battery pack to avoid print through. To aid the placing and insulation of the battery pack it was wet laminated with glass fibre weaves in the same mould as the final product resulting in a well-insulated and easily handled battery pack. Debunking was done sequentially after the first layer, after the battery pack was placed, after the beam core was placed, after the beam was finished, after every fourth layer at the spring tower connection and finally the whole laminate was debulked before curing at 80°C for 12h. The resulting laminate was found to have good surface finish.

The final demonstrator was the trunk lid for a Volvo S80 which contained active laminates using the supercapacitor approach developed at Imperial College London. For the cell fabrication, carbon fabrics were either used as received or modified using the CNT processing methods described in WP2 (Section 2). These were then fabricated into prepregs at Cytec using the multifunctional matrices developed in WP3 (Section 3), as described in detail in Section 4. Following production of the prepregs, these were laminated to make the cells. The tool used to make the cells was a flat steel plate which was covered with a PTFE film leaving a 25 mm gap around the periphery in order to be able to seal the tool. Subsequently the panels were laminated by first laying down the LSP on the tool, followed by a release film to prevent the LSP from being bonded to the carbon layer over its entire length. The carbon, two glass and final carbon fibre layers were then laid up, and finally a further strip of release film and LSP. Subsequently the laminates were bagged and debulked before autoclaving using the following cycle: 2 °C ramp per minute to 120°C with pressure to 90 psi at 5 psi per minute; dwell for 2 hours at 120°C and then cool to 50 °C at 5 °C per minute, venting pressure begins at 80°C.

The double cells were made using a similar procedure to that in the previous paragraph and after trimming to 180x280mm using a diamond coated unserrated circular saw, they were laminated and cured into a slab using GF/MTM57 prepreg as insulating layers. The double cells performed as expected both before and after being processed into a slab, although it was decided to produce single cells for the demonstrator due to significant electrical balancing issues. Subsequent batches of single cells were manufactured at Cytec using the same procedure as just described. A large number of this new batch did, however, exhibit shorting issues and consequently little or no capacitance was achieved. Either edge bridging by carbon fibres or LSP, which has a sharp edge when cut, were suggested as potential causes. Using a guillotine to trim inside the perimeter of the LSP did seem to resolve these shorting issues. Some cells worked prior to but not after the second cure during slab manufacture. This prompted the last batch of cells to be insulated with aluminium foil for moisture protection and mylar film for electrical insulation, all bonded together with
3M double sided tape to avoid any further exposure to curing. It was suspected that ionic liquid could have been absorbed into the MTM57 used with the GF/epoxy concept but this would need further work to verify. Overall, it is puzzling that the prototype slab concept worked consistently while most subsequent cells and slabs suffered badly from short circuiting issues while using the same processing procedure.

Two slabs made with GF/epoxy, one Device B and one Device E, were incorporated into the boot lid. A further two Device B slabs with Al/mylar separators were incorporated resulting in a total of four slabs each containing four single cells. It was found that the electrical terminals were mechanically too weak when formed by cutting the LSP to shape. The chosen solution was to cut all the excess (unbonded) LSP off, scrape off the anticorrosive protection locally and apply copper tape to form terminals. These were insulated individually with adhesive tape (as used in composite processing applications) and were mounted to a template for a consistent finish. The individual insulation enabled disconnection of cells rather than whole slabs when all 32 (2x4x4) terminals are brought through the inner skin.

A mould for the trunk lid was manufactured at Swerea Sicomp using wet lamination. The mould consisted of a first layer of black gel coat followed by layers of carbon fibre weave and finally building the thickness with heavy glass fibre fabrics. The matrix used was a two component epoxy suited for wet lamination (LY113). The outer skin of the trunk lid was manufactured as planned by laying up four layers of MTM57/CF3202 twill prepreg, bagging and curing at 100°C for 3h. Debubking was performed after the first, second and fourth layer. The foam cores needed were cut to size and the aluminium pieces needed for the mounting to the cars hinges were fitted. The complete foam core was bonded into one piece with Araldite 2012. A paste of LY113, silica and glass micro beads was used to glue the foam core to the outer skin and the whole assembly was bagged and allowed to cure overnight. Due to the added size of the slabs from the protective film there was only room to properly fit four multifunctional slabs to the trunk lid. It was also found that the film made it very hard to make a suitable foam core to go around slabs in any reasonable time frame therefore it was decided to just glue the slabs to the outer skin directly with Araldite 2012. Due to the risks of damaging the multifunctional slabs by applying pressure and heat the final two layers were wet laminated without bag rather than the intended pre-pregs. Wet lamination was performed with a 200g/m2 carbon fibre twill weave similar to the style of the prepregs and LY113 was used as the matrix. The inner skin was allowed to cure at room temperature overnight and the final part was demoulded and trimmed to desired size. Finally, the trunk lid was polished and fitted with a chrome trimming and a Volvo S80 decal to add a finishing touch. A custom LED-light was built and fitted to the trunk lid.

The FE model described in Section 7.1.2 was modified to reflect the actual stacking sequence and slab layout as described in the ‘skin’ Section. The slab layout consisted of two slabs in the vertical rear part and two slabs placed in the horizontal part. Only the critical torsion load case was repeated to assess the effect of the changes. It was evident that torsional stiffness has been lost due to the pure 0°/90° stacking sequence when considering the CFRP skin alone. This also affects the stiffness achieved with the stiffeners added and consequently the stiffness with stiffeners and MF slabs included. The torsional stiffness enhancement by adding the four MF slabs is now 7.4% while it was 33% with the original layout of six slabs. The main reason for this large drop in stiffness contribution is explained as follows. In the original six-slab configuration, the four slabs in the horizontal top section covered most of the area and almost connected with the upper transverse stiffener and the relatively sharp edge between top and rear
surfaces. In the four-slab as built configuration, the two slabs in the horizontal top section only covered a small proportion of the surface and much larger areas of monolithic laminate between these and any stiffening features in the boot lid. While the overall torsional stiffness had halved (mainly due to lack of angle plies), the boot lid would still serve its purpose.

7.3. WP7.3 and WP7.4 Demonstrator Testing and Assessment

7.3.1. Introduction

The final stage of the technology demonstration was the assessment of the components, the results of which are presented in Deliverables D7.3. Due to delays in the delivery of materials they had only been tested electrically and not mechanically to ensure that the demonstrators would not be damaged or destroyed. All demonstrators were shown in the PVH reception hall at VCC during the final meeting.

7.3.2. Main work performed, key findings and highlights of research

Firstly considering the small scale demonstrator, for which the clearly visible roof is a direct eye catcher that illustrate the intention of the project to develop multifunctional composites to be used in structural parts of a car. The structural supercapacitor roof was used to power the RC-car’s headlights. The car has been visible in a number of printed articles and videos on the Internet (these are collated and listed in WP8). The car was finished in time for the JEC show 2012 and the roof was still functioning at the date of the final meeting. The RC car had been stored at ambient conditions and had travelled around to a number of different occasions in Sweden, France and the UK (SSF conference in Stockholm, JEC show in Paris and the Imperial Festival Outreach event at Imperial College London). This gives an indication that even without environmental protection the laminates could withstand normal atmospheric conditions.

The plenum cover used commercial battery cells provided by ETC and was successfully mounted in a Volvo S80 in September 2012 and was still functioning without any problems at the time of the final meeting (June 2013). The car had been parked outside exposed to normal weather conditions in Gothenburg when not in operation and no evident problems from this could be found at the end of the project. The plenum cover offered considerable weight savings as compared to the system it had replaced with a weight reduction of 64%.

A cell from the same production batch as the cell used in the plenum cover (EiG, LiFePO4) was subjected to a curing treatment replicating the curing procedure of the composite plenum cover. A capacity test and a hybrid pulse-power capability test (HPPC) was performed before and after the heat treatment and both tests showed no loss in performance.

The trunk lid offered a considerable weight saving as compared to the steel part it was designed to replace. The trunk lid did not reach the same torsional stiffness as the steel counterpart but to achieve this would most likely only add 1-2 kg of material and the weight reduction would still be considerable. Another point to keep in mind is the fact that the trunk lid adds an electrical storage capability that the steel trunk lid does not offer.
Bench tests were performed on the structural supercapacitor laminates of the same type as those used in the trunk lid demonstrator. Multifunctional laminates (Device B) of 100x100 mm in size were subjected to electrical testing at ETC, using a PEC SBT0650 (s/n 10100056) in a climate controlled room held at 20.5 °C. Tests at other temperatures were performed in a climate chamber, Espec SU-241 (s/n 92008095). On arrival the laminates was adjusted by cutting excess LSP to allow for easier handling. To improve electrical contact the remaining LSP, covered with epoxy, was sanded slightly using 800 grain sandpaper. Electrical connection to the test equipment was made using single sided crocodile connectors. The energy measurements were performed at four different temperatures (-30°C, 0°C, 30°C, 50°C) and replicated three times (cycles) on six laminates. Further details of these test protocols are shown in Deliverable D7.3. At the lower temperatures the laminates could not be charged, leading to zero results for those tests. In fact, only a fraction of the performed tests produced non-zero results. The variation between different cells was small. There was a constant increase in energy when going from 0 °C to 30 °C and from 30 °C to 50 °C. However, for the power density, there was a decrease of about 20% when going from 30 °C to 50 °C. The inability to charge at -30 °C and 0 °C may be explained by viscosity changes in the electrolyte. The same phenomenon explains also why the energy storage ability is higher at 50 °C than at 30 °C. A lower viscosity of the electrolyte lowers the resistance and hence makes the resistive losses smaller. For a constant current charge the laminate can therefore run for a longer period of time before reaching end voltage. This supports the theory that the lower temperature causes the laminates to reach a higher voltage.

The power levels at various states of charges showed a slightly logarithmic correlation. This was likely caused by the self-discharge competing with the external circuit. The effect was directly reflected in the voltage of the laminates, during both charge and discharge. The lower powers at 50 °C compared to 30 °C only reflects the difference at different SOC levels. As the capacity was higher at 50 °C normalization to the same absolute capacity would show a different relation. However, the lower power at 100 percent indicates that the laminates keep a higher voltage after charged at 30 °C. The lower resistance at 50°C caused the cells never to reach 1 V before the time limit stopped the charge. Thus, the tests at 50°C would according to some definitions not really be at 100 % SOC.

Life tests were performed on two cells. Cell T13026_8 exhibited smoother behaviour than T13026_7 but both showed high variations and large peaks. Laminate T13026_8 was subjected to nearly 2000 cycles. It is clear that the peaks from the two laminates coincide in time suggesting that there was some external variation causing the behaviour. The large peak at the centre of the graph accounts extends for almost one week. The most apparent explanation would be temperature changes in the ambient air. However, the temperature and humidity was monitored and no deviations were recorded for the time of the test. There was a distance of about three metres from the point of monitoring to the test position which could allow for a local variation at the test which the monitor does not record. At the moment there is no viable explanation for the phenomenon.

However, there was also evidence of high self-discharge, which also increased with voltage. This competed with the charge process and at 30 °C the self-discharge would also occur at a higher rate than at 50 °C because the higher resistance caused a higher voltage to be reached much sooner. However, the highly fluctuating behaviour of the life tests makes it impossible to isolate any degradation. Any change in capacity is by far exceeded by the supposed external variation. The only thing to be concluded is that no
degradation could be found after 2000 cycles.

7.4. Summary of WP7 (Technology Demonstrators)

The project resulted in three demonstrators, one small scale RC car with a supercapacitor roof, one plenum cover with commercial Lithium-ion batteries and one trunk lid with supercapacitor laminates. The tests have revealed that there is still work to do on the electrical performance of the multifunctional materials but have shown that there is great potential for incorporating multifunctional materials and components in vehicle systems with great weight saving as a result (64% for the plenum cover and 60% for the trunk lid). The main benefit of the demonstrators was that they helped in visualising the concept of multifunctionality, which can often be a big hurdle for those unfamiliar with the concept.

Potential Impact:

8. Potential Impact

In this section we report on the socio-economic impact and the wider societal implications achieved by the successful execution of STORAGE.

8.1. Impact on the competitiveness of the proposers

Although we anticipate substantial impact on partner’s competitiveness from the project in a longer perspective, say in 15-20 years, we notice immediate benefits for the partners. Volvo Car Corporation has widened their high-tech profile beyond traffic safety and hybrid drivelines. This has been facilitated by a vast number of publications internationally in the open press. Volvo continuously monitors publications about the company and measures the value of such publications. They reported (orally) to the PC and APC that in May 2011 (merely 14 months after the start of STORAGE) the project had resulted in open press publications (e.g. CNN, New York Times, Ny Teknik, etc.) at a value exceeding 1 Billion SEK (about 110M€). Other partners, as well as the EU framework programme, in the project have also received great attention in the open press; however no analysis of the value of this has been done. For example, Imperial College London has been interviewed by the BBC and Swerea SICOMP has appeared on Reuters TV as a result of the project. As a result the partners have become more attractive as employers for young engineers and scientists.

In addition, Cytec has made them known to Volvo as a potential supplier of composites since they are to employ composites in their future cars. Also, Nanocyl, being a potential leader of nano-reinforcements for composite materials, have made valuable contacts in research and users and widened the potential application of the products and processes.

8.1.1. Direct applications and market prospects

Given the current state of the automotive Sector, this research was very timely and provides a considerable impact to the competitiveness of the proposers as described above. Although the technology did not reach the targeted maturity level, in particular for structural batteries, the realisation of technology
demonstrators up to full scale car components has built a lot of confidence in the technology and generated a deep understanding for the problems that comes with the systems level and industrialisation. It has also provided the composites and car manufacturers Cytec and Volvo with invaluable visibility of their technical capabilities. Furthermore, the project results have clearly shown that the field of nano-scale tailoring of composites is a promising area of research offering exciting opportunities for material development.

Swerea SICOMP has filed patent applications for their invention of carbon fibre batteries, partly developed within STORAGE. The technology, although ultimately aiming for realisation of structural batteries, can be employed in novel micro- and macro-battery concepts. Swerea SICOMP is now in the process to commercialise the technology for a non-structural thin-film battery application. Products with such thin-film batteries from carbon fibres may only be a few years from realisation.

The approach of addressing a combination of structural devices has proven very valuable. Although structural capacitors does not find an obvious application in automotive they may find extensive use in high voltage applications (civil or military) as they can store energy at many thousands Volts before electric breakdown. Also, the development of structural supercapacitors and batteries beyond STORAGE will benefit from technology developed for the other device. For example the short distance between electrodes developed for batteries may provide a route to increase power densities in structural supercapacitors. Also the structural polymer electrolytes developed for supercapacitors can find use in structural batteries. Finally, the possible combination of structural supercapacitors and batteries in hybrid devices arise from their use of common/similar electrolytes and benefits from a combination of reinforcement/electrode architectures on the fibre and laminate scales.

8.1.2. Economic justification

No detailed analysis of the statistics of sales of hybrid cars over the last years has been made. However, in September 2013 Volvo cars reported that to meet the increased demand for their C30 hybrid car they have maximised the output in their factories of the model and they are now pushing their suppliers to increase their capacities to deliver components to further increase the volume of vehicles.

All European car manufacturers currently develop carbon fibre composite cars. This is manifested in the four of EU FP7 projects in the SEAM cluster. In addition, companies outside the SEAM cluster, in particular BMW, Audi and Volvo, all have composite vehicles or components under development. Experience gained by Cytec from collaboration with Volvo is expected to be very valuable to them as they offer car industry their services in this development.

8.2. Contribution to Community societal objectives

The research performed in StorAGE is forecasted to have particular strong influence on the Community societal objectives concerning levels of employment and environment. Also, StorAGE is expected to contribute to increase the quality of life for the European citizens. However, it is too early to measure these effects at this point. Some examples are given below:
8.2.1. Quality of life

With the public demand for road travel continuing to increase in parallel to an increased environmental concern of the European citizens, there is a drive for cleaner and more efficient personal transportation vehicles. To meet this demand StorAGE offers a route for realising lighter and cleaner cars introducing a new type of structural component with dual power storage capability.

These lighter energy dense materials may reduce the operational costs for the car owner. This is realised through reduced fuel-burn and reduced maintenance costs of the non-corroding polymer composites. By this the citizens at-large will save money driving cars equipped with structural power storage components.

8.2.2. Health and safety

Health for European citizens may benefit from the results in StorAGE as they provide a key technology for future zero-emission vehicles. Hence, improved health will result from reduced air-pollution from the surface transportation sector. The benefits will be largest in highly populated areas and in cities, where toll systems can be used in combination promoting low-emission traffic only.

An important design driver for transport and automotive structures is that of crashworthiness; the ability to fail in a controlled manner under the rapid forces associated with collision impacts; i.e. absorbing and dissipating the kinetic energy of the vehicle through controlled fracture of the material. A concern with conventional energy storage devices is that under crash conditions, if the devices are damaged or penetrated, a rapid release of energy may arise. For lithium ion batteries, thermal runaway can develop leading to rapid heating of the device and the potential for release of volatile constituents, in particular from liquid electrolytes. At an ARPA-E workshop where STORAGE representatives gave a keynote lecture on structural energy devices it was identified that the use of solid polymer electrolytes may provide a route for energy storage in the crash zone of future electric vehicles.

8.2.3. Employment

STORAGE has had and will continue to have an impact on many levels of work, ranging from the research and development scientists, material manufacturers (fibre, resins and fabrics), battery manufacturers, design office, component manufacturers and car manufacturer’s final assembly. The project has trained four post-docs and two PhD-students (one of which are to graduate by the end of September 2013) in multifunctional materials. These students and post-docs have by the tasks given to them developed a deeper understanding for interdisciplinary research its obstacles and benefits.

The partners have also been able to widen their activities and improved their positions for the future. For example, Swerea SICOMP has established a new research area – multifunctional composite materials and by this employed researches with expertise in areas not previously considered, i.e. electrochemistry. Other partners have been able to grow faster by employing key staff on the basis of the resources provided by the project, e.g. ETC hiring a young battery expert.

8.2.4. Environment
Via StorAGE environmentally friendly vehicles may be realised by improved variants of the light materials of high strength and stiffness allowing superior structural integrity at the same time as they carry the electric energy for propulsion of the vehicle within. Although the StorAGE materials are still very immature, the undisputable benefits with the developed technology have been proven. Nevertheless, further research is needed to improve and mature the technology for use in future cars.

8.2.5. Gender issues

Two of the four post-docs involved in the project were women and one of the two PhD-students was a woman. Hence, the partners were successful in establishing a balanced project staff with respect to gender when appointing people active in the project.

8.3. Other relevant European or National funded research

ICL have had funding from the Ministry of Defence throughout the execution of the work in SotrAge which has underpinned the research. Similarly, Swerea SICOMP has had funding from the Swedish Agency for Strategic Research.

9. Main Dissemination and Exploitation

9.1. Introduction

INASCO was the exploitation manager of STORAGE, while ICL provided support via Innovations Group. INASCO throughout the duration of project had presented the PRO-GRID platform, a software tool developed that declares for each product/result of the project, its potential and benefits in the short and long term. All partners were provided with the instructions as to how to complete the Exploitation and Dissemination Templates in the beginning of the project.

ICL provided INASCO with a list of organizations and companies that expressed their interest for the project. Vehicles industries, aviation industries (AIRBUS UK), Universities, Institutes of material science etc. are most included into the list, as presented in full at the end of this report.

During the project, templates and queries from the partners were updated and sent to INASCO to be used as input at PROGRID exploitation tool. For each exploitable project result a relevant questionnaire had to be completed in order to declare its potential. A nomograph presenting all exploitable results including those with excellent exploitation potential was produced by PROGRID with the contribution of all partners’ exploitation and dissemination templates.

Small and large scale demonstrators were manufactured, while STORAGE results were presented in the JEC 2012 exhibition.

9.2. STORAGE logo
Within the first months of the project, Imperial introduced to all partners the very impressive and representative logo of the project.

9.3. STORAGE Website

Imperial was also responsible for the demonstration and maintenance of the STORAGE Website page, where all project meetings, reports and results had to be updated and uploaded. The Website was divided into two sections: a public view, which was open to anyone and a private view, where each partner through intranet had an account and a password that was necessary to have access. The public section included a brief summary of STORAGE and some more information about Structural Power Composites so that the viewer to become familiar with the STORAGE concept. Contact information, Partners that were involved in the project as well as publicity results were also included in the public section. The private section covered all aspects of project concerning the consortium (project meetings, agendas, deliverables, reports etc.)

The address of the website is http://www3.imperial.ac.uk/structuralpowerstorage.

9.4. Dissemination and Exploitation Tables

Exploitation and Dissemination Templates from all partners were updated throughout the project period. Other dissemination activities were also performed.

9.5. Industrial seminars, Exhibitions etc.

At the final meeting of STORAGE held in VOLVO cars in Sweden, an exhibition was planned for the dissemination of the project results inside the consortium and other organizations. The most important outcomes of each Work Package were collected together in nine posters which were presented in the exhibition hall of VOLVO facilities. People from VOLVO and had the opportunity to be familiarized with the STORAGE results. An electronic invitation was sent from the Swedish partners to whoever might be interested to attend to the exhibition and WP8 poster included statistics and publicity of project.

9.6. Posters, Leaflets etc.

STORAGE leaflet incorporated the most important outcomes from all work packages. Furthermore, the leaflet was sent electronically to all partners, so they could distributed it widely.

9.7. PROGRID results

All the exploitation tables along with the questionnaires that were filled in for each exploitation result for the time period of M1-M42 were assessed by weighted means by appropriate S/W tool. The exploitation criteria of the questionnaire were the following:

- Short Term The exploitation potential is high after project’s end.
- Medium Term The exploitation potential is high after 0-3 years of project’s end.
- Long Term The exploitation potential is high after 5 years of project’s end.
The SICOMP battery designs have excellent exploitation potential in short, medium and long term after the end of the project, while there are no results with poor exploitation potential.

9.8. Small and Large scale demonstrators

The project resulted in three demonstrators, one small scale RC car with a supercapacitor roof, one plenum cover with commercial Lithium-ion batteries and one trunk lid with supercapacitor laminates. The main benefit of the demonstrators was that they assisted in visualising the concept of multifunctionality, which can often be a big hurdle for those unfamiliar with the concept.

List of Websites:

http://www3.imperial.ac.uk/structuralpowerstorage

Dr Emile Greenhalgh CEng FIMMM
Reader in Composite Materials
RODH 362B, Aeronautics
Imperial College London, SW7 2AZ
Tel +44 (0)20 7594 5070
Email; e.greenhalgh@imperial.ac.uk

http://www3.imperial.ac.uk/people/e.greenhalgh

Related documents

[final1-storage-final-report.pdf]

Last update: 7 August 2014
Record number: 140464

Permalink: https://cordis.europa.eu/project/id/234236/reporting