Summary
Engineering issues have been addressed for a Multifunctional (MF) Carbon Fibre Reinforced Polymer (CFRP) capable of storing electrical energy and carrying mechanical load. The MF material was integrated into a technology demonstrator in the form of a car boot lid where the boot lighting was powered independently of the car main electrical system. Current collection was improved by using a thin copper mesh on the carbon electrodes while hole drilling was found to have a negligible effect on the laminate electrical performance.

1 Introduction
The goal of the Composite Structural Power Storage for Hybrid Vehicles (StorAGE) project is to develop multifunctional materials which have dual functionality, such that they are able to simultaneously store electrical energy and carry mechanical load. The specific energy storage capability and structural performance is continuously being developed, with a current focus on applications in the automobile industry where both weight and energy storage form important considerations during vehicle design. The final goal is a working demonstrator where a car boot lid will be replaced with structural power composite material [1], which poses a number of engineering issues.

Carbon Fibre Reinforced Polymer (CFRP) composites present a way of providing a light weight material with a high strength-to-weight ratio, which can also store electrical charge. In this particular system the carbon fibre layers act as electrodes and the polymer matrix acts as an electrolyte. In order to make the polymer matrix ionically conductive, ionic liquid and lithium salt are added to facilitate ionic transport between the two carbon fibre layers. This configuration essentially behaves like an electric double layer capacitor giving the ability to store energy within a high performance material which can carry mechanical load. Materials with high mechanical strength tend to also be stiff while materials with high ionic conductivity usually consist of mobile ions and are very compliant. The main challenge in developing structural power composites is to achieve a balance of good stiffness and mechanical strength while also having an electrolyte which exhibits good ionic mobility.

One issue that is being faced in this project is that the structural power composite material has a high equivalent series resistance (ESR), which reduces the desired energy and power densities being targeted. Conventional supercapacitors suffer from power loss during charge and discharge cycles. This loss is caused by resistances in electrical contacts, electrodes and electrolyte [2]. It is the sum of these resistances which is known as the ESR and is shown schematically in Fig. 1. The ESR prevents supercapacitors from achieving power densities closer to theoretical limits. Thus, determining how to lower the ESR of supercapacitors is an important part of research and development in the area of supercapacitors.

The specific issues addressed here are the need for a robust and lightweight solution to electrical collection on the laminates which minimises resistive losses. In practical applications it is often necessary to machine laminates including drilling holes for assembly purposes. The susceptibility of the energy storage laminates to machining is also addressed here.
2 Testing

2.1 Laminate configuration

All test panels were produced to a size of 180 mm x 180 mm with a nominal thickness of 0.8 mm, Fig. 1. The lay-up consisted of two 0.1 mm thick glass fibre separator plies sandwiched between single plies of 0.3 mm thick woven T300 carbon fabric oriented at 45°. Panels were manufactured using the resin infusion under flexible tooling (RIFT) method [2-4]. Some material specifications varied between panels used in the different studies, mainly due to further developments being included in the current collection studies while these developments were not deemed necessary for repetition in the machining study.

For the current collection studies a twill weave carbon fabric was used as the electrodes and the resin was prepared using poly (ethylene glycol) diglycidylether (PEGDGE), Triethylenetetramine (TETA) and 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide. TETA acts as a cross linker for the PEGDGE and the ionic liquid provides ionic conductivity through the electrolyte. Both Celgard [5] and ACG style 120 glass fibre were used as separators in different panels. For the machining studies a five harness satin woven carbon fabric was used with a Cytec MTM57 resin.

2.2 Current collection

In the baseline configuration two thin strips of copper with a conductive adhesive backing were attached to each electrode as shown in Fig. 1. For modest energy and power outputs, this solution can meet the requirements for current collection. However, as the systems approach the higher target energy and power densities through further development, a more efficient and longer term solution will be required to ensure low resistive losses. Lightning strike protection (LSP) material was selected as the most suitable alternative. This consists of a woven or expanded foil metallic mesh where the latter was considered here, Fig. 2. Dexmet 1.6EDCU12-100FA was chosen and added about 10% mass to the laminate when both outer carbon electrode surfaces were fully covered. However, when multiple cell stacks are used, this parasitic mass will diminish.

2.2.1 Corrosion

Corrosion is an issue for the metallic mesh when subjected to the electrolyte. As copper corrodes it forms copper oxide which acts as an insulating material and degrades the performance of the overall system by increasing the ESR. A way of passivating copper has been developed using Sun Chemical (Coates) Carbon Ink XZ302-1HV, a conductive ink with anti-corrosive properties. A layer of ink was painted onto the lightning strike material to prevent any corrosion of the copper mesh. Cyclic voltammetry was used to measure the specific capacitance and compare the performance with and without the anti-corrosion ink.

2.2.2 Results

Electrochemical impedance spectroscopy (EIS) measures the dielectric properties of a medium as a function of frequency. It is also an experimental method for characterizing electrochemical systems. This technique measures the impedance of a system over a range of frequencies, and therefore the frequency response of the system, including the energy storage and dissipation properties [6]. Data obtained by EIS is usually expressed graphically in a
Nyquist plot as shown in Fig. 3. Through EIS the ESR of a system can be determined by taking the high frequency intercept. Impedance measurements were made in the frequency range of 0.01 Hz to 200 kHz with an amplitude of 10 mV. The impedance results for Celgard samples are shown in Fig. 3. The device with copper tape connections had an ESR of 0.167 Ω/cm$^2$. Both samples with LSP material were shown to have lower ESR values of 0.908 Ω/cm$^2$ and 0.102 Ω/cm$^2$ for uncoated and coated LSP samples respectively. The higher ESR of the copper tape sample can be attributed to the in-plane resistance through the carbon fibre material. Copper tape connections were only placed on one side of each electrode and there was a resistance associated with the current moving through the carbon fibres which is not as electrically conductive as copper. The ESR values were lower in the case of LSP samples as the copper mesh covers the entire surface of the electrodes and the in-plane resistance through the carbon fibres was kept to a minimum. There is a slight difference in ESR values between coated and uncoated LSP samples which can be attributed to the thin layer of carbon ink on the coated LSP sample.

Chronoamperometry is an electrochemical method in which a step potential is applied and the current is measured as a function of time. The current – time response is comprised of two components: the current due to charging the double layer and the other due to an electron transfer reaction with the electroactive species. Fig. 4 shows the chronoamperometry results of the Celgard system with copper tape, uncoated lightning strike protection and coated lightning strike protection. Samples were held at 0V for 100s, followed by a step potential to 0.1V for a further 100s and finally back to 0V for 100s, using an Ivium-n-Stat potentiostat. At a first glance all three curves look much the same, however by integrating the curves from 200s – 300s the capacitance of each system can be calculated. The calculated capacitances are 78.64, 84.55 and 85.02mF/cm$^2$ for copper tape, uncoated LSP and coated LSP respectively. The capacitance values calculated from chronoamperometry measurements are different from those determined from cyclic voltammetry. The reason for this discrepancy is due to the fact that samples were not charged for a sufficient amount of time to measure the true capacitance as obtained from cyclic voltammetry. This technique was purely used as a way to compare the current-time response for each system. Results show that both samples with the LSP have higher capacitances than the copper tape sample giving further evidence that the use of LSP is preferable to copper tape as a current collector system.

Fig. 3. Nyquist plot of copper tape, uncoated LSP and coated LSP with the associated ESR values.

Fig. 4. Chronoamperometry of celgard systems with copper tape, uncoated LSP and coated LSP.

2.4 Machining

The aim of this study was to determine the effect of drilling on the electrical properties of structural supercapacitors. The key question to be addressed was whether holes drilled into multifunctional materials causes short circuiting or otherwise degrades the electrical performance. To study the effect of drilling on the electrical performance, two
electrical properties were chosen as indicators of the electrical characteristics, namely specific capacitance and resistance. These properties could be measured using chronoamperometry involving the application of a constant voltage until the supercapacitor was charged, followed by a discharge at zero volts (as per the previous section).

2.4.1 Materials, apparatus and procedure

The drilling studies were carried out on multifunctional laminates fabricated using two 5 harness satin weave carbon fibre plies separated by two Style 120 glass fibre plies oriented at ± 45°. The strips were cut to 25 mm x 180 mm leaving the 10 mm wide copper strips at the ends. Additional copper strips were attached over these copper strips, to allow connections to be made to the electrical test equipment via crocodile clips, Fig. 5. Two strips of MF laminate designated Bia1 and Bia4 were made available for testing.

An Ivium-n-Stat potentiostat was used to perform the electrical testing using the charge discharge technique by applying 0 V for 600 s, charging using a step voltage of 0.1 V for 600 s and discharging at 0 V for 600 s. The charge and discharge time was chosen to provide a sufficient time for the laminate to charge/discharge as much as possible while being short enough to allow the tests to be completed in a reasonable timescale. The voltage applied was chosen to be small enough to avoid any permanent changes in electrochemical properties but sufficient to give a measurable change in the current, which was recorded at intervals of 0.1 s.

The lower surface of the laminate was supported by a wooden base and the upper surface of the laminate was covered with a wooden block containing 8 pre-drilled 6mm diameter holes at an 18 mm pitch, i.e. three times the diameter. The strip was clamped between the wooden support blocks and drilled into using a 6mm Gandtrak GT-250 drill bit at a speed of 134 rpm (2.53 m/min), with a controlled feed rate of 0.179 mm/rev using a milling machine, Fig. 6. After each hole was drilled, the strip was tested by carrying out the 600 s chronoamperometry test. The day after the electrical testing of the strip containing all 8 holes, repeat electrical tests were carried out to check the inherent variability of the testing under the worst case conditions with all holes drilled.

2.4.1 Results

A set of chronoamperometry plots before and after drilling each consecutive hole are shown in Fig. 7 for strip Bia1 only. Inspection of the curves showed no appreciable differences in the charge-discharge characteristics from holes 0 (pristine) through to hole 8.

The transient response to charging and discharging was characterised by using the following equation to fit to the charging region of the current versus time plot [2].

\[ I(t) = \frac{V_0}{R_s} \exp\left(-\frac{(t-t_0)/\tau}{\tau}\right) + \frac{V_0}{R_p + R_s} \left(1 - \exp\left(-\frac{(t-t_0)/\tau}{\tau}\right)\right) \]

Where \( R_s, R_p \) and \( \tau \) were the series resistance, parallel resistance and time constants found by minimising the differences between the measured results and the curve fit. The capacitance was then calculated using the equation [2]

\[ C = \frac{\tau (R_s + R_p)}{R_s R_p} \]
The specific capacitance was found by dividing by the remaining area of multifunctional material, taking into account the area removed by drilling.

The calculated specific capacitance values are shown in Fig. 8 for both strips. For strip Bia1, the general trend was for the specific capacitance to increase slightly as additional holes were drilled. The maximum change in the specific capacitance was an increase of 23.9% between the tests with 0 holes and with 7 holes. For strip Bia4, the specific capacitance showed a marked increase after drilling hole numbers 4, 5 and 6 compared to the values for the other holes which appeared to show an approximately linear increase. The maximum change in the specific capacitance was an increase of 40.7% between the tests after 0 holes and 4 holes.

The inherent variability in the results was measured by twice repeating the electrical testing of both strips after all eight holes were drilled. These results are also shown in Fig. 8. For strip Bia1, the first test gave a capacitance of 0.89 mF/cm² and the second and third tests gave capacitances of 0.84 mF/cm² and 0.90 mF/cm²; a difference of 5.6% and 1.1% respectively compared to the original test. For strip Bia4, the first test gave a capacitance of 1.01 mF/cm² and the second test and third tests measured capacitances of 0.96 mF/cm² and 0.99 mF/cm²; differences of 5.0% and 2.0% respectively.

A measure of the resistance which characterised any electrical contact between the carbon fabric electrodes was calculated by taking the value of the parallel resistance $R_p$ from the curve fit to the charge discharge response. If a short circuit was caused by the drilling, then charging the laminate resulted in the current not returning to zero. The calculated resistance values after drilling each hole are shown in Fig. 9. For both strip Bia1 and Bia4. The resistance for strip Bia1 was over 1.80 MΩ cm² for all holes except after drilling hole 7 where it dropped to 1.40 MΩ cm². The resistance of strip Bia4 was above 1.59 MΩ cm² until hole 4 was drilled, where it dropped to 0.92 MΩ cm². And remained between 1.10 MΩ cm² and 1.40 MΩ cm² thereafter. The inherent variability of the resistance was as follows: For Bia1 the first test was 1.83 MΩ cm² and for the
second and third tests 1.62 MΩ cm$^2$ and 1.77 MΩ cm$^2$; differences of 11.5 % and 3.3 % respectively compared to the original test. For strip Bia4 resistance for the first test was 1.24 MΩ cm$^2$ and for the second test and third tests 1.27 MΩ cm$^2$ and 1.37 MΩ cm$^2$; differences of 2.4 % and 10.5 % respectively.

3 Technology demonstrator
Multifunctional panels have been incorporated into a composite variant of a Volvo S80 boot lid. The original part is made of pressed steel sheet (predominantly 0.9 mm thick) and comprises a two part outer skin joined above the licence plate 'scoop-out', Figure 13. The skin is bonded/seam rolled onto a complex inner which provides most of the boot lid stiffness and functionality such as mounting points for hinges, lock catch and stops. It also seals against the car body and carries a wiring loom for e.g. licence plate illumination. The total weight of the painted steel part without accessories is around 13 kg.

3.1 Design
The demonstrator boot lid is based on a CFRP skin with Multifunctional (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'. This has been smoothed out to enable easier incorporation of the MF laminate and simplify skin manufacture, Fig. 10. The complex inner was not replicated in the MF demonstrator boot lid but a simplified stiffening system replaced the inner. This enables mounting on a demonstrator car and maintains the opening/closing function albeit not a weather tight seal. At the time of writing, the demonstrator design had been completed, however, the actual manufacture had yet to take place.

3.1.1 Structure
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 will be laid up in the mould and autoclave cured at 120°C according to the recommended procedure for MTM57 resin. The chosen material system is T300/MTM57 plain woven prepreg with a nominal ply thickness of 0.3mm but a lighter surface ply was laid down first.

FEA has shown that a nominal skin thickness of 1.8 mm is sufficient to resist typical operational handling loads when combined with the MF laminates which add 33 % torsional stiffness, see Section 3.1.3. An outer skin of four plies (1.2 mm nom) was laid up and pre-cured in the mould. Pre-made MF laminates and a foam mask was then bonded to the skin while in the mould and covered by two additional plies of T300/MTM57 (0.6mm nom). A simplified stiffening structure was added to the skin and the full assembly post cured before removal from the mould. The stiffening structure consisted of a foam core bonded to the inner skin.

Fig. 10. CFRP skin with six MF slabs (grey) and Omega stiffeners (red) laid up over a foam core.
Four plies of T300/MTM57 fabric was draped over the core thus forming omega sections with a nominal wall thickness of 1.2 mm, shown in red in Fig. 10. 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.

3.1.2 Multifunctional laminate

Prototype MF laminates produced during the project typically consisted of two 0.1 mm thick glass fibre separator plies sandwiched between 0.3 mm thick single plies of woven T300 carbon fabric oriented at 45° giving a nominal cell thickness of 0.8 mm. The resin out-life is reduced drastically by modifications made to enable multi-functionality i.e. the ability to act as an electrolyte. Hence it was decided to pre-fabricate laminate units of 200 x 300 mm. These were originally specified as double cells to enhance the voltage which could be delivered. However, prototype studies showed that cell imbalance was significant and balancing via resistors was not deemed attractive here. Single cells were thus specified and a simple voltage booster deployed to ensure that a typical white Light Emitting Diode (LED) could be powered. The voltage booster has an efficiency of about 0.8, yet it enables much more of the charge to be used and thus shows a net benefit. The cells comprise lightning strike protection (LSP) expanded copper mesh ($t = 0.05$ mm) on the surfaces for current collection. Structurally, each cell consisted of two carbon plies and four glass plies. A cell should be able to charge/discharge to at least 1 V which is less than the nominal 3 V required for white LEDs which will be used for lighting the boot space. Cells were stacked four-fold through the thickness with 0.1 mm glass isolators between cells and on the surfaces of each slab. This resulted in a total thickness of 4.8 mm including the LSP. Six slabs were placed as illustrated in Fig. 10 with 30 mm gaps which were filled by a foam mask. Hence a total of 24 cells were incorporated into the design.

All cells were pre-fabricated and electrically tested prior to being assembled into slabs where typical 200 x 300 mm slabs with insulated copper tape terminals are shown in Fig. 11. The four cells were parallel coupled within a slab which had two copper tape terminals penetrating through the outer glass insulating ply and were connected to L-shaped connectors bonded to the outer skin as the slabs were bonded in. Slits were cut in the inner skin plies during layup of these. After final cure the six slabs were parallel connected with conventional wiring on the inner boot lid surface. This gives the opportunity to reconfigure the connections and isolate a whole slab should a fault develop.

3.1.3 Structural performance

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 100 N nominal point load was applied in various ways: 1) Bending, where a central load was applied to the bottom lip, Fig. 12 (top). This resulted in less than 1 mm maximum deflection. 2) Indentation, where a load was applied to the central upper skin, Fig. 12 (centre). The predicted indentation was here around 1.4 mm. 3) Torsion, where a load pair was applied in opposite directions, Fig. 12 (bottom). This generated deflections in the order of 12 mm 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 100 MPa.
3.1.4 Electrical performance

The discrete stack design is not optimal from a structural viewpoint but it does mitigate the implications should a fault develop because individual stacks can be disconnected from the system. It also allows testing of cells before assembly and finally different device types can be mixed.

A white LED was used as a light source for the boot lid lighting. White LEDs require around 3 V to function reliably. It was deemed risky to charge the cells beyond 1 V due to the presence of water in the laminates and hence the possibility of electrolysis resulting in cell degradation. To achieve the required voltage and to extend the operation time further, a DC voltage booster was employed, although these typically have an efficiency of around 80% yet a net gain in operation time can be anticipated due to the discharge characteristics of the MF laminate.

4 Concluding remarks

4.1 Current collection

While the power density for the present MF laminate is still below that anticipated in the future, it was shown that improved electrical performance can be achieved by using a distributed current collection system. The voltage limitation due to electrolysis is an issue which needs to be addressed in future work. Here expanded copper mesh, commonly used for lightning strike protection, was integrated into the laminate and formed good contact with the carbon electrodes. This improved the capacitance by lowering the equivalent series resistance relative to that achieved with discreet copper tape terminals. Potential corrosion issues were addressed by applying conductive coating to the copper prior to laminating.

4.2 Machining

Capacitance based on chronoamperometry tests appeared largely insensitive to drilling of the two laminate samples considered here. With the exception of one test, the inherent variability was greater than any trend resulting from drilling alone for one sample (Bia1) while the capacitance increased slightly with number of holes for the
second sample (Bia4) beyond the inherent variability. Both capacitance and resistance were affected significantly by ambient conditions where the effect manifested itself at known stages in the drilling process after the laminate samples had been subjected to changes in ambient conditions. Overall this study concluded that drilling did not affect the capacitance and hence multifunctional capability negatively for the laminates considered here.

4.3 Demonstrator

The design study has shown that adding MF laminates to an automotive composite part can enable electrical energy storage and save weight while maintaining an acceptable stiffness compared to the original steel part. The most important function of the demonstrator is perhaps to showcase the possibilities and issues faced when implementing multifunctional laminates in a real component. Some of these issues include the limited MF slab size which has reduced both the potential electrical storage capacity and structural performance. A discrete configuration is however more flexible from a systems point of view, albeit more time consuming to manufacture and integrate. Given further process development, continuous MF laminates are envisaged which will enable a more conventional layup process. The demonstrator boot lid has shown that it is possible to power a local consumer directly by a representative car component.

Acknowledgements

Research leading to these results has received funding from the European Community Seventh Framework Programme, Grant Agreement Number 234236. Supply of LSP material by Airbus UK is gratefully acknowledged.

References