



Novel high energy density, high reliability capacitors

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Future civil airframes will make much greater use of electrical systems for actuation of ailerons, flaps, rudder, landing gear, together with applications in de-icing, in-flight entertainment and air conditioning. These electrical systems will form part of a fully integrated power optimised aircraft design that is forecast to deliver substantial increases in the overall energy efficiency of the airframe. Consequently, as well as providing propulsion, aeroengines are forecast to generate up to 1MW of electrical power during flight. However, if this power is to be generated efficiently and without large weight penalties, a number of radical step-change technologies are required. One of these is a new reliable, lightweight power capacitor technology for elevated temperature applications. The current generated on-board requires various types of conditioning and manipulation before and during distribution and use. In many of these power systems, electrolytic capacitors are employed currently for various types of power conditioning. While electrolytic capacitors provide unmatched absolute capacitances, they suffer from catastrophic and unpredictable failure, and as power requirements increase, forecast electrolytic capacitor weight and volume will become problematical.

In the automotive sector, low emission electric vehicles make use of supercapacitors to provide short-term energy storage for energy harvested from regenerative braking systems, and the short-term high power discharge for acceleration. Supercapacitors work alongside batteries to provide the required balance of energy density (batteries) and power density (supercapacitors). Current supercapacitors are simple and reliable but offer considerable scope for further improvement. The thrust of the research is to explore novel and scalable manufacturing technologies to (1) combine the lightweight, high dielectric breakdown of polymers with the high dielectric performance (energy storage) capability of ceramics in a nanocomposite film capacitor, and (2) fabricate thin film porous nanostructures for use in improved supercapacitor configurations.

The project consortium brings together a university research group with expertise in capacitor technology and their manufacture (Oxford University, Department of Materials) with the leaders of the IeMRC flagship project on Power Electronics (Nottingham University, Department of Electronic and Electrical Engineering), a major end user (Rolls-Royce plc), a capacitor manufacturer (Norfolk Capacitors Ltd), a materials supplier (Scott Bader) and an industrial test-house (Nanon) in an integrated supply chain approach to increase the technology readiness level (TRL) 1/2 towards system/subsystem model or prototype demonstration in a relevant environment.

Objectives

- To investigate the manufacturability of polymer based nanocomposite and nanostructured porous films for capacitor applications at the near industrial scale.
- To investigate the manufacturability of novel matrix/nanoparticles combinations at the laboratory scale, with migration to large scale manufacture at the project mid-point.
- To undertake performance and reliability testing and to understand performance in terms of manufacturing approaches and microstructural features.
- To advance the technology readiness level towards system/subsystem model or prototype demonstration in a relevant environment.



Industrial relevance

The UK knowledge and manufacturing base for power and supercapacitors is small but strong, and requires additional investment to provide products that compete on performance achieved through innovation and a high intellectual content. Applications of more electric technologies are certain to grow, especially in the critical transport sector where there is increasing demand to reduce damaging emissions. It is essential that the UK remains competitive in the underpinning and enabling, high value added manufacturing technologies. This proposal seeks to make an important contribution to the field in the UK and to provide a foundation for further activities linked with UK industry.

Nanocomposite electrostatic film capacitors

A small scale web coater has been designed and built to mimic the larger facility at Oxford and can deliver in sequence or simultaneously a range of materials to the rotating web by thermal evaporation of metals, deposition of monomers, dc and rf sputtering, and e-beam curing. Both on this equipment and then on the larger scale webcoater, nanocomposite films of melamine containing Ag, Al and Ti based coevaporated and deposited particles have been produced successfully. The Al- and Ti- co-evaporated or reactively sputtered nanoparticles embedded in the melamine had high aspect ratio with dimensions of typically ~10nm in the long direction. The particles underwent internal oxidation to produce a "core and shell" structure. The films have reproducible dielectric constants of up to ~80 at frequencies up to 10kHz.

These values cannot be explained easily by simple composite theories based on the dielectric constant of the constituent materials. Ag nanoparticles did not undergo passivation and these composite films showed no significant dielectric enhancement. Consequently, the core/shell morphology is strongly implicated in dielectric enhancement. Current efforts are focused on reproducing this composite dielectric behaviour in a different polymeric matrix, consistently across and along very large web substrates, and detailed transmission electron microscopy studies of the Ti and Al containing nanoparticles. Spray deposition has focused on suspending barium titanate (BT) nanoparticles (~80nm) mixed with either acrylate monomer in a fugitive organic carrier or perfluoroalkoxy (PFA) particles in water onto a hot glass metallised substrate, and is novel approach developed at Oxford. Optimum conditions for all stages of manufacture have been developed successfully and polymer based nanoparticle films produced reproducibly with a range of BT volume fractions. The dielectric response of the nanocomposite films has been studied using impedance spectroscopy as a function of frequency and temperature, including the dielectric constant, dielectric loss and dielectric strength. These films have shown extremely exciting results that exceed comparable studies in the literature and indicate an energy storage capability of $>1.8\text{Jcm}^{-3}$

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Nanostructured porous supercapacitor electrode films

We have discovered that our spray deposition route for electrostatic capacitor composite films can be used to produce successfully supercapacitor electrodes based on meso porous entangled single and multiwall carbon nanotubes. This work has made very rapid progress and has recently been accelerated further through a separate DSTL/MoD MAST award to scale up the manufacturing equipment. The particular benefit of our approach is that it can produce thin film electrodes (a few microns) over large areas, free from binders that are usually required for much thicker meso porous graphite electrodes currently made by a hot pressing/slicing route. The addition of pseudo-capacitive nanoparticles into the nanotube electrodes to boost performance has been studied for Sn, Fe₃O₄, Fe₂O₃ in a range of volume fractions and morphologies, and provided power and energy density performance competitive with or exceeding the best in the literature. For both routes and type of capacitor, effort is now concentrated on achieving reproducible performance over areas ($>1\text{m}^2$) so that the flexible films can be packaged into commercially relevant capacitor formats for further testing. So far, we have published four journal papers, two are currently under review and two papers will be presented at the MRS Fall Meeting 2009, Boston.