Composites: Part A 46 (2013) 96–107

Contents lists available at SciVerse ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Structural composite supercapacitors

Natasha Shirshova [a], Hui Qian [a,d], Milo S.P. Shaffer [b,d], Joachim H.G. Steinke [b], Emile S. Greenhalgh [c,d,*], Paul T. Curtis [d,e], Anthony Kucernak [b], Alexander Bismarck [a,d]

[a] Department of Chemical Engineering, Polymer and Composite Engineering (PaCE) Group, Imperial College London, SW7 2AZ, UK
[b] Department of Chemistry, Imperial College London, SW7 2AZ, UK
[c] Aeronautics Department, Imperial College London, SW7 2AZ, UK
[d] The Composites Centre, Imperial College London, SW7 2AZ, UK
[e] Physical Sciences Department, Dstl, Salisbury SP4 0JQ, UK

ARTICLE INFO

Article history:
Received 16 May 2012
Received in revised form 10 October 2012
Accepted 13 October 2012
Available online 5 November 2012

Keywords:
A. Polymer–matrix composites (PMCs)
B. Electrical properties
D. Mechanical testing

ABSTRACT

This paper presents the development of multifunctional materials that perform a structural role whilst simultaneously storing electrical energy as a supercapacitor. Two structural carbon fibre woven electrodes were separated by a woven glass fibre layer, and infused with a multifunctional polymer electrolyte. Following characterisation of electrochemical and compressive performance, working structural supercapacitor prototypes were demonstrated. Since the relative mechanical and electrical demands are application specific, an optimisation methodology is proposed. Multifunctional composites were achieved, which had compressive moduli of up to 39 GPa and capacitances of up to 52 mF g^{-1}.

1. Introduction

1.1. Background and motivation

Weight and volume are at a premium on many structures and, in such applications, any material that does not contribute to the load-carrying capacity of a component is structurally parasitic. Current engineering design is increasingly sophisticated, requiring more efficient material utilisation; sub-system mass and volume are crucial application determinants. For example, consider a mobile phone that consists of structural materials, communication devices, sensors and power sources; the total volume (or weight) is limited and, therefore, compromises are made on parameters such as range, operating time and durability. Other examples include aircraft structures and electric vehicles that are required to maximise mechanical performance whilst minimising total structural weight. The conventional approach to system design pursues optimisation of the individual components often through the use of materials with improved specific properties. The alternative is to formulate multifunctional materials that can perform two or more functions simultaneously. Such materials could offer significant savings in system level mass and volume or performance benefits such as improved durability or redundancy. This design approach is in its infancy and faces significant design and material synthesis challenges [1], requiring the combination of disparate and often cross-cutting phenomena. This paper introduces a new multifunctional composite material that can simultaneously carry mechanical loads whilst storing (and delivering) electrical energy. Although at a very early stage, by adapting fibre reinforced composite structures to also store electrical energy, considerable weight or volume savings could be achieved in the future. Carbon fibre composites are an attractive starting point as carbon is commonly used both for electrodes and as high performance structural reinforcement. Although different forms of carbon are used, there is an opportunity to unify these roles with appropriate fibre modification. Similarly, polymers can be used both as a structural matrix and as an electrolyte; however, performing both roles simultaneously requires careful redesign.

Conventional approaches to electrical energy storage include batteries, (super)capacitors and dielectric capacitors. Batteries possess high energy density but modest power density due to the relatively slow kinetics of the redox processes involved. Dielectric capacitors offer limited energy density but high power density as only electrons are transported during charge/discharge. The focus of the research reported here is on supercapacitors, which provide a compromise between batteries and dielectric capacitors. These devices typically have energy and power densities of 5 Wh kg^{-1} and 0.2–10 kW kg^{-1}, respectively [2].

Double layer supercapacitors avoid solid state redox reactions, as charge is instead collected at high surface area electrodes. The

* Corresponding author at: Aeronautics Department, Imperial College London, SW7 2AZ, UK. Tel.: +44 (0)20 7 5945070.
E-mail address: e.greenhalgh@imperial.ac.uk (E.S. Greenhalgh).

1359-835X/$ - see front matter
http://dx.doi.org/10.1016/j.compositesa.2012.10.007

electrical performance of supercapacitors makes them desirable as short term storage and high power density energy sources. In particular, they are useful for load-levelling applications; when used in conjunction with a battery, they provide for peak power demands that cannot be supplied efficiently by the battery. Substantial improvements in battery life have been reported using this strategy [3]. Supercapacitors consist of two electrodes, a separator and an electrolyte [4]. The two electrodes, usually made of activated carbon to provide a high surface area, are separated by a layer that is ionically-conducting but electronically insulating. The energy is stored by the accumulation of charges at the boundary layer between electrode and electrolyte; the nanometre separation of the charges gives rise to high capacitance. The amount of stored energy is a function of the available electrode surface, the size and concentration of the ions and the electrolyte stability to oxidation and reduction; the latter limits the voltage difference between the two electrodes to a few volts (typically 4 V).

Multifunctional materials and structures, in general, have been widely studied and were reviewed by Gibson [5]. Two configurations have been pursued in order to simultaneously carry mechanical load and store electrical energy. The *multifunctional structural* approach packages distinct constituent components together to minimise mass or volume; for example, embedding or even printing thin batteries into a composite laminate such that the mechanical stress on the battery is negligible [5]. Researchers have demonstrated improvements in performance, but such an approach is perhaps limited and presents a number of practical challenges such as delamination at the device/composite interfaces and restrictions in processing conditions. A more challenging, but potentially more beneficial approach, is to synthesise a truly *multifunctional material*, in which the constituents simultaneously and synergistically undertake two roles; electrical energy storage and structural performance. Polymer composites have now reached a level of maturity at which adventurous material configurations can be considered. Furthermore, the laminated architecture of fibre composites, at a fundamental level, mirrors the electrode configuration of many current electrical storage devices. Carlson et al. [6] and Lin [7] have demonstrated structural dielectric capacitors whilst Wetzel [1,8,11], Hucker [12] and Liu et al. [13] have developed structural batteries. The multifunctional electrolyte is perhaps the most challenging aspect of this class of materials, since it must provide both mechanical robustness and allow ion diffusion. Various approaches have been taken [8], including polymerised vinyl ester derivatives of poly(ethylene glycol) (PEG) in which lithium trifluoromethanesulfonate was dissolved. It should be noted that electrolyte developments for structural batteries can also be pertinent to structural supercapacitors, although requirements are slightly different. However, structural supercapacitors have not yet been studied significantly, other than an initial assessment in collaboration with ARL [9], utilising the original concept developed by the authors [10]; in that work, the resulting electrical and mechanical properties were poor, particularly limited by modest reinforcement surface areas, delamination issues and the low stiffness of the electrolyte matrices. As with conventional supercapacitors, increasing the surface area of the reinforcement was recognised as essential for achieving high electrical capacitance [9].

1.2. Aims of research

The study reported here demonstrates a carbon fibre reinforced polymer composite, which can act as a supercapacitor whilst sustaining mechanical loads. This investigation compares the electrical and mechanical properties of different matrix formulations for structural supercapacitors. In particular, it explores the effects of enhanced reinforcement surface area, which is expected to play a key role in improving energy density. Polymer composites offer a variety of architectures for multifunctional materials which have different processing implications and ionic diffusion distances, and hence potential performance. The embodiment described here is a laminated architecture which conveniently maps onto the electrode sequence of a supercapacitor using electrically conducting carbon fibre weaves as electrodes and glass fibre weaves as separators (Fig. 1). Ions thus migrate from and through the electrolyte matrix and accumulate at the carbon fibre surfaces.

To achieve multifunctionality, the two constituents need to have additional properties over those associated with conventional structural composites. Firstly, the reinforcement (carbon fibre) is not only required to have excellent stiffness and strength but also a high (electrochemical) surface area to enhance electrical energy storage; the amount of charge stored is generally proportional to the specific surface area of the electrode [14]. For the multifunctional matrix, there are conflicting requirements; it must be compliant enough to allow ions to diffuse but stiff enough to ensure efficient load transfer and lateral support to the fibres. The latter is vital to inhibit failure modes such as fibre microbuckling [15]. Finally, the interface between the fibres and matrix is critical to the performance of the multifunctional composite. The interfacial strength controls delamination resistance and consequently the damage tolerance [15]. However, it is within this interface that the energy can be stored in the form of the electrical double layer around the fibres. The work reported here does not profess to offer the optimal solution to these considerable challenges, but to be a first step in formulating a novel material configuration.

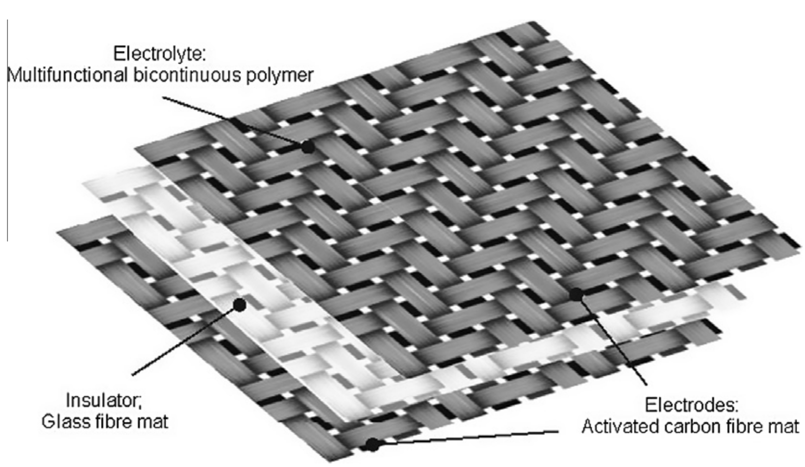

Fig. 1. Illustration of configuration for the structural supercapacitor.