



## Research Paper

# Investigations of Activated Carbon Fabric-based Supercapacitors with Different Interlayers via Experiments and Modelling of Electrochemical Processes of Different Timescales



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## ABSTRACT

This study includes a novel approach of applying an equivalent electric circuit model of two resistors and three constant phase elements (CPEs) to the galvanostatic charge-discharge of supercapacitors which provides virtual monitoring of the electrochemical processes taking place in parallel at different timescales and offers remarkable insights into the coexistence composition and cascade of such processes during the charge-discharge of cells at different current densities. This modelling method has been applied to analyse the performance of high energy density supercapacitors based on a microporous, phenolic-derived, activated carbon fabric (ACF) with different interlayers with the current collector (CC). Associated experimental studies deal with the challenge of overcoming the high contact resistance between the ACF and the current collector (CC) by employing innovative interlayers containing conductive features or structures to fill or bridge the interface gaps between the ACF fibers and the CC foil and the pores of the activated carbon (AC) fiber surface. Such interlayers involve tree-like microstructures of carbon black nanoparticles or deflocculated graphite platelets or multiwall carbon nanotubes (MWCNTs) deposited electrophoretically on the aluminium foil and the ACF. The use of PEDOT:PSS binder in such interlayer raises performance to maximum 44 Wh/kg and 9 kW/kg for electrolyte 1.5 M TEABF<sub>4</sub>/AN. These are further raised by 17% and 13%, respectively, using electrolyte 1.5 M SBPBF<sub>4</sub>/AN, and by 19% (both) using a thin polyolefinic separator against the thicker, cellulose-based separator.

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## 1. Introduction

Supercapacitors and other energy storage devices based on porous carbon fabrics have been of particular interest in recent years for the possibility of incorporating them in cloths and fabric accessories for wearable electronics [1–5], in structural energy storage due to the continuous fabric structure [6–8], and in energy storage curved surfaces due to the flexible nature of woven and knitted fabrics with single and double-curvature drapeability [9,10] and ability to conform onto complex-shaped, curvilinear surfaces [7]. A major advantage of supercapacitors based on activated carbon fabrics (ACF) against supercapacitors based on activated carbon (AC) coatings is that the polymer binder between particles in coatings may cover the micropores of carbon particles, drastically reducing their specific pore surface area (BET) [11], whereas the woven or knitted fabrics are self-supported 3d

structures that do not require any binder for their structural integrity.

On the other hand, we have found out that the lack of binder creates huge contact problems between a highly porous carbon fabric and the current collector which make it a real challenge for any device to behave as a supercapacitor, especially large scale devices for which is very difficult to maintain homogeneously good contact for a large interfacial area. This was realised early in the development of highly microporous ACFs and during the efforts of incorporating them in electrochemical double layer capacitors (EDLCs). Various solutions have been proposed in the literature which have resulted in small supercapacitors with still relatively high contact resistance. Aluminium current collector was plasma sprayed on one side of the ACF and the so modified electrodes were used to fabricate very small EDLC disc cells of 5 mm with  $R_{CT} = 5\text{--}20\text{ ohm}$  [12] or larger EDLC disc cells of 20 cm<sup>2</sup> with  $R_{CT} = 0.85\text{ ohm}$  [13] equivalent to  $R_{CT} = 4.25\text{ ohm}$  for disc cells of 4 cm<sup>2</sup> as used in the present study. A hybrid ACF-current collector was fabricated with yarns consisting of twisted phenolic-derived activated carbon fibers (Kynol) and titanium or aluminium wires; small EDLC

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disc-shaped cells of 10 mm diameter had  $R_{CT} = 0.8 \text{ ohm}$  [12]. Hu and Wang [14] used ACF electrodes pasted with a conductive graphite paste forming an interlayer between the ACF electrode and a graphite substrate current collector and they optimised this conductive interlayer at 40 wt% PVDF; however, they found that such high content of PVDF blocked the pores of the ACF electrode and acted as insulator. Therefore, the present study has devised interlayers with conductive structures to fill the gaps between the ACF electrode and the current collector foil without the inconvenience of an insulating binder blocking the micropores of ACF.

ACFs have been manufactured from polymer precursor-based fabrics, such as regenerated cellulose (rayon or viscose fiber fabrics), poly-acrylonitrile (PAN), pitch or phenolic resins [15,16]. Depending on the particular polymer precursor, carbonisation and activation treatment, ACFs can reach different maximum BET and pore size distributions. Cellulose-derived AC fibers can reach a BET of 1450 to 2500  $\text{m}^2 \text{g}^{-1}$  [17,18] with bimodal pore size distributions below and above 1 nm pore size [19,20]. PAN-derived AC fibers reach a BET of 800 to 1000  $\text{m}^2 \text{g}^{-1}$  [17,18]. Pitch-derived fibers reach a BET of 400–1500  $\text{m}^2 \text{g}^{-1}$  [21]. Phenolic-derived ACFs reach a BET of 2500  $\text{m}^2 \text{g}^{-1}$  with narrow pore size distribution of pore width around 2 nm [22,23]. Recently, AC fiber was produced from graphene oxide dispersion exhibiting a BET of 1476  $\text{m}^2 \text{g}^{-1}$  with a pore size distribution around 1 nm [24]. In general, ACFs are considered to have a large proportion of micropores (around 1 nm) whereas granular AC powder has a large proportion of macro- and meso-pores [21].

The present study has been oriented to medium and high voltage applications of supercapacitors, which led us to investigate organic electrolytes. Aqueous electrolytes traditionally reach a maximum operating voltage of 1.1 V although this has been raised to 2 V by charge balancing the active electrode masses [25] or with  $\text{Mn}_3\text{O}_4$ /reduced graphene oxide electrode in asymmetric supercapacitor [26], and even to 2.4 V by using a Na-doped  $\text{MnO}_2$  electrode in an asymmetric supercapacitor [27]. Considering organic electrolytes with relatively larger ions than those of inorganic salts, a phenolic-derived ACF with high BET (2000  $\text{m}^2 \text{g}^{-1}$ ) and relatively large micropores around 2 nm slit width [22,23] has been selected as the active electrode in this paper. Organic electrolytes include TEABF<sub>4</sub> dissolved in propylene carbonate (PC) or in acrylonitrile (AN) with an operating voltage window up to 3 V [28,29] from which AN will be preferred as the solvent in this study as it has a smaller molecule and lower viscosity than PC and would contribute to high ion mobility and packing density, and also has lower density than PC [30]. SBPBF<sub>4</sub> has even smaller cation size than TEABF<sub>4</sub> [31,32] and will be investigated as an alternative organic electrolyte.

The aim of this study is to develop high energy density symmetric EDLC supercapacitors based on activated carbon fabrics (ACFs) for medium or high voltage applications. The first challenge was to eliminate the contact resistance with the current collector foil by researching different innovative interlayers with conductive features or structures that would bridge the interface gap and also the micropores of the ACF fibers. The next step was to investigate the two different organic liquid electrolytes, TEABF<sub>4</sub> in AN and SBPBF<sub>4</sub> in AN, of different relation of electrolyte ion versus electrode pore size. The final stage of development of the ACF-based supercapacitors involved an investigation between different types of separator: two thin, polyolefin porous separators and a thicker, cellulose-based paper separator. The second part of this study comprised the analysis of the cascade of electrochemical processes taking place at different timescales in the charge and discharge of the investigated types of supercapacitor cells at different rates via computer simulations. An equivalent electric circuit (EEC) model of resistors and constant phase elements (CPEs) was first fitted to the electrochemical impedance

spectroscopy data for each type of supercapacitor cell. Then a novel procedure was developed for the application of this model in computer simulations of the galvanostatic charge-discharge tests at different current densities and the virtual monitoring of the overall voltage profile against time (predictions) as well as the time-profiles of the voltage difference across each component of the EEC representing a corresponding type of electrochemical process. In this manner, this paper contains a unique analysis and discussion of different features of the investigated types of ACF-based supercapacitor cells in this study and illustrates their quantitative relation to electrochemical processes of different timescales and the relative weighting of these processes at different rates of charge-discharge (i.e. at different current densities or at different power densities of the supercapacitors).

## 2. Materials and Experimental Procedures

The activated carbon fabric (ACF) was ACC-507-20 supplied by Kynol Europa GmbH. It was a plain woven fabric, phenolic-derived and activated to a BET specific pore surface area of 2000  $\text{m}^2 \text{g}^{-1}$ , and had an average areal density of 8.5  $\text{mg cm}^{-2}$  and a nominal fabric thickness of 0.5 mm. ACC-507-20 fibers have been reported [22,23] to have a narrow pore size distribution of pore half-widths less than 1.5 nm, averaging at 1.1 nm. ACF strips of 4  $\text{cm}^2$  area ( $2 \times 2 \text{ cm}$ ) were cut for the supercapacitor test cells, using a guillotine. The ACF strips were subjected to a pre-treatment process whereby each strip was dipped into a beaker containing acetonitrile (AN) (HPLC-grade, Fischer Scientific UK), until it was fully wet, then placed on a hotplate at 120 °C to evaporate the AN. This was repeated three consecutive times for each strip. Then, the ACF strips were mounted inside a fan convection oven at 120 °C for 4 hours. Thereafter, the ACF strips were ready for assembly in the EDLC cell fabrication.

The EDLC cells fabricated and tested in this study were of 4  $\text{cm}^2$  area and symmetric consisting of aluminium foil-based current collectors as the two outer layers, an ACF layer adjacent to each current collector with or without an interlayer, and a porous separator membrane in the middle plane of the cell. The cell was then infused with the electrolyte. Two different electrolytes were investigated in association with the ACC-507-20 fabric of this study: 1.5 M TEABF<sub>4</sub> (tetraethyl ammonium tetrafluoroborate) in AN (acetonitrile) (>99% purity from Sigma Aldrich; anhydrous with >99.8% purity from Alfa Aesar Ltd, respectively); 1.5 M SBPBF<sub>4</sub> (spiro-(1,1')-bipyrrolidinium tetrafluoroborate) in AN (Japan Carlit Co., Ltd; anhydrous with >99.8% purity from Alfa Aesar Ltd, respectively). All EDLC cells were tested at room temperature (RT), 25 °C. Three different separators were investigated in this study: a cellulose-based paper separator NKK TF4060 (NKK – Nippon Kodoshi Corp) of 60  $\mu\text{m}$  thickness; a polyolefin-based, PP (polypropylene) monolayer micro-porous membrane Celgard 2500 (Celgard LLC) of 25  $\mu\text{m}$  thickness; a polyolefin-based, PP (polypropylene) coated with a surfactant, micro-porous membrane Celgard 3501 (Celgard LLC) of 25  $\mu\text{m}$  thickness.

Plain aluminium foil, used as current collector in bare form (denoted as Nol) or coated with an interlayer, was of >99.3% purity and H18 hardness (purchased from MTI Corporation with product code “EQ-BCAF-15U”). I1 interlayer involved the coating of Al foil with a thin layer of acetylene carbon black (CB) (from Alfa Aesar with specifications of average particle size of 42 nm, specific surface area of 75  $\text{m}^2 \text{g}^{-1}$  and bulk density in the range of 170–230  $\text{kg cm}^{-3}$ ) and 10 wt% PVDF (polyvinylidene fluoride) binder ( $M_w = 534,000$ , Sigma Aldrich), where a slurry in NMP (1-methyl-2-pyrrolidinone, anhydrous form, >99.5% purity, Sigma Aldrich) was used for the coating; the current collector-I1 interlayer was then thermally bonded with the ACF under pressure of 50  $\text{g cm}^{-2}$  at 180 °C for 30 min. I2 interlayer involved the coating of Al foil with a

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