SHORT TERM SCIENTIFIC MISSION (STSM)
SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CA17107

STSM title: Development of hybrid solid-state supercapacitors based on AC/TiO2 cotton fabric electrodes as potential wearable energy storage devices for smart textiles

STSM start and end date: 09/09/2019 to 27/09/2019

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PURPOSE OF THE STSM:

The present proposal has as objective the development of textile-based structures using environmentally friendly materials that can be used to the fabrication of flexible energy storage devices with high energy density, wide operating voltage window and high electrochemical performance. During this STSM, has been designed and produced several textile-based electrodes, made with titanium dioxide (TiO_2), manganese dioxide (MnO_2) nanoparticles, and carbon structures (i.e. carbon black and carbon nanofibers), which were deposited onto cotton woven fabrics that were used as substrates. Thereafter, the prepared flexible electrodes were characterized for electrochemical features by cyclic voltammetry, galvanostatic charge-discharge, electrochemical impedance spectroscopy and analysed separately in three-electrode cell and two-electrode cell configurations (i.e. as a final supercapacitor).

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

100% cotton woven fabric: 14.9 x 20.2 warp x weft yarns linear density (tex), 0.26 mm thickness at 18 Pa was used as base-substrate of the electrodes. Conductive electrodes were produced at first step. The cotton woven fabric was first discoloured. An ink was prepared by dissolving carboxymethylcellulose sodium salt (Aldrich) and sodium dodecilbenzensulfonate (Tokyo chemical industry). Then, carbon black (CB) shawinigan acetylene black was added to the solution. This ink was spread onto each side of the cotton fabric by screen-printing. These samples were called as CWF@CB.

After this first deposition, two different types of electrodes (positive and negative) were produced. The TiO_2-based active layers for negative electrodes were prepared by spreading onto the CWF@CB samples a slurry consisting of: 70 wt % of TiO_2 (Aeroxide® P90), 10 wt % of CB, 10 wt % of Pyrograf III PR 24 LHT XT carbon nanofibers (CNF), 10 wt % of PVDF solution in DMAc. The sample was dried at 70 °C for 24 hours, after which, a further heat treatment of 1 hour at 120 °C followed by 20 minutes at 160 °C, was carried out. This process was repeated two times. At the end, the sample was hot-pressed at 160 °C and 20 bar during 10 minutes with the aim of decreasing their total thickness. The MnO_2-based active layers for positive electrodes were prepared similarly by spreading onto the CWF@CB samples a slurry consisting of: 70 wt % of MnO_2 (prepared previously by a simple co-precipitation method based on chemical reaction in aqueous solution), 10 wt % of CB, 10 wt % of CNF, and 10 wt % of PVDF solution in DMAc. The sample was dried at 70 °C for 24 hours, after which, a further heat treatment of 1 hour at 120 °C followed by 20 minutes at 160 °C, was carried out. These two types of MnO_2 and TiO_2 based electrodes were investigated by three-electrode cell configuration to obtain the first electrochemical characteristics.
The positive (i.e. based on MnO_2) and negative electrodes (i.e. based on TiO_2) were then assembled with sodium exchanged Aquivion®E87-05S membrane in order to study a full supercapacitor (two-electrode cell

configuration) by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), electrochemical impedance spectroscopy (EIS). All electrodes were cut with circular shapes and areas of 2 cm^2, whereas Aquivion®E87-05S membrane (2.5 cm^2) were cut slightly larger than 2 cm^2 to prevent lateral short circuits. All electrodes were impregnated with 1M Na_2SO_4, and before assembling, the Aquivion®E87-05S membrane was exchanged in Na^+ form by treatment with 1M Na_2SO_4 (18 h) under slow stirring. At the end, the loading of active layer for the MnO_2 based electrode (positive electrode) was 3.10 mg cm^{-2}; whereas the loading of active layer for the TiO_2 based electrode (negative electrode) was 7.29 mg cm^{-2}.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The positive and negative electrodes were studied separately in the three-electrode cell configuration through cyclic voltammetry measurements at voltage sweep rate of 5 mV s^{-1}. The results of the test, with data of current converted in specific capacitance, are reported in Fig. 1.

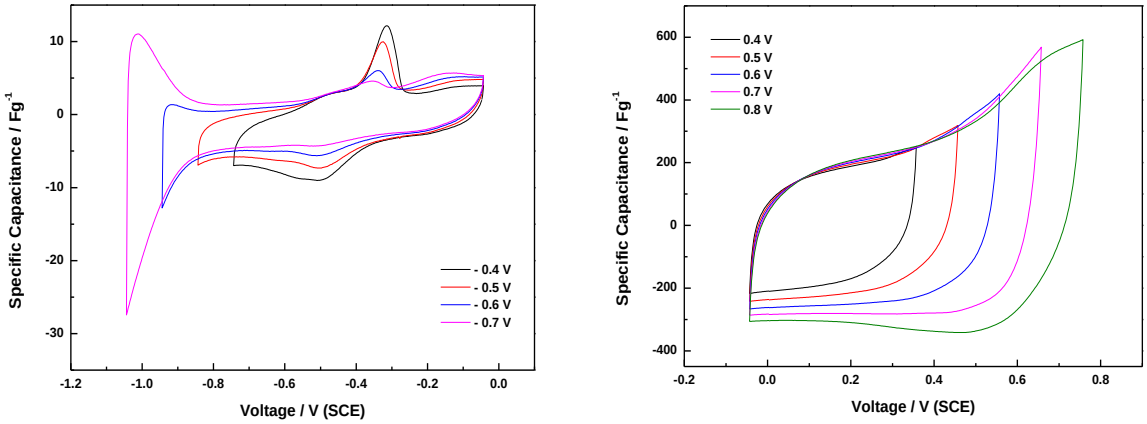

Fig. 1. Comparative voltammograms (CV) of positive MnO_2 based (right plot) and negative TiO_2 based (left plot) electrodes at variable potential ranges and scan rate of 5 mVs^{-1}.

Fig. 2. shows the specific capacitance versus cell voltage, obtained by CV, of the solid-state hybrid SCs at constant voltage sweep rate of 20 mV s^{-1}. The original values of current in CV plots were converted in capacitance per mass one electrode by using the equation C (F g^{-1}) = [(I (A)/dV dt^{-1} (V s^{-1})]/mass capacitor (g)] × 4; where dV/dt is the scan rate and I is the current.

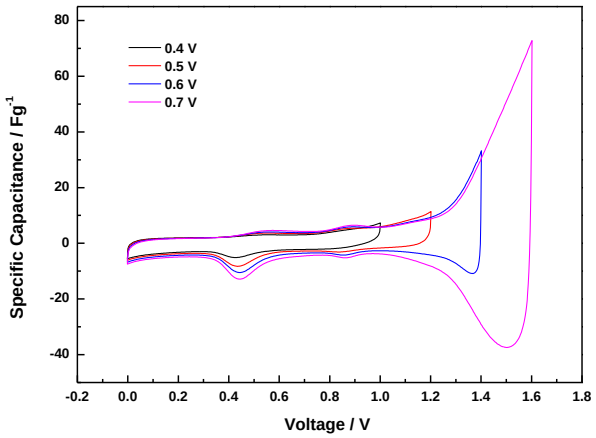

Fig. 2. Specific capacitance versus cell voltage for the hybrid solid-state SC, at variable potential ranges and scan rate of 20 mVs^{-1}.

Outcomes: In summary, a series of different electrical conductive electrodes based on cotton-substrate and metal oxide materials were produced. They were made from low-cost materials and simple methodologies. Besides, the MnO_2 positive showed very high performance (e.g. 300 F g^{-1}), whereas the TiO_2 negative electrodes need further improvements, before that, they can be coupled with a polymer electrolyte and thus allow for the manufacture of excellent flexible energy storage devices.
Though, it is not expected that the results of this STSM can be directly employed for an oral presentation at International Conference and/or a Journal research paper, thanks to the work performed during the STSM further investigation will be developed and a scientific publication is expected to be produced.

Acknowledgements:
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FUTURE COLLABORATIONS (if applicable)

Future collaboration between 2C2T (Portugal) and CNR-ITAE (Italy) will concern the completion of STSM research activities in the development and fabrication of flexible and hybrid supercapacitors based-on cotton textile substrate, MnO_2 and TiO_2 for positive and negative electrodes, respectively. Moreover, further collaboration between 2C2T and CNR-ITAE will be considered for the participation at European funding calls in the areas of functional nanomaterials and smart energy storage devices.