DEVELOPMENT OF MULTIFUNCTIONAL STRUCTURAL ENERGY STORAGE DEVICES USING GRAPHENE NANOPLATELETS

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Abstract

Graphene, a class of two-dimensional allotrope of carbon-based materials, is emerged as exciting novel material that has notable application in various fields. Due to its high specific surface area, good chemical stability and outstanding electrical properties, graphene is one of ideal candidates for next generation storage devices. In the present investigation, various types of hybrid formation electrodes, consisting of graphene nanoplatelets and different weight ratios of MnO_2 particles were fabricated for application to supercapacitors, to achieve higher specific capacitance combined with mechanical robustness. The morphology and thickness of the graphene electrodes were characterized by Scanning Electron Microscopy. Experiments on structural integrity and energy storage capacity of the electrodes were also carried out. Quasi solid-state electrolytes, consisting of different wt% loadings of succinonitrile (SN) as plasticizer and the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF4) entrapped within the structure of copolymer poly vinylidenefluoride-hexafluoropropylene (PVDF-HFP), were prepared to be utilized as ionic conductors in supercapacitors. The ionic liquid concentration varied to investigate the effect on the ionic conductivity of the device while the addition of the plasticizer produced a more compact device. Differential scanning calorimetry (DSC) was used to characterize the thermal stabilities of the electrolytes. DSC studies confirmed that polymer electrolytes remain stable in the same phase over a wide temperature range of -40 to 100 °C. The configuration of supercapacitor started by impregnating carbon fibers with the graphene paste, creating this way composite electrodes. Polymer electrolyte was then applied and solidified between graphene electrodes. A compact supercapacitor was assembled finally by using glass fibers as separator impregnated with electrolyte to avoid contact of the electrodes. The electrochemical behavior of the supercapacitors was evaluated by cyclic voltammetry and galvanostatic charge/discharge. The maximum value of specific capacitance achieved using polymer electrolyte was ~160 F/g. Finally, tensile experiments were performed at ambient conditions to determine the mechanical behavior of the supercapacitors. The results of this study are very promising for the development of materials with high performance in the field of energy storage with applications to wearable electronics.

1. Introduction

The development of polymer fiber composites over decades resulted the application of these materials to a wide range of applications from civil to military and especially to aerospace industry. Their comparative advantages offer the feasibility of more efficient structural design for lighter structures due to their high specific mechanical properties. Also, the manufacturing processes of polymer fiber composites are suitable for the design and production of tailor-made materials with optimum stiffness and strength. The last years, extensive efforts have been consumed on the development of polymer composites with enhanced multifunctionality. Multifunctional composites combine the unique properties of structural fiber composite materials with at least one additional critical functionality. The advantages that occur from the development of multifunctional composites have attracted high research and industry interest over the last years for a variety of applications that demand enhanced mechanical, electrical, electromagnetic, optical, electromagnetic and chemical properties. Nanotechnology contributed an important role on the development of multifunctional composite materials high enhanced properties [1]–[3]. The research on nano-enabled hierarchically multiscale reinforced composites led to the development of materials with high-end integrated technological functionalities such as self-sensing [4]–[6] based on the exploitation of the piezoresistive behavior of nanomaterials. Also, nanotechnology has opened the opportunity of the further research of multifunctional materials with integrated energy functionalities [7]–[12]. The idea of moving the necessary energy devices of a structure into the structure in order to save space and weight for additional energy storage or payload increases the endurance and the capabilities of the mission that the referenced structure is able to conduct. In a wide range of industry applications such as electronics, automotive, UAVs, spaceships, portable and wearable electronics multifunctional structural-power composite materials can be applied to improve their performance in an overall systemic approach.

Carbon nanomaterials and especially carbon nanotubes and graphene nanoparticles have found several applications in the field of nano-enabled composite materials due to their extraordinary properties (mechanical, electrical, thermal etc.). A wide range of multifunctional composites have been developed by the usage of carbon nanomaterials in different forms [18]–[21] and for several different applications such as enhanced fracture toughness [22], [23] electrical [24], [25] and thermal conductivity [26]. In parallel, carbon nanomaterials also exhibit unique properties for their application to energy conversion and storage devices [27] and have attracted wide interest of the research for the development of high performance solar cells, fuel cells, batteries and supercapacitors. Especially, after the discovery of graphene with its ideal properties for energy applications [28], [29], such as high aspect ratio, rich electronic states, high electrical conductivity, high thermal conductivity, large surface area, high chemical resistance and robust mechanical properties scientists have consumed a lot of effort to prove in multiple studies to produce high performance energy devices with graphene. Graphene is a 2D planar nanostructure with thickness of one atom with carbon atoms packed in honeycomb crystal lattice. The structure of graphene consists the basic modular structure of all carbon allotropes (buckyballs, carbon nanotubes, graphite) which widely have been used in the formation of electrodes for energy applications. Graphene monolayer nanosheets and graphene nanoplatelets with few graphene layers due to their structure and their properties are very effective electrode materials for fuel cells, rechargeable batteries and supercapacitors.

In this study, graphene nanoplatelets and metal oxides (MnO_2) with polymer binder (PVDF) have been utilized to form self-standing electrodes in the form of films over a current collector and composite carbon fabric electrodes for supercapacitors. Graphene nanoplatelets in this study serve as a conductive substrate of the double layer and pseudocapacitance mechanism of MnO_2 in order to form a hybrid supercapacitor electrode. The electrodes were tested with liquid electrolyte (KOH) and solid-state polymer electrolyte. The fabrication of graphene/MnO_2-carbon fabric with solid electrolyte was used to form robust supercapacitor devices where can be used as structural energy devices. Carbon fabric in this device serves as the current collector of the system and in parallel the carrier of the mechanical load. The electrochemical performance of the produced electrodes and devices was studied with potentiostatic and galvanostatic techniques (Cyclic Voltammetry and Charge-Discharge). The microstructure of the electrodes observed with Scanning Electron Microscopy (SEM). Finally, tensile tests performed to characterize the structural integrity of these multifunctional composite energy devices.

2. Experimental

2.1. Materials

1-Methyl-2-pyrrolidinone (NMP, ReagentPlus® grade, 99%, Sigma-Aldrich), pellets of poly(vinylidene fluoride) (PVdF, Mw ~180,000, Mn ~71,000, Sigma-Aldrich), graphene nanoplatelets with 8-15nm average thickness (GNPs, 97%, , CheapTubes), activated manganese(IV) oxide powder (MnO_2, , ~85%, <10 μm, Sigma-Aldrich), carbon fabric (plain,160 gr/sqm, FIBERMAX LTD), co-polymer poly(vinylidenefluoride hexafluoropropylene) (PVdF-HFP, Mw ~400,000, Sigma-Aldrich), ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMImBF4, ≥98.0%, Sigma-Aldrich) and succinonitrile (SN, 99%, Sigma-Aldrich), acetone (ACS reagent, ≥99.7%) and glass fabric (280 g/m2, twill weave, R&G Germany) have been used without further purification.

2.2. Preparation of Graphene Nanoplatelet-MnO_2 Electrodes

The slurry preparation was initiated by magnetic stirring of the polymer binder PVDF with NMP solvent, until the complete dissolution. The GNPs and MnO_2 particles were then added, and their dispersion was carried out by sonication until a macroscopically homogeneous mixture was obtained. The mixture was then casted of aluminum substrate and left for drying of the solvent for 3 h. Finally, three compositions of films were prepared as electrodes for supercapacitors, as listed below :

Table 1: List of hybrid MnO_2/GNP electrodes.

Sample Type	*GNP % wt.*	*MnO_2 % wt.*	*PVDF* % wt.
MnO_2-1	68	12	20
MnO_2-2	52	28	20
MnO_2-3	40	40	20

2.3. Preparation of SN-based gel polymer electrolytes

Quasi-solid-state electrolytes of copolymer PVdF-HFP with ionic liquid BMImBF4 and plasticizer SN have been prepared by means of solution mixing method using acetone as solvent. Specifically, 500 mg of PVdF-HFP were separately dissolved in 8 ml acetone under continuous magnetic stirring in sealed glass vessel. Different wt% loadings of SN and IL were prepared in another vessel. Each IL/SN mixture was then mixed with the PVdF-HFP solution and stirred continuously for 5 hours until their complete dissolution. The weight ratio of the PVdF-HFP to IL/SN was kept at 1:4. The electrolytes were finally stored in sealed vessels until their incorporation in supercapacitors.

2.4. Assembly of solid-state supercapacitor cells

Stepwise fabrication of solid-state supercapacitors with different composition of gel polymer electrolytes is illustrated in Figure. In order to get optimum graphene/MnO_2-electrolyte interface, instead of sandwiching a membrane between two carbon electrodes, each electrode was impregnated with electrolyte, while in a low viscosity solution form, before assembling the supercapacitors. Impregnation of fiber composite electrodes was performed by adding a diluted acetone electrolytic solution into porous graphene electrodes using a micropipette. Before the completely evaporation of acetone, a glass fabric was put over the liquid electrolyte solution and impregnated with this. Here, the soaked glass fabric allows the ion movements and separates the electrodes from any danger of undesirable short-circuits. Finally, a drop of electrolytic solution was added before the two identical electrodes were assembled in a planar configuration to form the solid-state cell. In all cases, the supercapacitors active area was 1 cm2 and the active mass of each electrode was 0.6-1.5 mg/cm^2. As a counter electrode in any case was used an electrode which was formed with GNPs and PVDF (80% wt. GNPs and 20% PVDF) without MnO_2. The purpose of the usage of this kind of counter electrode is to use the same conductive substrate in both electrodes. A slurry was formed with GNPs and PVDF and was injected on carbon fabric to the carbon fiber electrode and in the case of film electrodes was tape-casted on aluminum substrate. So, the final formation of the supercapacitor is a non symmetrical supercapacitor with a hybrid GNP/MnO_2 and a GNP electrode.

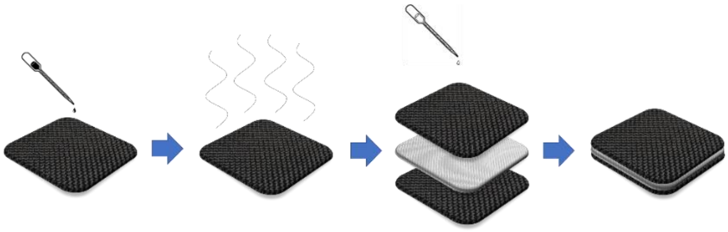

Figure 1: Manufacturing process of carbon fober/GNP/MnO_2 electrodes and assembly of the supercapacitor.

2.5. Measurements

Differential scanning calorimetry (DSC) was used to test the thermal stability of the gel electrolytes. DSC was performed from -80 to 200 oC at a heating rate of 10 oC/min in a static nitrogen atmosphere using DSC 2920 (TA Instruments). The microstructure and morphology of the porous graphene-based composite electrodes was estimated by SEM (LEO SUPRA 35VP). Electrochemical performance of the supercapacitor cells was tested by cyclic voltammetry (CV) and galvanostatic charge-discharge method using an AUTOLAB potentiostat/galvanostat analyzer (PGSTAT302N - High Performance). The electrochemical performance of the liquid state supercapacitor cells was performed in a 3-electrode configuration set-up, using 1M KOH electrolyte. To estimate the capacitive response of the fabricated solid-state supercapacitors with the different compositions of gel electrolytes, a set-up with two symmetrical Cu contacts in a parallel configuration was assembled. The CV was carried out at different scan rates (10, 20, 50, 100, 200 mV/s) between a potential range of 0 and 2.5 V.The galvanostatic charge/discharge tests were performed at different constant current density from 0.3 A/g to 8 A/g in the potential range of 0 - 2.5 V. To estimate the mechanical behavior of the solid-state supercapacitors, the Instron 8872 fatigue testing system was used. Tensile experiments were carried out at ambient conditions with elongation rate of 1 mm/min.

3. Results and Discussion

Electrolytes with good mechanical stability are a necessary prerequisite for the fabrication of structural supercapacitors. The fundamental concept of solid-state electrolytes involves the immobilization of ionic liquids, with high electrochemical potential window and low vapor pressure, using a small amount of polymer materials. The copolymer PVDF-HFP has been shown to be a promising matrix for an electrolyte material due to its good mechanical properties. However, since the electrochemical devices involve ion movements in the cell, the high crystallinity of PVDF-HFP leads to the decrease in ionic mobility and subsequently to lower power performance of the devices. In this way, the solid plasticizer SN was used to enhance the ionic conductivity of the polymer electrolytes. Plastic-crystalline SN possesses high molecular diffusivity, waxy nature, and good solvating power via low melting temperature and high dielectric constant ($\varepsilon \sim 55$) which help to reduce the crystallinity of PVdF-HFP. Finally, gel polymer electrolytes with high ionic mobility and good dimensional/mechanical stability were prepared. An optical image of a self-standing electrolyte film, which combine both flexible nature and transparency is shown in **Figure 9**.

The microstrure of the film electrodes and the carbon fiber electrodes was investigated by SEM. In **Figure 2** (magnification ~600x) was captured the cross sectional area of the film electrode through the thickness, the thickness of the film was measured at approximately 30 μm. In **Figure 3** to **Figure 5** at higher magnifications is presented the internal microstructure of the film electrodes were the GNP and MnO_2 particles are distributed uniformerly all over the structure of the film. The morphology of the carbon fabrics after the impregnation process that was followed to deposit GNP/MnO_2 particles over the fiber surface is presented in **Figure 6:** and **Figure 7**. Also, in this case GNPs and MnO_2 are distributed all over the carbon fabric.

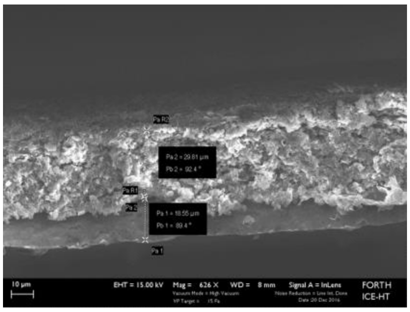

Figure 2: Magnification ~600x, cross section of the film electrodes

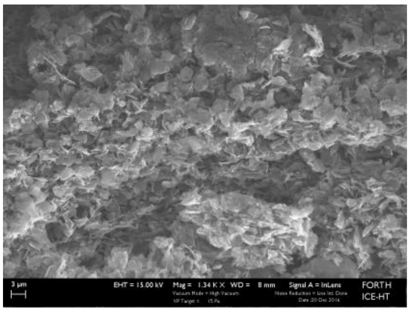

Figure 3: Magnification ~1.3Kx, microstructure of the film

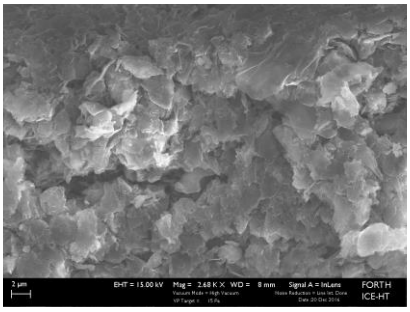

Figure 4: Magnification ~2.7Kx, microstructure of the film

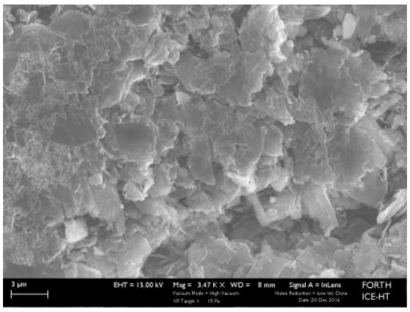

Figure 5: Magnification ~3.5Kx, microstructure of the film

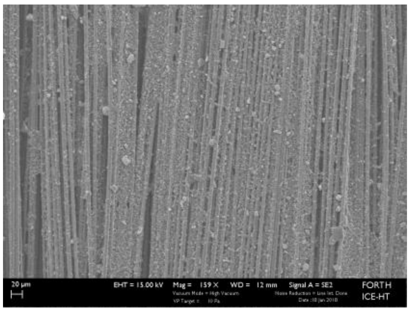

Figure 6: Magnification ~160x, distribution of the GNP/MnO_2 particles over the carbon fabric

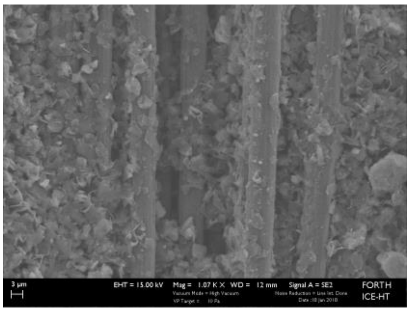

Figure 7: Magnification ~1Kx, microstructure of the carbon fiber electrode

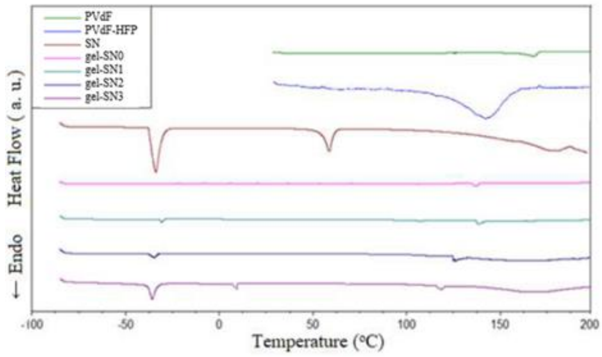

Figure 8: DSC curves for different compositions of polymer electrolyte

Figure 9: Morphology of the solid polymer electrolyte

The thermal stability of the SN-based gel polymer electrolytes was tested by DSC. DSC curves were obtained from first run heating. **Figure 8** shows the DSC thermograms of the different compositions of PVdF-HFP/IL/SN gel electrolytes, as well as of the polymer PVdF, the host co-polymer PVdF-HFP and the pure SN. Pure SN shows two characteristics peaks at -35 ^oC and 60 ^oC. The peak at ~ -35 ^oC corresponds to the glass transition temperature, and the peak at ~60 ^oC is assigned as melting temperature of SN. The endothermic peak at 168 ^oC corresponds to the melting point of crystalline phase of PVdF. The host polymer PVdF-HFP shows melting point at 142 ^oC, due to the amorphous phase of HFP. By adding IL, the melting point of the different compositions of PVdF-HFP/IL/SN gel electrolytes is decreased in a temperature range from 135 to 120 ^oC, and this is attributed to the presence of liquid components that causes an increase in the amorphous content in the overall phase of the electrolytes. On addition of SN, there is no melting peak of SN appears for gel-SN1 and gel-SN2 whereas for gel-SN3 the melting peak of SN shifted from 60 to 9 ^oC. The most thermostable composition of the polymer electrolyte obtained in the sample SN1 with melting point at ~135 ^oC.

The electrochemical behavior of the produced electrode materials was characterized with potentiostatic and galvanostatic measurements. Cyclic voltammetry and charge-discharge tests were conducted to measure the specific capacitance of the electrodes and to evaluate their overall electrochemical behavior. Film electrodes were characterized with a three electrode setup and liquid electrolyte (1M KOH) and for the solid state electrolyte tests were assembled asymmetrical supercapacitor cells. From **Figure 10** to **Figure 12** are presented the results of cyclic voltammetry tests for the film elctrodes (MnO$_2$-1, MnO$_2$-2, MnO$_2$-3). In all cases pseudocapaciatance mechanism was confirmed by the curves exported from cyclic voltammetry. Most intense pseudocapacitance mechanism was observed in sample MnO$_2$-2 **Figure 11**. The maximum specific capacitance obtained from the film samples is 141 F/g, 266 F/g and 318 F/g respectively. In sample MnO$_2$-3 specific drops abruptly as the scan rate increases. From **Figure 13** to **Figure 15** presest the curves that obtained from charge-discharge tests with the same liquid electrolyte at potential window of 0.55V. In **Figure 17** are concentrated the values of specific capacitance that calculated from charge-discharge tests correlated with the current density. It is confirmed that sample MnO$_2$-3 has an abrupt dropage of the specific capacitance as current density increases and also has a very high specific capacitance of ~450 F/g at 0.3 A/g current density. More stable behavior with retention of high specific capacitance values is sample MnO$_2$-2. The formulation of sample MnO$_2$-2 was selected to supercapacitor with polymer electrolyte.

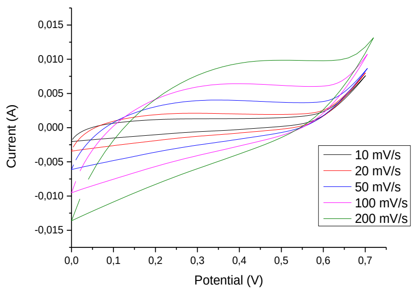

Figure 10: CV curve of sample MnO$_2$-1

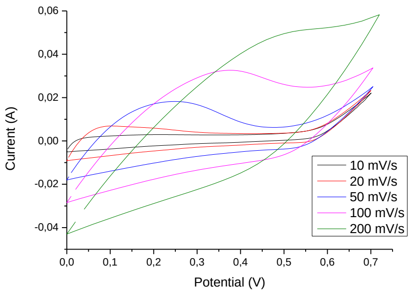

Figure 11: CV curve of sample MnO$_2$-2

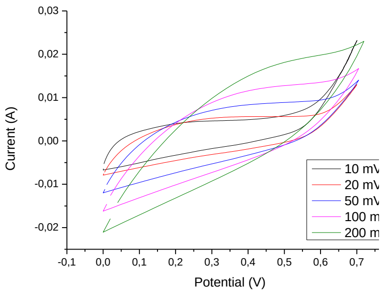

Figure 12: CV curve of sample MnO$_2$-3

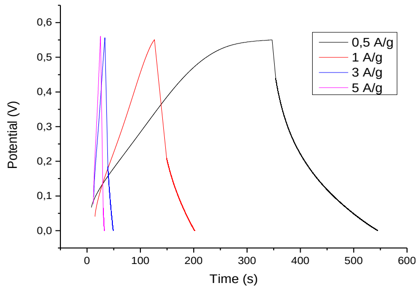

Figure 13: Charge-Discharge curve of sample MnO$_2$-1

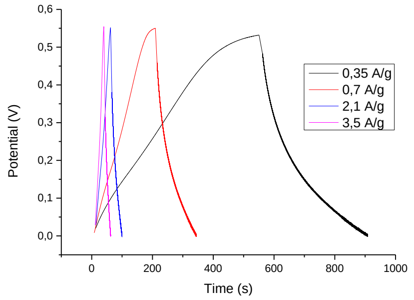

Figure 14: Charge-Discharge curve of sample MnO$_2$-2

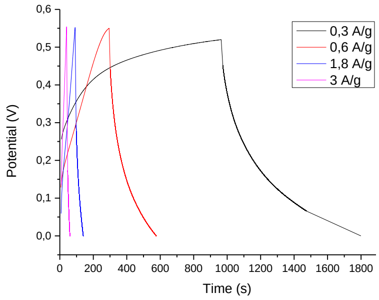

Figure 15: Charge-Discharge curve of sample MnO$_2$-3

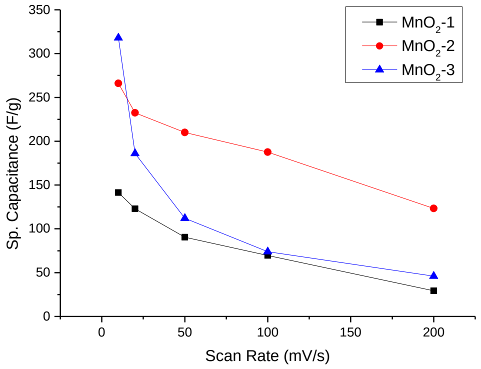

Figure 16: Specific Capacitance evolution vs Scan Rate

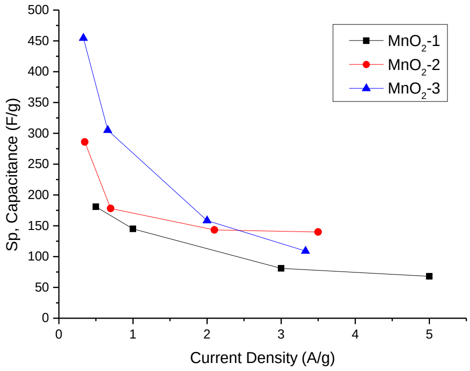

Figure 17: Specific Capacitance evolution vs Current Density

For the assembly of the polymer solid electrolyte supercapacitor (SESC) used MnO$_2$-2 samlpe and a counter electrode consisted of GNPs and PVDF (80% GNPs). In **Figure 18** in presented the CV that obtained at the same scan rates that used for the aqueous liquid electrode but in this case in wider potential window (0-2.5V) that is operational for the polymer electrolyte. The elecrochemical behavior of the sample differs from the behavior that obtained for the same sample with aqueous liquid electrolyte. The pseudocapacitance mechanism is restricted by the limitations that insert the solid electrolyte on the ionic mobility and as a result the maximum specific cpapacitance measured at ~151.2 F/g. **Figure 19** presents the CV curve of the carbon fiber composite solid electrolyte supercapcitor (CF-SESC) which is similar to the curve extracted for the sample without carbon fibers. The specific capacitance measured at the same level approximately 164 F/g. In **Figure 21** and **Figure 22** are the charge-discharge from samples SESC and CF-CESC respectively where it is observed a scalar drop of the potential at the start of the discharge, this scalr drop is observed due the higher internal resistance of the supercapcitor cell as an effect of the higher resistance of polymer electrolyte. In **Figure 23** it is shown that the CF-SESC has slight higher specific capacitance at the same current density with the SESC. It is very promising that the specific capacitance remained at the same or even higher level in the case of using carbon fibers as current collectors and this overall structure can be used for the development of multifunctional structural supercapacitors.

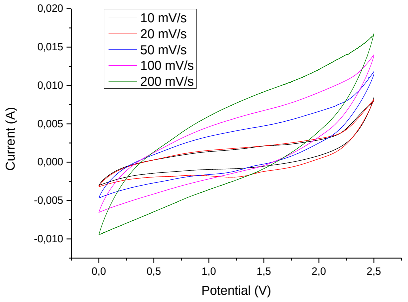

Figure 18: CV curve of Solid Electrolyte Supercapacitor (SESC)

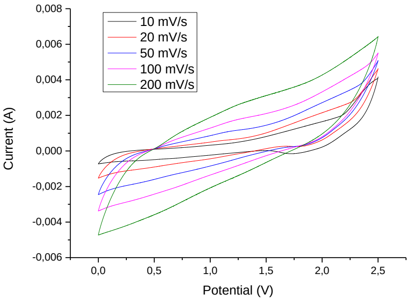

Figure 19: CV of Carbon Fiber Solid Electrolyte Supercapacitor (CF-SESC)

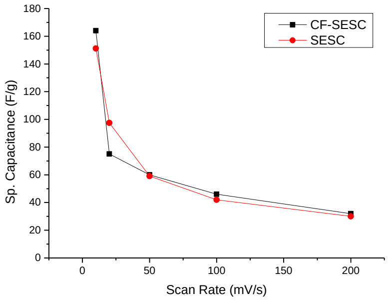

Figure 20: Specific Capacitance vs Scan Rate

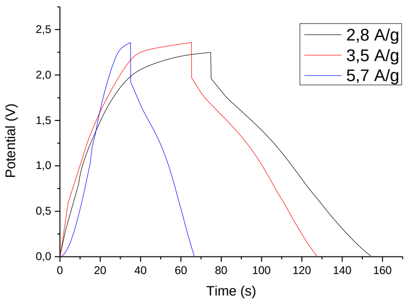

Figure 21: Charge – Discharge curves of sample SESC

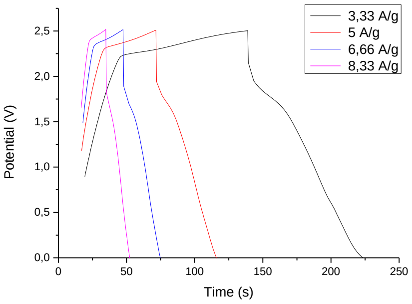

Figure 22: Charge – Dicharge of sample CF-SESC

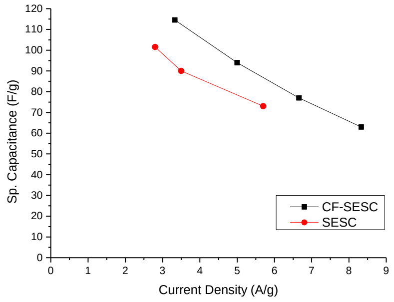

Figure 23: Specific Capacitance vs Current Density

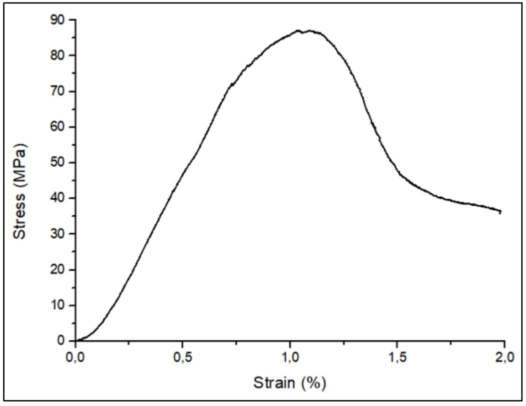

Figure 24: Curve obtained from tensile test of the CF-SESC.

Generally, the attribute of high surface area generally conflicts with the demand of good mechanical properties of materials. So, ideal composite electrodes with both merits have rarely been reported in literature. Here, a structural supercapacitor was assembled that can bear mechanical load while maintaining high storage performance. The structure of the supercapacitor included an impregnated glass cloth with the optimal gel electrolytic solution, sandwiched by two graphene-MnO_2 fiber composite electrodes. The mechanical properties of the material of the compact supercapacitor was quantitatively examined using tensile test. The Stress–Strain curve is presented in **Figure 24** and demonstrates that the supercapacitor exhibits a typical plastic deformation under tensile loading at room temperature. The supercapacitor can withstand a maximum tensile stress as high as 87 MPa at elongation of 1.2% with Young's Modulus of 11 GPa. The initiation of the mechanical failure of the material is a result of the failure of the intermediate layer of electrolyte/glass fibers.

4. Conclusions

In this study it was developed a structural fiber composite structure with energy storage capabilities as supercapacitor. The idea of developing materials that can store energy and in the same time operate as structural elements is very promising as it can lead to lighter structures where the space that it was saved by integrating the energy storage elements into the structure will be used for additional functions. The stepwise process that it was followed in this study was first to develop an efficient material formulation that it will then be applied to the surface of carbon fibers and will be assemblied as a supercapcitor. So, first it was developed the electrode formulation and the polymer electrolyte formulation then a first assembly of them was developed without fiber reinforcement in order to describe the energy operational limits of the structure. Finally, the selected formulations of the electrode and the polymer electrolyte applied to carbon fiber and glass fiber respectively and assembled to a composite material energy storage structure. The value of specific capacitance of this structure measured at 164 F/g, where combined with the fact that can withstand a tensile mechanical load of ~90 MPa, it is very promising for further research on the applications of these type of multifunctional materials in a wide range of industry applications from UAVs to wearable electronics.

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