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Tuning the Ionic and Dielectric Properties of Electrospun Nanocomposite Fibers for Supercapacitor Applications

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ABSTRACT

This study reports the fabrication and characterization of electrospun polyvinylidene fluoride (PVdF)and polyvinylpyrrolidone (PVP) nanofiber separators embedded with carbon black nanoparticles. Different weight percentages (0, 0.25, 0.5, 1, 2, and 4wt%) of carbon black nanoparticles were dispersed in N, N-dimethylacetamide (DMAC) and ethanol using sonication and high-speed agitations, and then PVdF and PVP polymers were added to the dispersions prior to the mixing and electrospinning processes. The morphological, dielectric constant, ionic conductivity, and surface hydrophobic properties of the PVdF/PVP nanofiber separators were analyzed using various techniques. SEM micrograms showed that the fiber diameter was around 100-200 nm. The ionic conductivity test clearly revealed a significant increase in conductivity valueof 4.28×10^{-4}S/cm for 4 wt. % carbon black loading. However, the contact angle values were decreased with increasing weight percent of carbon black particles. The dielectric constant was increased with the carbon black loading. As can be seen, overall physical properties of the nanocomposite separators were significantly enhanced as a function of carbon black inclusions, which may be useful for supercapacitor separators and other energy storage devices.

***Keywords**: Carbon Black Nanopowders, Electrospun Nanofibers,Ionic Conductivity, Supercapacitor Separators.*

I. Introduction

1.1. General Background

Supercapacitors or electrochemical capacitors have been considered as alternative energy storage devices. They can be utilized as backup source devices due to their high power levels, large specific surface area, low electrical resistivity, high charging-discharging rate, and long cyclic lives compared to conventional capacitors and conventional batteries. They have demonstrated great potential in a wide range of applications such as power backup for mobile phones or laptops, and a power source for hybrid vehicles[1-8].Research on novel energy storage devices has attracted substantial attention recently. Traditional batteries have slow discharge rates and a high energy density; therefore, it is important to develop storage devices having high energy density and high power density. Electrochemical supercapacitors possess high power density and reasonably good energy density. Currently, researchers have focused their attention on increasing the energy density of supercapacitors by finding suitable materials for the separator/electrode and lowering the overall cost [9]. Many researchers have fabricated separators/electrodes for supercapacitors using a wide variety of materials, such as metal-based oxides, graphene, carbon nanotubes, carbonized wood, etc. Some researchers have used carbonaceous compositions and metal oxides, and incorporated them with various polymers for separator applications [3-12]. Carbon-based nanocomposites with conducting polymers have high capacitance values and better cyclic performance in supercapacitors. They also possess high capacitance values due to their functional groups containing phosphorus, nitrogen, and oxygen, which are referred to as thepseudocapacitance effect [13].

Electrospinning is a promising technique used to fabricate nano/micro membrane separators in a very short period of time with minimum investment. Polymeric separators fabricated by the electrospinning possess a unique texture with micro and/or nanosize fiber arrangements, flexibility, and high surface area and porosity. This can be a promising material for various types of separators.The main focus here is the fabrication of a separator with high ionic conductivity and electrochemical stability. Among many polymers, PVdF has presented better results due to its high electrochemical stability and particularly excellent electrical properties, which can be useful in supercapacitor applications,although the flexibility of PVdF is not sufficient due to its high crystalline structure and may eventually cause some difficulties [14].

Electrospun polymer such as PVdF and its derivatives, can be used as nanofiber mats in separators of Li-ion batteries, due to its nanoporous structure leading to increased ionic conductivity [15]. Uniform electrospun PVdF membrane thickness and fiber diameter can be obtained by using high polymer concentrations and electrospinning at relatively high spinning voltage. This improves mechanical strength and provides the PVdF separator with charge and discharge capacities that generally exceed commercial polypropylene separators, while resulting in little capacity loss [15].

Karabelli et al. [16] prepared PVdF separators for supercapacitor applications, and studied the different properties of PVdF separator such as thermal, mechanical and ionic conductivity. Polymeric materials are widely used as separators and as electrodes in batteries and in ultracapacitors. PVdF contains various phases, the most common being the α-phase. The pyroelectric and piezoelectric features of the β-phase of PVdF provide better material properties [17]. The purpose of this study was to fabricate separators for supercapacitors using the electrospinning technique and investigate their ionic, dielectric, and surface properties.

1.2. Electrospinning

Electrospinning is an effective method to produce woven and non-woven micro/nanoscale fibers from a polymeric solution. The process parameters can be optimized to prepare separators having extraordinary properties. The resultant fibers generally have a large surface area, flexibility, and uniform porosity [18, 19]. Some conventional fiber-spinning methods, such as melt spinning, dry spinning, and gel spinning, are capable of producing fibers with diameters in the range of micrometers, but the electrospinning technique produces non-woven polymeric fibers in the micro to nanometer range. It also presents a high surface area compared to conventional fiber-forming methods [20].

In electrospinning, a high-voltage or high-electric field is used to overcome the surface tension of the polymeric solution. When the intensity of the electric field is increased beyond a certain limit, called threshold intensity, the hemispherical surface of the polymer solution at the tip of the capillary tube begins to elongate into a structure known as the Taylor cone.Electrospun fibers form from the plastic stretching of a polymeric solution jet while the solvent evaporates, and the polymer solidifies at micro and nanolevels. In this technique, a polymer solution is transferred into a syringe, and a continuous filament is drawn from the nozzle to the collector by utilizing a high electrostatic field. A charged polymer jet is ejected from the nozzle due to electrostatic repulsion. Afterward, the filaments are deposited on the collector surface, which is located some distance from the capillary tube [20].

Lewandowski et al. [21] studied the electrochemical performance of a totally solid state electric double – layer capacitor using a polymer electrolyte and an activated carbon powder as electrode material in which polymer electrolyte serves as separator as well as electrode material. Sivaraman et al. [22] reported all-solid-supercapacitor based on chemically synthesized polyaniline (PANI) and sulfonated polymers having fluorinated ethylene propylene copolymer grafted with acrylic acid and sulfonated (FEP-g-AA-SO_3H) membrane (separator). Electrospun polymers such as polyvinylidene fluoride (PVdF) and polyacrylonitrile (PAN) and many other, can be used as nanofiber mats in separator applications in electronic devices [15]. These separators provide nanoporous structure leading to increased ionic conductivity of membrane soaked with liquid electrolyte [15]. A separator should be mechanically, chemically, and thermally stable and should allow ions to transfer, but prevent electrical short circuit. However, a separator has two main functions: the first one is to provide electronic insulation between electrodes of opposite polarization and the second one is to allow ionic conduction from one electrode to another.

A uniform electrospun PVdF membrane thickness can be achieved by using high polymer concentration and carrying out electrospinning at high voltage. This provides mechanical strength and also results in charge and discharge capacities that exceed many commercially available separators [15]. High crystallinity of PVdF generally impedes conductivity. Therefore, PVP was added in polymeric solution in order to account for conductivity limitation caused by PVdF high crystallinity and also it increases electrospinnability of polymeric solution.PVP is ahydrophobicizer and stabilizer, and it can greatly improve membrane oxidative stability and chemical stability [23, 24].Qiao et al. [23] determined the chemical stability of PVA/PVP membrane by immersing it in different concentration of KOH at elevated temperature, in order to test the tolerance of the membrane at elevated temperature in KOH solution.

Conventional capacitor technology has focused on minimizing the area of electrode plates and then combining these plates with thin layers of insulating separator having high dielectric constant possibly resulting in high capacitance values [25]. This methodology has certain limits, as separator film can be of minimum thickness before it fails and there are also limits on the dielectric constant of film material [25]. Usingthe electrospun PVdF and PVP membranes incorporated with carbon black not only increase the surface area of separator and wettability, but also provide the mechanical stability to the separator and increase the dielectric constant values of separators, as well. Figure 1 shows a schematic illustration of an electrospinning process. Fibers produced by this method can be used for many industrial applications, such as sensors, filters, biomedical purposes, compositereinforcement, solar cells, fuel cells, batteries, supercapacitors, and membrane technology [20, 26].

II. Experimental Procedure

2.1. Materials

PVdF and PVP with molecular weights of 180,000 g/mole and 130,000 g/mole, respectively, were purchased from Sigma-Aldrich and used without any modification or purification. Carbon black (ELFTEX8) was purchased from the Cabot Company and used as reinforcement nanoparticles (15–60 nm). N, N-dimethylacetamide (DMAC) and acetone, were purchased from Fisher Scientific and used as solvents. Figure 2 shows SEM images of the carbon black powder. As can be seen, the particles are mainly aggregated and need to be dispersed prior to the electrospinning process.

2.2. Methods

2.2.1. Fabrication of Nanocomposite Fibers

Different weight percentages (0, 0.25, 0.5, 1, 2, and 4 wt%) of carbon black nanopowders were dispersed in the DMAC/acetone solvent and sonicated for 90 minutes; then PVdF and 2 wt%of PVP were added separately to the dispersions. The weight ratio was 80 wt. % solvents (including DMAC and acetone, were 70/30 in weight proportions respectively) and 20 wt. % of polymers (including 18 wt. % PVdF and 2 wt. % PVP). The solution was constantly stirred at 550 rpm and 60°C for five hours before the electrospinning process. Special care was taken to ensure a homogeneous blend of the mixture. The dispersed solution was transferred to a 10 ml plastic syringe connected to a capillary needle having an inside diameter of 0.5 mm. The electrospinning parameters of voltage, distance between tip and collector, and syringe pump speed were 25 kV DC, 25 cm, and 2 ml/hr, respectively. The theoretical density of polymeric solution with 4 wt. % of carbon black was calculated as 1.069 g/cm^3, based on rule of mixtures. Electrospun fibers were then collected on an aluminum screen and dried in an oven at 60°C for eight hours to remove all residual solvents.The theoretical density of electrospun fibers with 4 wt. % of carbon black was calculated as 1.72 g/cm^3, based on rule of mixtures. PVP is a very good adhesive agent and it is used in batteries as a special additive. PVP is used to glue the membrane together for efficient electrochemical performance of supercapacitors. The reason for using PVdF is that it generally performs significantly better in many applications where strength, resistance to solvents and heat are required. PVdF is also used as insulator on electrical wires due to its combination of low weight, low thermal conductivity and high thermal and chemical resistance. Additionally, PVdF is a binder material usually used in the production of composite electrodes in lithium ion batteries. Figure 3 shows the SEM images of PVdF/PVP nanofibers incorporated with carbon black nanopowders, indicating that most of PVdF nanofibers are in nanosize(100 and 200 nm). However, some beads were formed during the electrospinning of 4 wt% carbon black, as shown in Figure 3(f), which may have been due to the mixture’s high carbon content. A good combination of PVdF/PVP and carbon black nanopowders is observed in all samples.A membrane thickness of 0.5 mm was used in this experiment. As can be seen in all SEM images (Figure 3), there was no pronounced difference in the fiber diameter as the weight % of carbon black increased. In electrospinning, the fiber diameter depends on the viscosity of the polymeric solution and the distance between the capillary tube and collector screen distance. The viscosity generally depends on the molecular weight of the polymers and solvent types used for dissolution. In the present study, a constant distance of 25 cm was maintained between the capillary tube and collector screen throughout the experiment. A higher distance will lower the intensity of the electrostatic field. There could be some shrinkage during the heat treatment at 60°C for eight hours to remove all residual solvents and polymer change alignments. However, this shrinkage is very minute, so fibers retained their shape and morphology after the heat treatment. The average diameter of fibers was observed to be between 100 and 200 nm in all the cases.

2.2.2. Capacitance Measurements

The dielectric constant values of the PVdF/ PVP nanocomposite fibers as a function of carbon black were calculated using a parallel-plate capacitor. An Andeen Hagerling 2550A Ultra Precision capacitance bridge was used to measure the capacitance of the parallel-plate capacitor. Figure 4 represents a schematic of the dielectric constant measurement following the ASTM D 150 test. The dielectric constant ε_r can be obtained from the measured capacitance C with the help of electrodes of a known cross-section area A, layer thickness d, and vacuum dielectric constant ε_o

(8.85 x 10^{-12} pF/m), using the following equation [18]:

$$\varepsilon_r = \frac{C.d}{A\varepsilon_0} \qquad (1)$$

The metal parallel-plate capacitor was composed of 0.5-cm-thick aluminum. PVdF/PVP nanocomposite fibers samples containing different weight percent of carbon black were placed between the aluminum conductor plates, which were tightly held together by hard and rigid plastic clips to ensure a complete contact between them and the fiber samples. After the setup was completed, the conductor plates were connected to the capacitance bridge, which also served as a DC power supply. As the current flowed, the aluminum plates connected to the positive and negative electrodes of the capacitance bridges were negatively and positively charged, respectively, creating a potential difference between the plates.

2.2.3. Water Contact Angle Measurements

The water contact angle values of the PVdF/PVP samples as a function of carbon black concentration were determined with an optical contact angle goniometer, purchased from KSV Instruments Ltd. (Model #CAM 100). This compact, video-based instrument is used to measure contact angles between 1° and 180° with an accuracy of ±1°. Computer software provided by KSV Instruments Ltd. precisely measured and also took pictures of the contact angles. Samples were cleaned with deionized water and dried in a vacuum overnight. Then they were placed on the goniometer stage, and a droplet of water was gently dropped on the sample from a syringe attached to the goniometer.

2.2.4. Ionic Conductivity Measurements

Electrochemical impedance spectroscopy (EIS) is an important tool for defining the electrical properties of materials. A Gamry instrument (Reference 600, Potentiostat/Galvanostat/ZRA) was utilized to characterize the ionic conductivity of the PVdF and PVP electrospun nanofibers. An aqueous solution of 6M KOH, which is a common electrolyte for liquid supercapacitors [2, 3, 23], was used during the ionic conductivity measurements. The conductivity values of the polymeric fibers were calculated using the resistance obtained from a slope of the I-V plot, a known area of the film (A), and the measured thickness of the film (L) [27] using the following equation:

$$\sigma = \frac{L}{RA} \qquad (2)$$

Where*R* represents resistance obtained from the slope of the I-V plot.

III. Results And Discussion

3.1. Capacitance Measurement Tests

Dielectric materials are used in almost all electrical equipment. They have low conduction and the capability of storing an electric charge. The dielectric properties of polymers are very important in many industrial applications, such as cable insulation, encapsulates for electronic components, and wiring board materials.Dielectric materials can store an electric charge in different forms depending on theirstructure [18, 28]. Higher filler material loadings will generally increase the dielectric constant values to a notable limit, so that the material can be used for various industrial applications. However, some properties of composites, such as thermal, electrical, and mechanical, may degrade due to higher filler loadings. Accordingly, the weight percentage of carbon black nanopowders was limited to 4 wt% in the present studies.

Figure 5 shows the dielectric constant values of the obtained PVdF/PVP nanocomposite fibers as a function of carbon black concentration. As can be seen, the addition of carbon black in PVdF/PVP nanofibers results in higher dielectric constants. Generally, the dielectric propertiesof a polymer depend on temperature, frequency, structure, and composition of the polymer and filler materials.

The measured dielectric constants of the nanocomposite fibers remarkably increased from 1.59 to 3.97, when the carbon black concentration reached 4 wt% in the PVdF/PVP nanocomposites. As observed in Figure 5, the dielectric constant values of PVdF/PVP samples were significantly increased by adding 1 wt% of carbon black in the fibers. By increasing the carbon black weight percentage to 4 wt% in the PVdF/PVP fibers, the dielectric constant values were slightly enhanced to 3.97.

This drastic improvement in dielectric constant values of PVdF/PVP fibers is attributed to the charge carrier concentration of carbon black embedded into the polymer structures [27]. The addition of carbon black to a polymer will certainly increase the charge carrier concentration, thereby increasing the polarizability of the electrospun fibers [18]. The relationship between the dielectric constant ε_r and the molecular polarizability α_t is given by [29]

$$\varepsilon_r = 1 + (\frac{N\alpha_t}{\varepsilon_0}) \qquad (3)$$

Where *N* is the concentration of molecules, and ε_0 is the permittivity of free space.

According to this relation, the dielectric constant must increase by increasing the polarizability.

3.2. Surface Hydrophobicity

Contact angle measurements were conducted on the PVdF/PVP nanocomposite samples in order to determine the effects of carbon black nanopowders on the surface properties of the fibrous separators. Hydrophobicity and hydrophilicity are terms related to the behavior of solid surfaces when placed in contact with water droplets. A hydrophobic surface is one on which a droplet of water forms a contact angle greater than 90^o, whereas a hydrophilic surface is one on which a droplet of water forms a contact angle less than 90^o [30]. Polymer surfaces with contact angles between 150^o and 180^o are called super-hydrophobic. This phenomenon is also known as the “lotus effect”, which exhibits self-cleaning and anti-contamination features [31].

The hydrophobicity or wettability of a separator plays an important role in the performance of a supercapacitor because a separator with high wettability can retain the electrolyte solutions and facilitate the diffusion of electrolytes. Table 1 shows the contact angles of PVdF/PVP fibers at different carbon black loadings.

Contact angles values of the PVdF/PVP fibers were slightly decreased by adding carbon black nanopowders. However, nanocomposite fibers indicated hydrophobic behaviors when the carbon black concentration reached 0.5 wt%. Then, increasing the carbon black percentages in the PVdF/PVP fibers exhibited hydrophilic behaviors, which may be more suitable for supercapacitor separators. The addition of 4 wt% of carbon black into PVdF/PVP fibers improved the wetting property of the surface and showed a contact angle of 78.51°.

PVP has higher wettability characteristics than PVdF because the surface tension of PVP (68 mN/m) fibers is much higher than that of PVdF (33.2 mN/m). Therefore, it is obvious that a combination of PVdF and PVP can provide better properties for supercapacitor separators. Increasing the carbon black content improved the surface wettability of membranes which might be due the high surface area of carbon black (1500 m^2g^{-1}), surface energy and accessible surface to perform higher hydrophilicity [7, 32, 33]. The membrane should soak quickly and completely in typical aqueous electrolytes to transport ions, but should not dissolve in the electrolytes and change the physical and chemical properties during charging and discharging.

3.3. Ionic Conductivity Tests

Generally, encapsulation of a polymer matrix with conducting elements can also increase the ionic conductivity [34, 35]. Figure 6 shows the ionic conductivity values of PVdF/PVP nano composite fibers as a function of carbon black nanoparticles. As can be seen, the ionic conductivity of the carbon black-based PVdF/PVP nanocomposite fiber samples increased 76.86% at 4 wt% carbon black loading.The calculated ionic conductivity values of PVdF/PVP nanofibers are given in Table 2.

Test results clearly indicate that the incorporation of carbon black raises the ionic conductivity, which may considerably increase the functionality of supercapacitor separators. The measured ionic conductivity value for the PVdF/PVP fibers without the addition of carbon black was 2.42×10^{-4} S cm^{-1}, which increased to 4.28×10^{-4} S cm^{-1} by adding 4 wt% of carbon black to the fibers.Increasing the ionic conductivity with a higher carbon black percentage is also confirmed with a higher value of capacitance in the presence of 4 wt% carbon black compared to PVdF/PVP fibers without the addition of carbon black. The high ionic conductivity may be attributed to the interconnected pores by carbon black nanopowders and the molecular structure of PVdF. Carbon blacknanoparticles are found to be highly branched with open structures, and high porosity which might assist ionsto move faster, resulting in higher ionic conductivity at higher carbon black contents in the microstructure [7].Porous separators with an accessible transportation path will provide better movement for ions between anode and cathode electrodes. Due to their nanoscale size, conducting polymer nanostructures are expected to improve performance and shorten the diffusion path length for transporting ions.

IV. Conclusions

The electrospinning method was employed to fabricate various polymeric PVdF/PVP separators incorporated with different percentages of carbon black nanoparticles for supercapacitors with high porosity, surface area, and ionic conductivity. Following the electrospinning process, the nanofiber samples were characterized using SEM, the capacitance bridge, the water contact angle, and GAMRY/EIS. The PVdF/PVP nanofibers were mainly nanosize (between 100 and 200 nm). The ionic conductivity of the PVdF/PVP electrospun membranes reached 4.28×10^{-4} S cm^{-1} by adding 4 wt% of carbon black. The dielectric constant values of the fibers were significantly increased in the presence of carbon black nanopowders, which may have been the result of the charge-carrying nanoinclusions embedded into the polymer structure. The wettability of the PVdF/PVP nanofibers improved by adding carbon black nanoparticles in the polymer structure. The present study clearly shows that electrospun nanocomposite fibers have excellent physical and chemical properties, which may be effectively utilized for the fabrication of supercapacitor separators.

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Table Captions:

Table 1: Water contact angle values of electrospun PVdF/PVP nanocomposite fibers as a function of carbon black concentrations.

Table 2: Ionic conductivity values of electrospun PVdF/PVP nanocomposite fibersas a function of carbon black concentrations.

Figure Captions:

Figure 1: Schematic view of electrospinning process.

Figure 2: SEM images of carbon black (ELFTEX8) powderat low (left) and high (right) magnifications.

Figure 3:EDX SEM images: (a) electrospun PVdF/PVP fibers, and incorporated with (b) 0.25wt%, (c) 0.5wt%, (d) 1wt%, (e) 2wt%,and (f) 4 wt%carbon black.

Figure 4: Schematic view of capacitance measurement of dielectric materials using ASTM D 150 test.

Figure 5: (Color online) Dielectric constant values of PVdF/PVP fibers as a function of carbon blackconcentrations.

Figure 6: (Color online) Linear sweep voltammogram curves for PVdF/PVP nanocomposite fibersas a function of carbon black concentrations.

Table 1:

Carbon Black Concentration (wt %)	**Water Contact Angle (^{o})**
0	112
0.25	111
0.5	95
1	81
2	80
4	78

Table 2:

Carbon Black Concentration (wt %)	**Ionic Conductivity (Scm^{-1})×10^{-4}**
0	2.42±0.04
0.25	2.90±0.03
0.5	3.56±0.04
1	3.87±0.05
2	4.05±0.03
4	4.28±0.05

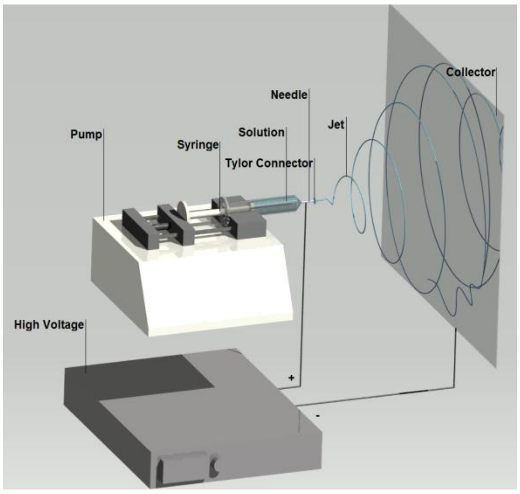


Figure 1:

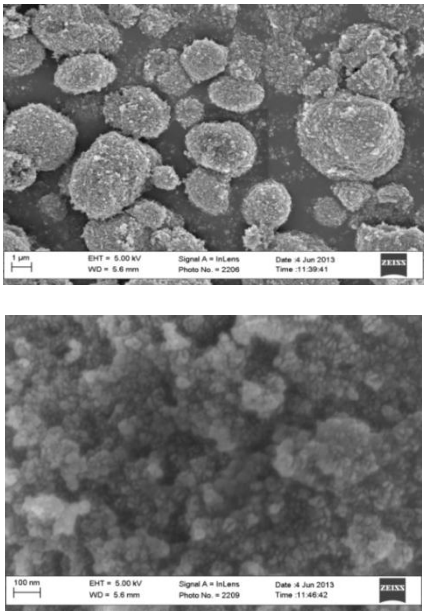
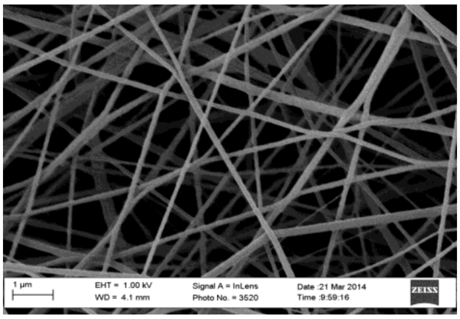
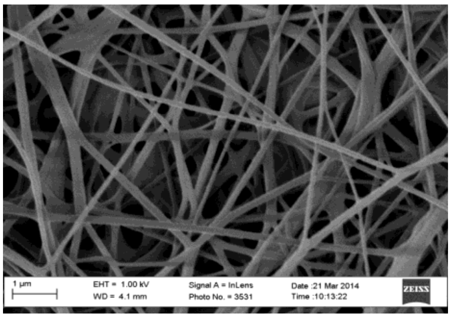


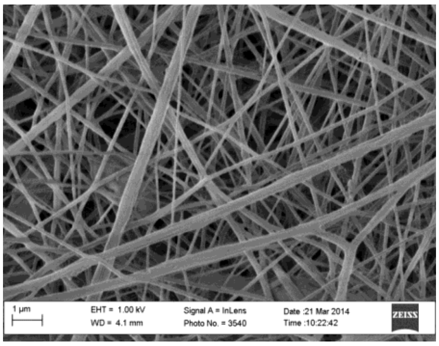
Figure 2:



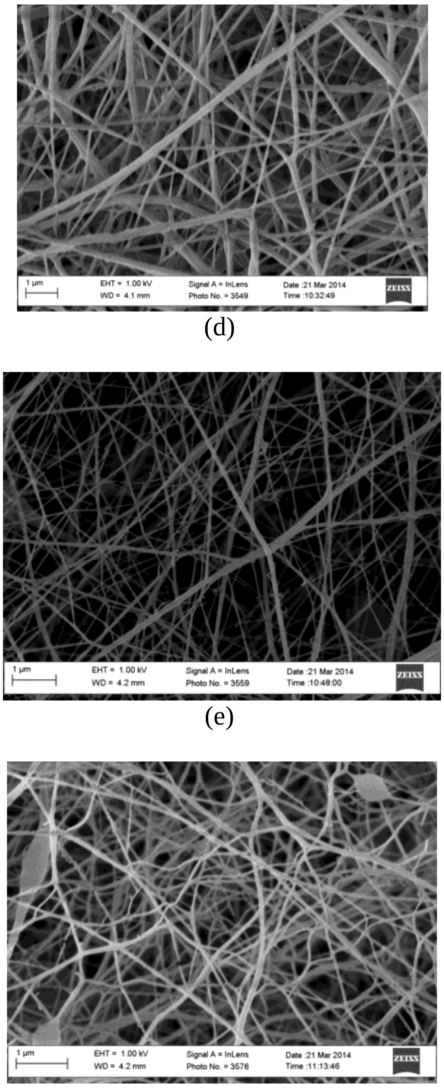
(a)



(b)



(c)



(d)

(e)

(f)

Figure 3:

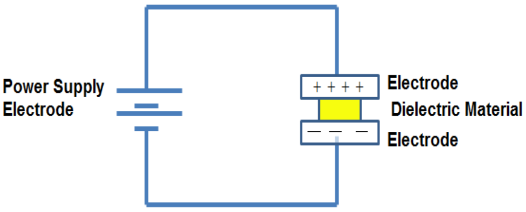


Figure 4:

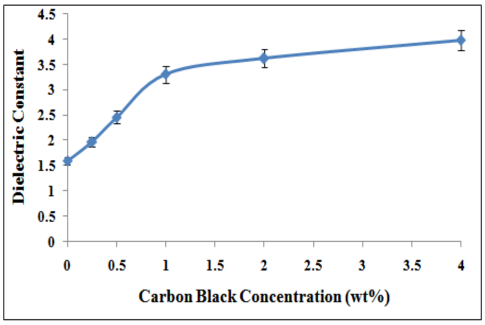


Figure 5:

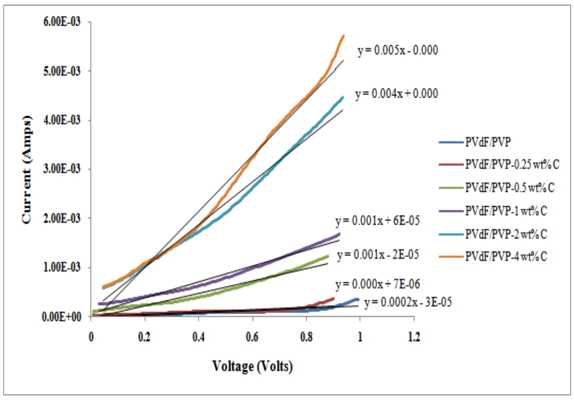


Figure 6: