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Development of electrospun fibrous activated carbon based electrodes for supercapacitor application

MASTER THESIS

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Aktiveeritud süsinikul põhinevate fiibriliste elektrokedratud elektroodide arendamine superkondensaatori rakenduseks

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ABSTRACT

Supercapacitors have drawn extensive attention during last years. Electrodes of EDLC-s are usually made of carbon allotropes that have high specific surface area. In recent years, the electrospinning process has found application in supercapacitor technology studies owing the high surface area of fibrous material, which is related to the performance of supercapacitors at high frequencies. This process involves formation of dry fibers from polymer solution using high voltage. Electrospun fibers have good mechanical properties, including resistance to cyclic loading and vibrations. Another advantage of electrospinning is the flexibility of making fibers which can be produced from a large assortment of different polymers and polymeric composites. In this study porous coconut shell activated carbons (AC) have been mixed with polymer solution and electrospun into fibrous membranes. Polyacrylonitrile (PAN) has been chosen as the polymer matrix due to its good mechanical properties, electrospinnability and good ion permeability. ACs have been preliminarily grinded to the particles size below 500 nm in order to be smaller than expected diameter of the fibers obtained via electrospinning. The ACs have been dispersed within electrospinning polymer solution by ultrasonic treatment in presence of ionic liquid. The ratio of AC to polymer in composite membrane has been varied. To improve the conductivity, carbon black and conductive carbon nanotubes composite have been added to ACs. Solution preparation, electrospinning and compacting conditions have been adjusted to get the best fibrous electrode with required characteristics. For prepared electrode membranes their electrochemical parameters, like electrochemical stability window (V), internal resistance, cell and specific capacitance (F/g) have been evaluated. The capacitance of 64 F/g for fibrous electrode has been reached which is comparable with 78 F/g for conventional EDLC electrodes.

INTRODUCTION

Interest in electrochemical capacitors (ECs), especially supercapacitors, has intensively increased during the last years thanks to their noticeable power density (fast charging/discharging within seconds) and high life cycle (>10^6 cycles) in comparison to batteries and fuel cells. To store energy ECs use either ion adsorption (electrochemical double layer capacitors, EDLC) or fast surface redox reactions (pseudocapacitors). If high power delivery or uptake is needed, ECs can complement or replace batteries in electrical energy storage and harvesting applications. [1]

Throwbacks of ECs involve suffering with low energy density and high production cost. To solve this problem one of the most intensive approaches is the development of new materials for EC electrodes. Most popular electrode materials today are various carbon allotrope particles that have high surface area accessible for charge storage casted into polymer matrix or deposited onto the metal foil electrodes. The surface area of the electrodes is a crucial factor to increase capacitance, therefore, activated carbons (AC), having a large specific surface area in addition to objectively good electric conductivity, electrochemical inertness, and lightweight properties are the perspective candidate to be used in EDLC electrodes.

Nowadays, an electrospinning method has received a great attention because of its special characteristics [2, 3]. Electrospinning allows producing fibres with a diameter of few hundred nanometres. Fibrous form of EC electrodes can provide a number of physical properties [3, 4]. The biggest benefit of electrospinning method stays in high specific surface area of the fibrous material, which is directly related to capability of the supercapacitor to operate at high frequencies if the surface can participate in the double-layer capacitance. Such fibres may have also good mechanical properties including resistance to cyclic loading and vibrations. Another benefit of electrospinning is flexibility of producing fibers from different polymers and their composites.

Therefore, development of activated carbon electrodes in fibrous flexible form by means of electrospinning is of high priority to be used in supercapacitors under applied specific environmental conditions (high frequency, as example) without significant loss of capacitance.

AIM OF THE STUDY

The main aim of this study is to develop fibrous EDLC electrodes by electrospinning which has simultaneously high enough capacitance, large operating voltage window and durability by combining porous coconut shell activated carbons (AC) with polymer matrix (polyacrylonitrile) and ionic liquid (IL).

Highly porous ACs have been mixed with polymer solution and electrospun into fibrous membranes. The polymer polyacrylonitrile (PAN) has been selected owing to their good mechanical properties, good solubility and good ion permeability. IL is used both as dispersing media for ACs in polymer solution and electric conductivity enhancing agent. Additionally, carbon nanotubes (CNT) and conductive carbon black (CB) are used to improve electric conductivity of final electrodes. ACs have been preliminarily grinded to nanoscale of the particles (below 500 nm) to be fairly below expected diameter of the fibers in electrospinning. High concentration of porous carbons in composite electrodes gives extraordinary specific surface resulting in high enough EDL capacitance.

The tasks of the study were:

- To develop a method for preparation of homogeneous composite polymeric dispersion with high content of activated carbons AC which can be further electrospun and used as electrodes in EDLC devices.
- To evaluate the electric, morphological and electrochemical behavior of electrospun fibrous PAN/AC/(conductive additive) electrodes in dependence on:
    - different AC content in composite electrodes;
    - different type and content of conductive additives (CNTs and CB).

To the best of our knowledge, there are no reports on electrospinnability and electrochemical evaluation of electrospun composite PAN/AC nanofiber membranes as electrode materials for supercapacitor applications.

1. LITERATURE REVIEW

1.1. Electrospinning

Nanomaterials have gained more and more interest during recent years and one of these types of materials are nanofibers. There are different methods for producing fibers, which have one dimension, usually thickness, in nanoscale. Most of those known methods, like melt fibrillation and nanolithography give excellent results, but can only be used in scientific research, because for industrial production they are too expensive. One of the most prominent technologies for industrial making of nanofibers is electrospinning, which has relatively low cost and quite high production rate [5]. Unfortunately electrospinning still has smaller production rate than other spinning techniques, which are widely used in production even though they give larger diameter fibers [6].

The electrospinning technique is often described as a variant of the electrospinning spraying (electrospraying) since both of them use high voltage to induce the formation of the liquid jet, but in electrospraying the electrified liquid jet is broken into small droplets and in electrospinning, a solid fiber is generated by stretching the jet using electrostatic repulsion. The process of electrospinning was first patented in 1934 by Formalas and it included apparatus for producing polymer filaments by using electrostatic repulsions between surface charges [7]. The process of electrospinning was almost forgotten until the 1990s, when the field of nanotechnology started to gain popularity. The researchers started looking for new (and old) ways to produce nanofibers and now there are hundreds of universities and research institutes worldwide studying various aspects of the electrospinning [5].

Electrospinning setup consists of three components, which are: a high-voltage power supply, a spinneret and a collector. As a high-voltage (usually in range 1 to 30 kV) power supply in electrospinning direct current (DC) power supplies are usually used, alternating current (AC) can also be used for some applications [7]. The spinneret can be a capillary tube with a pipette or needle of small diameter and the collector is made of some kind of conductive metal [8]. The spinneret is connected to the syringe, which is filled with the solution. The syringe is usually connected to the pump, so the solution can be fed at a controllable rate [7]. The basic setup is shown in Figure 1.1 [7].

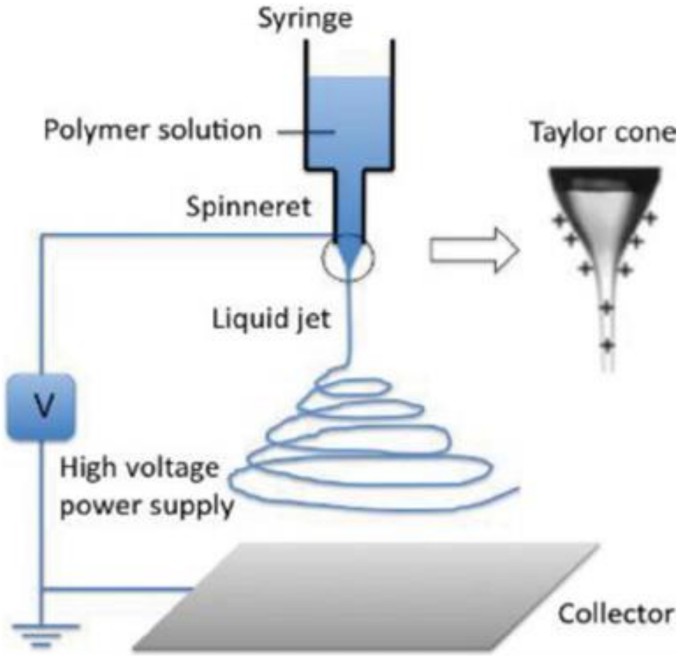


Figure 1.1 Schematic illustration of the basic setup for electrospinning [7]

In the process of electrospinning, static electrical charges are induced on the molecules of a solution. The density of this solution has to be suitable so that the self-repulsion of the charges would cause the liquid to stretch into a fiber in an electric field. When there is no breakage in the stretched solution, a single thread of continuous fiber is formed after the solvent evaporates [6].

During the process of electrospinning high-voltage is applied and when it is done, the pendent drop of solution (usually some sort of polymer) at the nozzle of the spinneret is electrified and those induced charges are uniformly distributed over the surface. This drop will experience two different types of electrostatic forces: first one is the electrostatic repulsion between charges on the surface and the second is the Columbian force applied by the external electric field. With these electrostatic interactions, the solution drop will be distorted into conical shape, which is called the Taylor cone (see the inset of Figure 1.1). When the strength of electric field is sufficient, the electrostatic forces can overcome the surface tension of the solution and then the liquid jet can be ejected from the nozzle. After that the liquid jet is stretched and whipped, during which the solvent evaporates, to form a long and thin fiber. The diameter of the fiber can be from hundreds of micrometers to just tens of nanometers [7].

In electrospinning, the interaction between the electric field and the surface charges on the jet causes the liquid to accelerate towards the metal collector. A higher charge density on the jet causes more instability, if we do not take into account the stiffness and viscosity of the solution. In a perfect dielectric jet, the non-uniformity of the jet’s radius along its length results in surface charges gathering on the protruding regions. The jet is destabilized by the self-repulsion of the charges and stabilized by tangential stress acting parallel to the flow. At a high charge density, the self-repulsion exceeds the tangential stress, which results in bending instability that can become so chaotic that loops of single jet unite into a cross-linked network. The series of close loops may hinder the motion of the electrospinning jet and form a fluffy cylindrical column with a diameter of a few millimeters [6].

1.1.1 Characteristic and applications of electrospun nanofibers

In electrospinning the diameter of the fibers and the morphology of them are the most researched and fundamental topics. These are dependent on numerous processing parameters that can be divided into three larger groups [7]:

1. Solution properties - viscosity, concentration, elasticity, electrical conductivity, polarity, molecular weight of the polymer, conformation of the polymer chain, surface tension of the solvent [7, 9].

2. The operational conditions - polymer feed rate, capillary size, applied voltage, distance between spinneret and collector [7, 9].

3. The surroundings properties - temperature, humidity [7].

The diameter of the fiber is mostly dependent on the stretching and acceleration of the fiber before its solidification. In the literature there are several models suggested to predict fiber diameter based on surface tension and electrostatic charge repulsion. For example in the model developed by Fridrikh *et al.* solution conductivity and viscosity are also taken into account in predicting the diameter of the nanofiber [10].

One way to control the morphology of the electrospun fiber mat is to use patterning, because the geometry of the collector effects the alignment of fibers. There are several types of collector, which can be seen in Figure 1.2 [9].

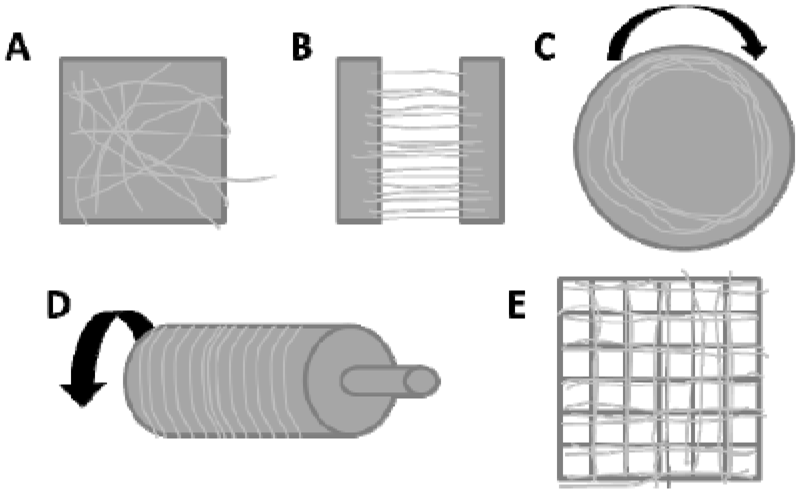


Figure 1.2 Collector geometries for electrospinning: A) static plate; B) parallel electrodes/plates; C) rotating disc; D) rotating mandrel; E) grid [9]

When using static plates, like grounded metal plate, the result of electrospinning are randomly oriented fibers. Electrodes separated by a gap or rotating mandrel and discs are good ways to generate oriented fiber mats. Conductive grids are used to make micro- or macro-scaled patterns of nanofibers [9]. In this work, rotating mandrel is used in electrospinning to get oriented nanofiber mats.

For certain applications, like the tissue engineering, filtration, batteries and fuel cells, fiber mat porosity or the surface area is extremely important and that is why it has been studied a lot [7, 9]. There are different ways to control the pore size in nanofiber mats. These include the addition of salt particles or ice crystals to the electrospinning solution, making of composites made of electrospun fibers and electrosprayed polymer beads that can be later removed, or the generation of micron-sized fiber diameter scaffolds [9].

Since electrospinning is quite simple technique for generating ultrathin fibers from many materials, its resultant structures are attractive for numerous applications from different fields. In biomedical usage these nanofibers are used in growing tissues (porous membrane for skin), prosthetics, wound dressing, skin cleansing, drug delivering. Nanofiber mats are also used for different sensors, filters, optical devices and several electronical applications, which regarding this work is the most interesting one [7, 8]. Porous mats made of electrospun fibers are good matrices for electrolytes and when soaked in electrolyte solution, this mat exhibits enhanced ionic conductivity. For example carbon nanofibers can be used as electrode material for supercapacitors [7, 11]. In this work, electrospinning is used in making electrodes for supercapacitors.

1.2. Supercapacitors

Electrical energy storage is required in more and more applications. These include telecommunication devices, like smartphones, stand-by power systems, and electric/hybrid vehicles. These energy storage devices must have good energy storage (W h), high maximum power (W), be lightweight and small, have long durability and relatively low cost. At the moment, the most common energy storage device is the battery, which has several shortcomings. As an alternative to pulse batteries, supercapacitors are used [12].

Electronic capacitors were first patented in 1957. They did not get much interest, until in 1989 a program was initiated to develop ultracapacitors (supercapacitors) [13]. Supercapacitor is a kind of electrochemical device which stores and releases energy at extremely high rate (from 0,1 s to 30 min.), has high power density (1 to 10^5 W/kg), long cycling life (more than 100 000 cycles), requires low maintenance, exhibits low self-discharging and can be used in wide temperature range [11, 14]. These excellent characteristics are the reason why supercapacitors could have many applications and why so many research groups are working with them.

A supercapacitor unit usually consists of two porous carbon electrodes, which are immersed in an electrolyte and isolated from each other by a porous separator. The current collectors, made from metal foil or carbon-polymer composites for example, are used to conduct electrical current from each electrode. The separator and the electrodes are impregnated with an electrolyte, which means ionic current can flow between the electrodes and also at the same time prevent discharging of the cell. Supercapacitors are divided into two groups: the electrochemical double-layer capacitors (EDLCs) and pseudocapacitors or redox supercapacitors. The first type can be based on activated carbons with capacitance proportional to the electrode surface area. The other type uses transition metal oxides or electrical conducting polymers as electrode materials, with the charge storage depending on the fast-Faradaic redox reactions. Electrical double-layer (EDL) supercapacitors share a similar principle with a dielectric capacitor, but there are still some big differences. The biggest difference is that the insulating barrier in a dielectric capacitor is replaced by electrolytes in a supercapacitor. Another difference is that dielectric capacitors rely on a dielectric material to store a charge, while EDLCs rely on the charge of the adsorbed double layer. The capacitance of traditional dielectric capacitors is limited by the thickness of the dielectric material and the thinnest of those are 2,5 mm in thickness. In the case of EDLCs, charging is achieved by separation of ions in the electrolyte, resulting in charge separation distances on the order of 1 nm, which occurs inside the pores of high surface area carbon materials [11].

The usual structure of a supercapacitor can be seen in Figure 1.3 [13].

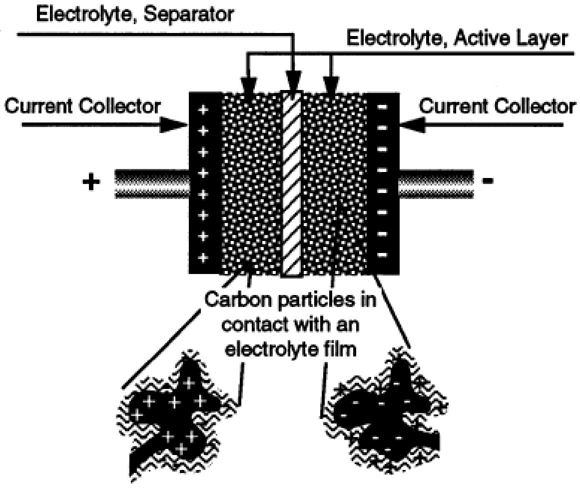


Figure 1.3 Principle of a double-layer capacitor [13]

Electrospinning can be also used in the production of supercapacitors, specially flexible supercapacitors [14]. Electrospun fiber mats can be used as electrodes in supercapacitors. Depending on the charge storage mechanism and active materials used, the supercapacitors, where electrospun nanofibers are used as electrodes, can be mainly divided into three groups: electrical double-layer capacitors (EDLCs) based on carbon nanofiber with high surface area; pseudocapacitors based on conducting polymers and hybrid capacitors based on carbon materials and transition metal oxides. Also, when nanofibers are used as the electrodes, they are immersed in electrolyte. Schematic of a supercapacitor using electrospun nanofibers as electrodes can be seen in Figure 1.4 [11].

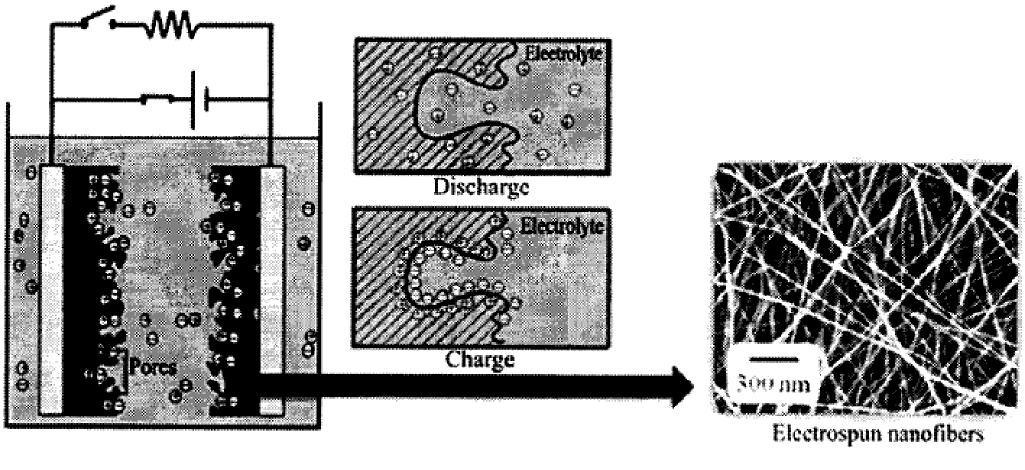


Figure 1.4 Scheme of supercapacitor using nanofibers as electrodes [11]

Electrospun nanofibers, especially carbon nanofibers, seem to be a good material for electrodes in supercapacitors, where their unique properties contribute to product’s functionality. These fibermats have high surface area and fibers have diameter in nanoscale, also other chemicals can be incorporated to the fibermats. In the structure of the supercapacitor the material of electrodes is extremely important − it has to be conductive and have high surface area, but it is not the only thing. The operating voltage of the supercapacitor is limited by the choice of electrolyte. Supercapacitors have an operating voltage of about 1 V when using aqueous electrolyte, this is limited by the electrochemical decomposition of water. Organic electrolyte-based supercapacitors can be operated in a voltage range of 2,5−3,5 V. Ionic liquid based supercapacitors give the best results - operating voltage can be up to 4 V [11].

1.2.1 Flexible supercapacitors

In today’s world, electronics, devices and needs are in constant change. One interesting field is flexible or space-saving electronic devices, like displays, sensors and mobile phones are desirable. Limits to their usage at the moment are production constraints. To power-up these portable electronics, the development of flexible energy storage and conversion devices need to catch up with the growth of the demand for flexible electronics. For that reason, flexible energy storage devices with higher energy density and power density are needed, where the first one must be able to provide sustainable energy and the second one able to provide a high-rate current output. For such of energy storage devices, improving the electrochemical performance of supercapacitors with higher energy density has been proven to be an interest of study to meet the growing demand. But it is challenging to produce very flexible supercapacitors with great electrochemical properties. [15]

Flexible supercapacitors usually require thin-film electrode materials with high flexibility integrated on soft-matter. These devices also need to have high mechanical integrity upon bending, folding or even rolling with a compact lightweight design. In particular the choice of electrode materials for flexible supercapacitors is extremely important [15]. Flexible electrodes are primarily based on carbon materials thanks to their good variety of geometric shapes from a macroscopic point of view. Based on the carbon networks, flexible electrodes can be divided into two categories: single carbon electrodes and carbon composite electrodes. Single carbon electrodes, which consist only carbons, can be produced via weaving, chemical vapor deposition (CVD), printing, filtration, evaporation and dipping-drying - these methods create carbon networks from 1D or 2D particles [16]. The composite electrode can be made of metal oxides coated onto carbon networks or from carbon and polymer mixture. The latter ones can be prepared using electropolymerization, chemical polymerization, coating and of course electrospinning. [15, 16]

1.3. Polyacrylonitrile

Polyacrylonitrile (PAN) is a synthetic resin prepared by the polymerization of acrylonitrile. As a member of the family of acrylic resins, it is a hard, rigid thermoplastic material that is resistant to most solvents and chemicals, burns slowly and has low permeability to gases. [17]

The structure of PAN can be seen in Figure 1.5 [18].

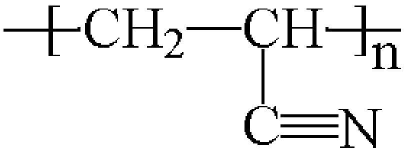


Figure 1.5 Structure of PAN. [18]

Acrylonitrile(CH_2=CHCN) is a flammable liquid, highly toxic if ingested and carcinogenic. PAN has none of the hazardous properties of the monomer [17]. Acrylonitrile was first synthesized in 1893 by Moureu and it was based on dehydration of acrylamide or ethylene cyanohydrin. The latter one was also used in early industrial productions. Since 1960s industrial scale manufacturing of acrylonitrile has been based on catalytic ammonoxidation of propylene. Nowadays almost two-thirds of manufactured acrylonitrile is used to prepare PAN fibers, the rest is used in acrylic rubbers production [19].

Although the polymerization of acrylonitrile had been known since the 1890s, commercial production of PAN, more specifically its fibers, did not begin until the 1940s after Ray C. Houtz of E.I. du Pont de Nemours & Company (now DuPont Company) found suitable solvents that could dissolve the polymer and make it spinnable. DuPont introduced its trademarked Orlon acrylic fiber in 1948 [18]. PAN is soluble in aqueous solutions of ethylene carbonate, in some mineral salts and in polar solvents like *N,N*-Dimethylformamide, dimethyl sulfoxide and *N,N*-Dimethylacetamide [20].

PAN has a unique molecular structure. This is due to strong repellent dipole-dipole interactions between intramolecular nitrile groups in parallel position, which force the polymer backbone into an irregular helical conformation. Also strong dipole-dipole interactions between antiparallel nitrile groups of different chains cause parallel orientation of the individual irregular helices [19]. That kind of structure leads to a stiff polymer chain, high crystalline melting point (317 °C), limited solubility and good mechanical properties [20].

The commercial/technological uses of PAN have been widely studied for almost a century now. Recently its processing and fiber forming technologies have gained the most interest. Among those new fields is the production of carbon nanofibers. There are various precursors for producing them, but from the polymers, PAN is the most used one. This is mainly due to relatively high carbon yield, which is up to 56%. Other attractive properties of PAN as the precursor include: the ability to tailor the structure of final carbon nanofibers, the ease of obtaining stabilized products and attractive mechanical properties. [20]

The route of getting carbonized structure of PAN can be seen in Figure 1.6. This involves three main steps: electrospinning, oxidative stabilization and carbonization. This is one of the most used ways to manufacture carbon nanofibers from PAN. Properties of obtained nanofibers are highly depend on the properties of PAN and thus on the synthesis process. The quality of commercially available PAN precursors is fluctuating and due to that there are problems with obtained nanofiber properties, especially with the mechanical ones. [20]

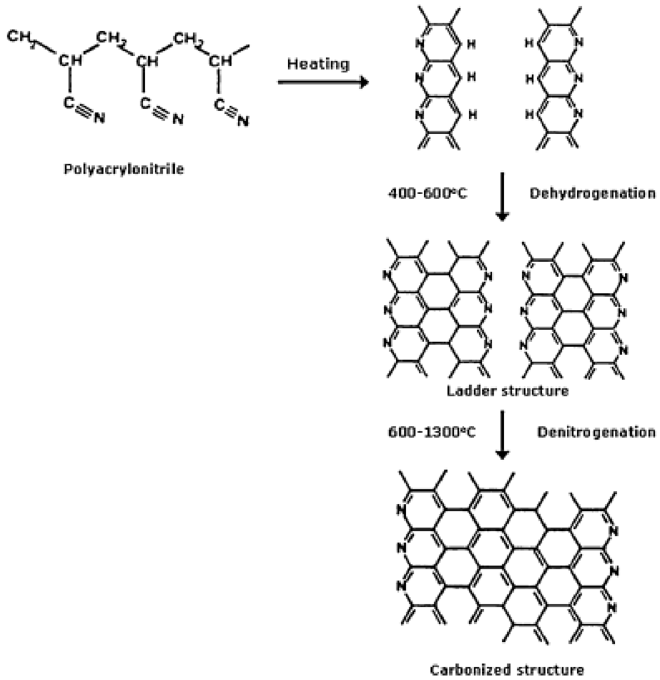


Figure 1.6 Schematics of the formation of carbonized structure from PAN fibers [20]

To increase the electrical and mechanical properties of PAN derived carbon nanofibers, carbon nanotubes can be added. Then the carbon nanotubes will act as a reinforcement, but effectiveness depends on their alignment. That kind of composite fiber mats containing PAN and carbon nanotubes can be used for example as supercapacitor electrodes. The high capacitance has been achieved, but there is still a problem with low power density [20]. More scientific work needs to be done to fix the power density issue.

In this work the latter version of producing PAN and carbon nanofibers is used and that due to inadequate mechanical properties of carbonized PAN fibers. These composite fibers containing PAN and carbon additives are done via electrospinning procedure.

1.4. Ionic liquids

Ionic liquids can be defined as ionic liquids as salts with a melting point below the boiling temperature of water. They are completely ionic and are often called “molten salts” in older literature. Ionic liquids usually contain organic cation and an inorganic, polyatomic anion. There are very many different ionic liquid with different characteristics due to the amount of known cations and anions, which can be combined in the ionic liquid. Since ionic liquid vary in components and thus properties, there are many applications for them [21].

The first so called ionic liquid was synthesized in mid 1800s and was named “red oil”. At the beginning of the 20th century, some alkylammonium nitrate salts were found to be liquids and the same thing happened with copper (I) chloride and alkylammonium chlorides in the 1960s. In 1963, Major (Dr.) Lowell A. King at the U.S. Air Force Academy initiated a research project to find a replacement for the LiCl/KCl molten salt electrolyte used in thermal batteries and since then there were continuous projects engaging ionic liquids. Ionic liquids were not popular until the beginning of a new millennium with the found usage as reaction solvents [21].

The synthesis of ionic liquids quite often involves basic types of chemistry, usually organic chemistry and protonation of suitable starting material is still the simplest method, even though it can be used with quite a small range of useful salts and for most of the applications more complex synthesis routes are needed. Since ionic liquids contain only certain anions an cations, the most common cations are shown in Figure 1.7 [21].

Room-temperature ionic liquids (RTIL) like the name suggest are ionic liquids, which are in liquid state at room temperature. First RTIL was identified in 1914 by Walden, who studied electrical conductivity of ethylmmonium nitrate. Even back then RTILs were used in electrochemistry. Nowadays electrochemical applications of RTILs include their usage as electrolytes in artificial muscles, photoelectrochemical cells, lithium-ion batteries and supercapacitors. [22]

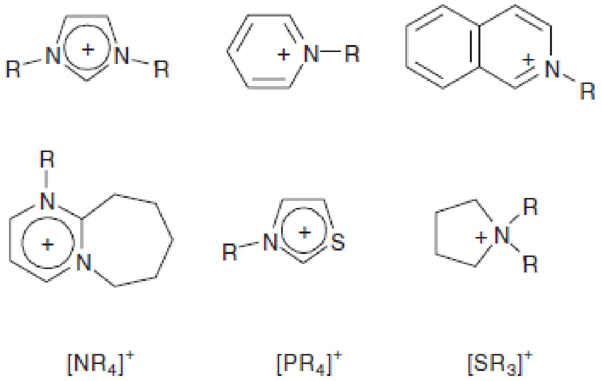


Figure 1.7 Examples of most common cations used in ionic liquids [21].

In this work, imidazolium type of RTILs are used, more specifically 1-ethyl-3-methylimidazolium tetrafluoroborate (EmimBF_4). This ionic liquid was prepared first in 1992. Since then it has been increasingly used due to its good properties. These include: low melting point (12 °C), relatively easy preparation, relative moisture stability, immiscibility with many organic solvents and good conductivity. [23]

1.5. Carbon materials

Carbon materials have long been used in electrodes of energy-storage devices as electro-conductive additives, supports for active materials, electron transfer catalysts, intercalation hosts, substrates for current leads and as agents for the control of heat transfer, porosity, surface-area and capacitance. For these reasons, carbons are suitable as electrode materials for EDLCs. Carbons have unique combination of chemical and physical properties, which make them feasible to use in supercapacitors [24]. These include:

- high conductivity,
- high surface-area range,
- good corrosion resistance,
- high temperature stability,
- controlled pore structure,
- processability and compatibility in composite materials,
- relatively low cost. [24]

1.5.1 Activated carbon

Activated carbon (AC) or activated charcoal is a nano-carbon material, which contains small pores. An easy way to describe the material is that it is assembled from defective graphene layers [25]. The pores in activated carbons are in the 0,4–4,0 nm range, and the pore size distribution is generally relatively wide [26]. Due to the reason that it has a large surface area (up to more than 2000 $m^2 g^{-1}$), it is used in numerous applications. AC is already used in the industry at a large scale - its capacity is about 500 000 tons per year. They are mainly used for air and water purification and separation of gas mixtures. [25]

Activated carbons can be made of many natural resources, including hard wood, coconut shell, fruit stones, coal and also from synthetic macromolecular systems [25]. ACs with better developed porosity, reproducible properties and more uniform microstructure and pores are produced from synthetic polymers. AC is made from raw materials using activation process. Activation can be done thermally or chemically. Thermal or mechanical activation involves carbonization of a precursor (removal of non-carbon species by thermal decomposition in inert atmosphere) and selective gasification of carbon atoms. Chemical activation is usually done by using phosphoric acid (or KOH, $ZnCl_2$, H_2SO_4 or others) at elevated temperature. Chemical activation of carbons usually leads to more uniform pore size distribution, smaller pores and higher specific capacitance. [25, 26]

Although activated carbons are popular, it is quite difficult to characterize them. Depending on the raw material, the properties tend to vary a lot. They are complex in terms of shape, size and variability of its pores. To completely characterize one material, several methods need to be implied, these include: techniques of adsorption from gases and liquids, kinetics and energetics studies, assessment of surface polarities, X-ray and neutron scattering. [25]

Activated carbons in powder form are already widely used in EDLCs due to their well-developed manufacturing technologies, easy production in large quantities, relatively low cost and great cycle stability. To form an electrode, AC is mixed with polymer binder and then casted on current collector foil. Commercial ACs offer specific surface area of 700 to 2200 $m^2 g^{-1}$ and specific capacitance in the range of 70–200 $F g^{-1}$ in aqueous and 50–120 $F g^{-1}$ in organic electrolytes. [26]

1.5.2 Conductivity enhancers

Supercapacitor electrode materials need to have good conductivity and good capacitance. When activated carbons take care of the latter, the conductive part also needs to be incorporated. Not all carbon materials have good conductivity, but with wide range of them available, suitable additives, conductivity enhancers for electrodes, can be found.

Carbon has four crystalline (ordered) allotropes: diamond (sp^3 bonding), graphite (sp^2), carbyne (sp^1) and fullerenes (sp^2). With increasing proportion of conjugated carbon in the sp^2 state increases the conductivity of the starting material as electrons associated with π-bonds are delocalized and become available as charge carriers. Electrical conductivity increases when separate conjugated systems also become interconnected to form a conducting network. [24]

In this work, two carbon materials were chosen as conductivity enhancers, to test whether these would work with activate carbon to produce supercapacitor electrodes. These materials are carbon black and carbon nanotubes (commercially available composite material).

Carbon black

Carbon blacks are materials that have near spherical carbon particles of colloidal sizes. They are produced by the partial combustion or thermal decomposition of hydrocarbons (like gases, oils, or distillates) in the gas phase. During production, the colloidal carbon particles coalesce into chemically fused aggregates and agglomerates with varying morphologies. The properties of carbon blacks vary with precursors and manufacturing conditions and they are usually classified according to their method of preparation or intended application. Due to that reason, the surface area of carbon blacks covers a wide range - from less than 10 to greater than 1500 $m^2 g^{-1}$. [24]

The conductivity of carbon blacks is typically in the range of 10^{-1} to 10^2 S cm^{-1} and is influenced by the relative ability of electrons to jump the gap between closely-spaced aggregates (electron tunneling) and by graphitic conduction via touching aggregates. Highly conductive carbon blacks have so-called high structure − aggregates with a highly branched, open structure. They should also have high porosity, small particle size, and a chemically clean (oxygen free) surface. [24]

Carbon blacks are used quite a lot in energy storage applications, like batteries and supercapacitors, where they are mainly used as conductive fillers/conductivity enhancers. Thanks to the fine and highly branched structure, the carbon blacks are ideally suited for filling inter-particle voids created between large particles. Addition of carbon black does not only improve the conductivity of electrodes, but can also improve capacitance. The inter-particle void volume in carbon electrodes can make ∼25–40% of the total electrode volume. Partially filling these voids with a porous carbon black will provide additional capacitance and also displace excess electrolyte that would otherwise completely fill the voids and increase weight of electrode and thus ultimately the cost of cells. [24]

Carbon nanotubes

Carbon nanotubes (CNTs) are carbon allotropes with cylindrical 1D structure. They consist of either one rolled-up graphitic sheet (single-walled CNT) or several coaxial ones (multi-walled CNT). CNTs are commonly made using catalyst assisted chemical vapor deposition (CVD) technique from hydrocarbon-based gaseous precursors, like methane, acetylene, propylene, and others.[26]

The nanoscale tubular morphology of CNTs offers a unique combination of low electrical resistivity and high porosity. There is interest for the application of carbon nanotubes as electrode materials for supercapacitors and other energy-storage devices. Both single- and multi-walled CNTs have been used as electrode materials in aqueous and non-aqueous electrolytes. The specific capacitance of CNTs depends highly on their morphology and purity. For purified nanotubes (without residual catalyst or amorphous carbon), the specific capacitance varies from 15 to 80 F g^{-1} and surface area ranges from 120 to 400 $m^2 g^{-1}$. [24]

2 EXPERIMENTAL PART

2.1 Materials

In this work poyacrylonitrile (PAN) with average molecular weight of 150 000 g mol^{-1}, was used as a polymer matrix. Dimethyl sulfoxide (DMSO) of 99,9% purity was used as a solvent. Both were purchased from Sigma-Aldrich Inc. Ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($EmimBF_4$) was purchased from Iolitec Ionic Liquid Techonologies GmbH.

Three different carbon materials were used in this work. As the active material the porous coconut shell activated carbon (AC), YP-80F, purchased from Kuraray Co.,Ltd has been used. As conductivity enhancers carbon black (CB) and conductive carbon nanotubes composite (CNTs) were used. Used carbon black was Super C65 (purchased from TIMCAL Ltd.). CNTs with tube length of 10−15 µm, tube diameter of 60−80 nm and specific surface area of 55−75 m^2 g^{-1} were purchased from Cheap Tubes Inc. This material contains mainly multi-walled carbon nanotubes with addition of carbon black.

AC was grinded using planetary Ball Mill PM 100 (Retsch). 200 mill balls (5 mm diameter) from zirconium oxide were used to grind 2 grams of AC. The samples were ground at 300 rpm for 5 h.

2.2 Solution preparation

To prepare solutions suitable for electrospinning procedure several different methods were used and compared. All prepared solutions contained 8% PAN in DMSO and 10% (or other) of ionic liquid $EmimBF_4$ to the weight of the whole solution was added. The amount of carbon additives (both activated carbon and conductivity enhancers) was varied. The exact steps of solution preparation regarding two main methods will be discussed in *Results and Discussion*.

Since carbon materials tend to agglomerate in solutions the sonication treatment was applied in addition to mechanical mixing. As a sonication device Bandelin Sonoplus HD 2070 with probe VS 70T (diameter 13 mm), purchased from BANDELIN Electronic GmbH & Co. KG, was used.

2.3 Electrospinning

To produce nanofibers, the electrospinning process was used. Typical set up of electrospinning apparatus was used, which consists of: a high voltage power supply (Glassman High Voltage with 0–40 kV power range), a syringe pump (New Era Pump Systems), a syringe with needle diameter of 0,6 mm and a drum collector covered with foil or special textile, where the nanofibers were collected as a fiber web. In this research electrospinning was conducted at room temperature with atmospheric conditions. The prepared solution was loaded into the syringe and this liquid was extruded from the needle tip at a constant rate by using a syringe pump. Used parameters for electrospinning were: pumping rate of 0,15 to 0,3 ml h^{-1}, distance of 10 cm and applied voltage of 12,5 kV.

The picture of used setup can be seen in Figure 2.1 and an example of obtained nanofiber mat can be seen in Figure 2.2.

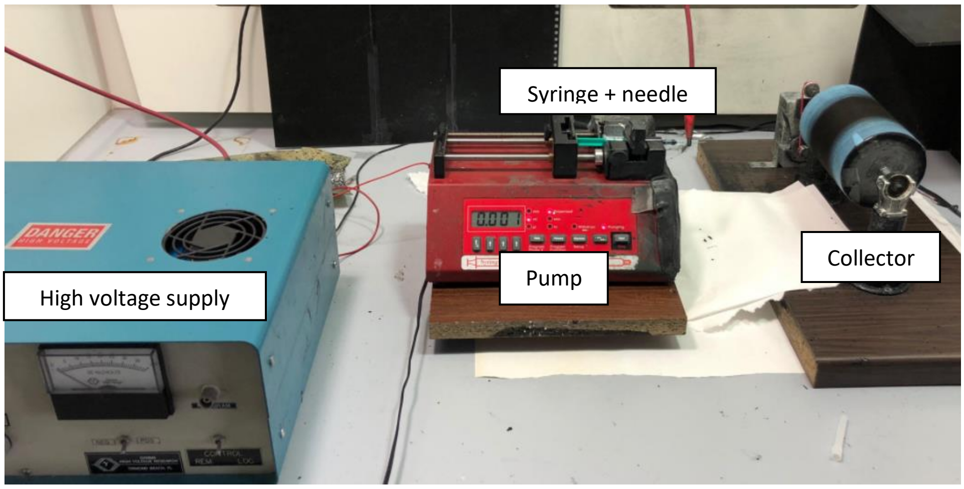


Figure 2.1 Used electrospinning setup

Figure 2.2 Example of electrospun nanofiber mat containing polymer, ionic liquid and carbon additives

2.4 Characterization

Solution electric conductivity

Before electrospinning the prepared solutions were measured for their conductivity using Seven Compact conductivity measuring device (Mettler Toledo Inc.). This was done at room temperature. The average value of 5 measurements was calculated.

Figure 2.3 Device used for measuring

Electric conductivity of fibrous mat

The conductance of fiber mats was measured using high resistance and low conductance meter HR 2 (Alpha Lab Inc.). The thickness of the mat was measured using a device purchased from Sony Magnescale Inc.

Figure 2.4 Conductance measuring device

The thickness of mats was measured from at least 3 different places and the average value was used in the calculations. The conductance was measured using a two-point method. Before conductivity measurements the mat has been pressed at room temperature and pressure 50 bars.

From the conductance, the conductivity was calculated using a formula (2.1):

$$\sigma = G \times \frac{L}{A} \tag{2.1}$$

Where σ is conductivity, G is conductance (S), L is the length between testing electrodes (cm), and A is the cross-sectional area of the specimen (cm^2).

Morphology study

To study the morphology of received fiber mats and measure the diameters of fibers, Hitachi Tabletop TM-1000 (purchased from Hitachi Ltd.) scanning electron microscope (SEM) was used. The samples were magnified in 500, 1000, 2000 or 3000 times and from highest magnified images, the diameters of fibers were measured and average values calculated (agglomerates were excluded).

Electrochemical properties

Electrospun mats (chosen ones) were also measured for their capacitance using a cell. Cellulose based separator (Ion-permeable separator paper Nippon Kodashi with thickness 50 µm) was used in measuring EDLC cell.

From electrospun mats, electrodes of suitable size were cut. These were firstly heat treated under vacuum to get rid of any excess moisture present. Electrodes were then pressed at 85 bars and 75°C before assembling into the cell. After that the electrodes were transferred into a nitrogen-filled glove-box, where the measuring cell was assembled. To provide better electric connection with cell, double side carbon coated aluminum foil was used as a collector. The assembled cell firstly was dried under vacuum and 105 °C during 72 h and then filled with standard electrolyte 1.8 M TEMABF4/ACN. This high conductive electrolyte has been chosen because it is most common organic electrolyte in carbon based ultracapacitors. Filled cell was left for the next 24 h for electrode impregnation. The electrochemical properties of fully assembled cells were determined using cyclic voltammetry (two-electrode experiment).

In the cyclic voltammetry (CV), the current at the working electrode versus the applied voltage is plotted to give the cyclic voltammogram. It is used to find information about the forward and the reverse reaction. Cyclic voltammetry applies a linear potential over time and at a certain potential the potentiostat will reverse the potential applied and sweep back to the beginning point. The measuring of current is usually done using different sweep rates. From the CV curves, the cell capacitance in Farads (F) is first calculated and after that specific capacitance in F/g can be re-calculated.

The cell capacitance is calculated using formula:

$$C_{cell} = \frac{I}{\nu} \tag{2.2}$$

where C_{cell} – cell capacitance in F,

I – current in Amperes,

ν – sweep rate in V s^{-1}.

Specific capacitance from CV curve is calculated by formula:

$$C_{sc} = \frac{2\times(q_a+q_c)}{m_t\times\nu\times\Delta V} \tag{2.3}$$

where C_{sc} – specific capacitance, F/g,

q_a, q_c – anodic and cathodic charge, C, found by intergrating CV curve,

m_t – mass of active material in both electrodes, g

ΔV – voltage window used, V.

The simplified way to find apparent specific capacitance is by using formula:

$$C_{cs} = \frac{4\times C_{cell}}{m_t} = \frac{4\times I_{disc}}{\nu\times m_t} \tag{2.4}$$

where I_{disc} – current taken from discharge curve of CV, A.

3 RESULTS AND DISCUSSION

3.1 Grinding of the carbons

AC powder has been grinded using planetary ball mill device to particle size below 1 μm. This is vital for having high specific surface and nano-fibrous structure in electrospinning. Average particle size should be fairly below expected diameter of the fibers in electrospinning, which is expected in range 300–700 nm. The sample was ground at 300 rpm for 1 h, 2 h, 3 h, 4 h and 5 h to investigate the optimum time condition to achieve homogeneously ground sample with particles size in nanoscale. Before every grinding process the carbon sample was vacuumed and filled with inert atmosphere (pure nitrogen) to avoid the contact with air during grinding process. The vacuuming and the filling with nitrogen were carried out in the desiccator.

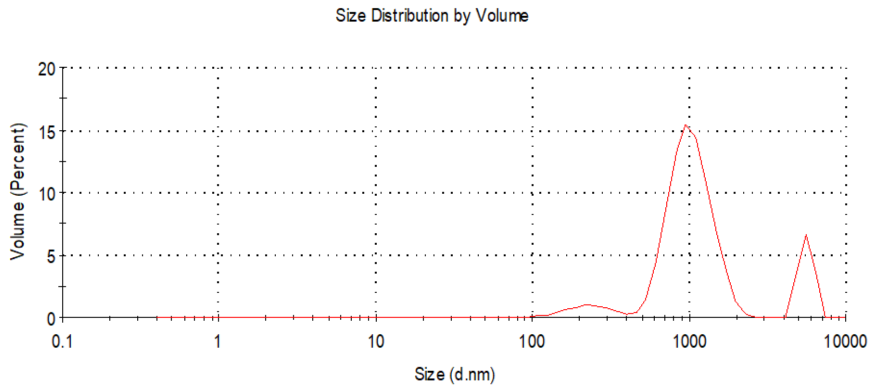
To estimate the success of the grinding the specific surface area and the particle size of carbons materials were measured before and after grinding. The Brunauer-Emmett-Teller method (BET) was used to measure the specific surface area. Dynamic light scattering (DLS) technique was used to analyze of particle size distribution.

Table 3.1 Average particle size depending on the grinding time

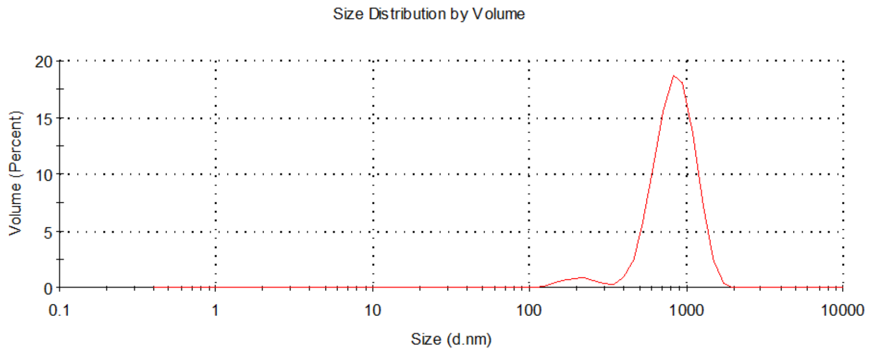
Grinding time, h	**Average particle size, nm**	**Homogeneity of the grinding**
0	2019	no
1	750	no
2	560	no
3	484	no
4	590	no
5	480	Yes

The results of the particle size distribution analysis of YP-80F activated carbon have shown that after 1 h grinding there were not significant changes in the particle size. The average particle diameter was still in microscale. The results of the particle size distribution analysis have shown that the decrease of the particle size to nanoscale occurs after 2 h grinding. If the particle average size of the initial sample was 2 µm then after 2 hour grinding the average particle size was measured 750 nm, see Table 3.1. But the sample was not ground homogeneously. The part of the sample was still with particle average size in microscale.

After 5 h grinding the result presented in Figure 3.1 shows more homogeneously ground sample with particle average size 480 nm compared to initial sample. Otherwise, despite the increase of the grinding time up to 5 h there is still some of the sample left to be unground properly with particle size in both nano and microscale as can be seen from the Figure 3.2 where SEM image of 5h ground AC is demonstrated.



(A) Initial distribution of AC



(B) Distribution of AC particle sizes after 5 h grinding

Figure 3.1 Particle size distribution of initial AC sample (A) and 5 h ground sample (B)

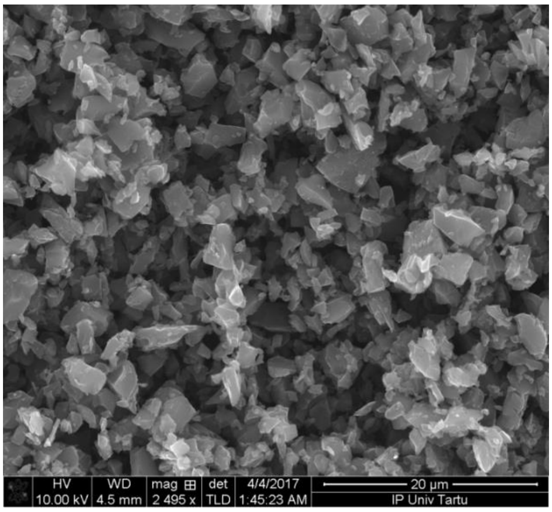


Figure 3.2 SEM image of 5 h ground AC

Basing on the results achieved by grinding the sample for 5 h BET analysis was performed to estimate the influence of grinding time on the specific surface of the sample. The results are presented in Table 3.2. From the results it can be seen that the specific surface area was not destroyed during applied grinding.

Table 3.2 BET analysis of 5 h ground Kuraray YP-80F

Sample	**Grinding time (h)**	**BET**		
		Sa (m^2/g)	**V (tot), cm^3/g**	**V (micro), cm^3/g**
Initial Kuraray YP-80F	0	2500	1,40	1,20
Ground Kuraray YP-80F	5	2174	1,08	0,15

As can be seen from the results that 5 h of the grinding is enough to achieve the particle size distribution in nanoscale without significant loose of specific surface area. Therefore, 5 h ground sample has been chosen for further study.

3.2 Choosing of ionic liquid

Activated carbon is often used in supercapacitors. However, the unsuitable dispersion of AC in polymer matrices presents major challenges due to the inconsistency between AC and polymer matrix, especially for large-scale industrial applications. The improved dispersion can be reached by the covalent modification of AC surface; however, the surface modification usually disturbs the π-electronic structure of carbons and diminishes the mechanical, electrical and capacitive properties of carbons. ILs have been found to have strong 'π-cation' interactions with carbons, and therefore can be used as a good dispersive and conductive additive to fabricate non-covalent Polymer/AC composites. [27]

Ionic liquids (ILs) are composed exclusively of organic cations and organic/inorganic anions. The nature of cations/anions plays a key role in determining the physicochemical properties of ILs, and consequentially affects the structure and capacitance of EDLs. The conductivity of an ionic liquid mainly depends on the mobility of its cation because in general the diffusion coefficients of ILs cations are higher than anions. Ionic liquids based on imidazolium cations usually show the highest ionic conductivity (~1 and 10^{-1} S/m) [28]. However, the highest conductivities can lead to the lowest electrochemical stabilities. When conductivity and electrochemical stability are both required in an application, such as in supercapacitors, imidazolium-based ILs with stable anions e.g., tetrafluoroborate (BF4) or acetates (Ac), halogens are applied.

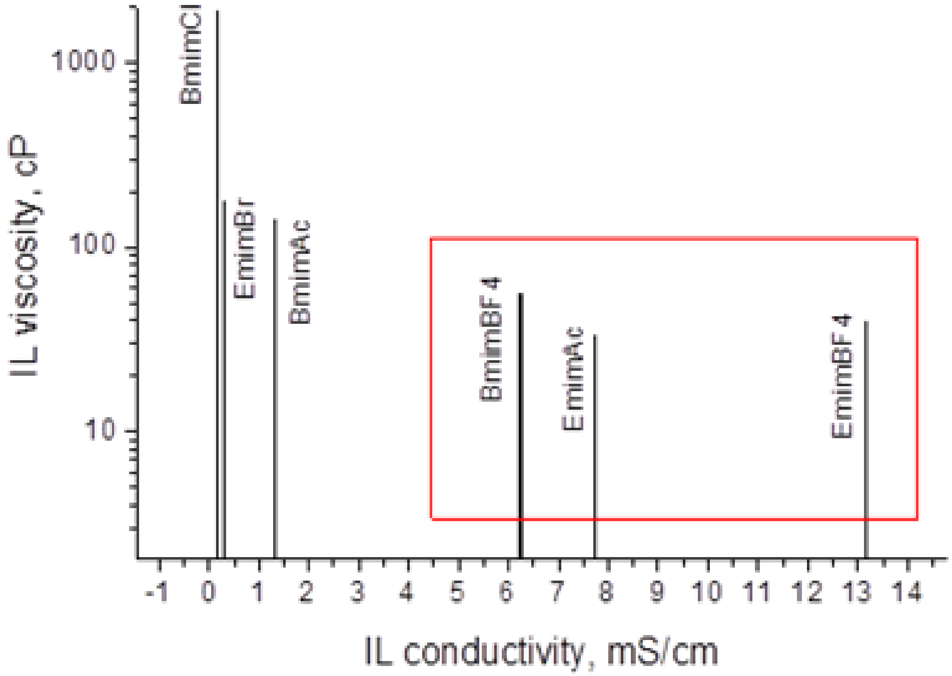


Figure 3.3 Plots of viscosity of ionic liquid (IL) vs. electrical conductivity of IL

In our work several imidazolium-based ILs with different anions (chloride, bromide, acetate, BF4) were used and their physical properties were evaluated. Imidazolium cation was also varied: 1-ethyl-3-methylimidazoilum (Emim) and 1-butyl-3-methylimidazoilum (Bmim) cations were used. Figure 3.3

shows the plot of IL viscosity vs. IL electric conductivity. As it is seen the ionic liquids with acetate (EmimAc) and BF4 anions (EmimBF4 and BmimBF4) show the lowest viscosities and in the same time the highest conductivities which make them the promising candidate for using in EDLs.

However, before using these ILs in flexible EDLs the electrospinnability of ILs with polymer matrix should be evaluated.

For testing ionic liquids were added to polymer solution to see how they work with PAN. All prepared solutions contained 8% PAN in DMSO (by weight) and 5% of IL to the weight of the whole solution. This solution was mixed mechanically for 24h at 50 °C. Firstly, the conductivity of solution was measured. Obtained values can be seen in Figure 3.4. Polymer solution had a conductivity of 0,02 mS cm^{-1}, so it is clear from the figure, that addition of IL greatly increases the conductivity of solution. The ionic liquids with BF4 and bromide anions showed the best results. $EmimBF_4$ was of the highest conductivity.

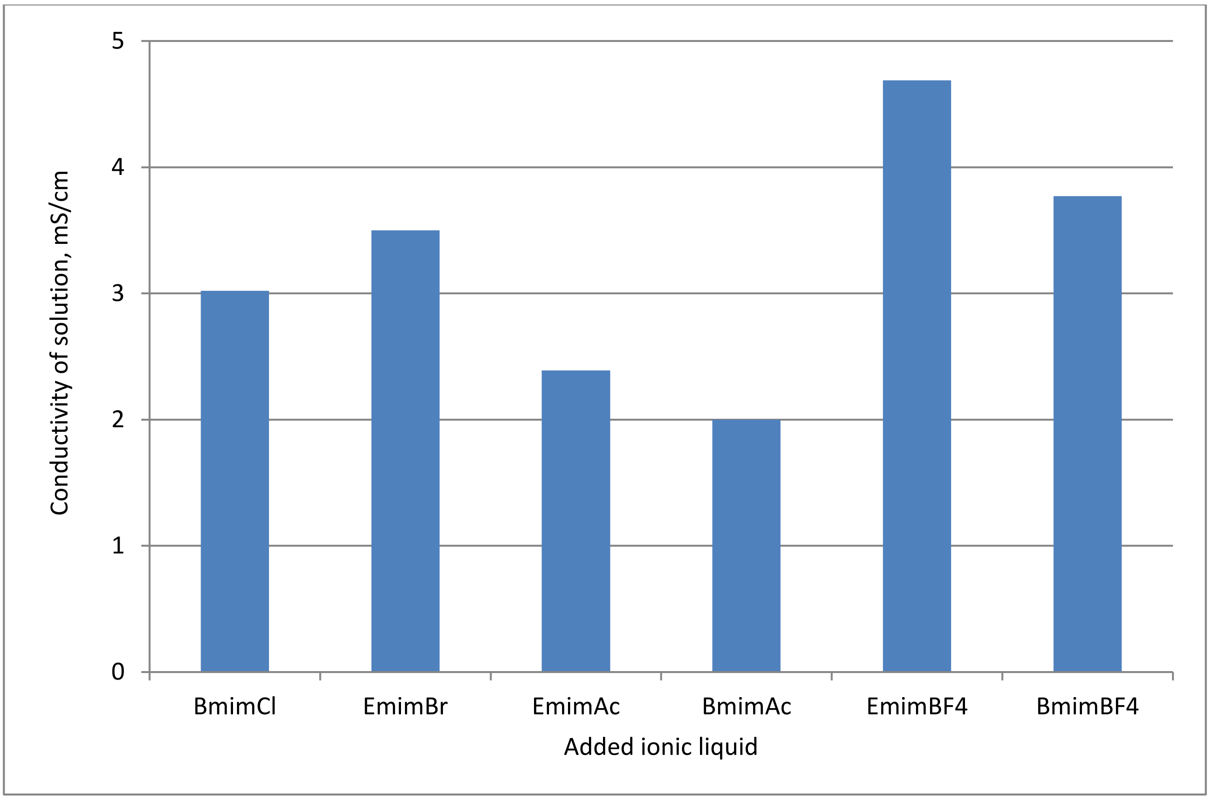


Figure 3.4 Conductivities of solutions containing 8% PAN in DMSO + 5% IL

All listed ILs were electrospun with polyacrylonitrile (PAN) at identical solution and electrospinning conditions. Figure 3.5 shows the SEM images of PAN+IL electrospun membranes.

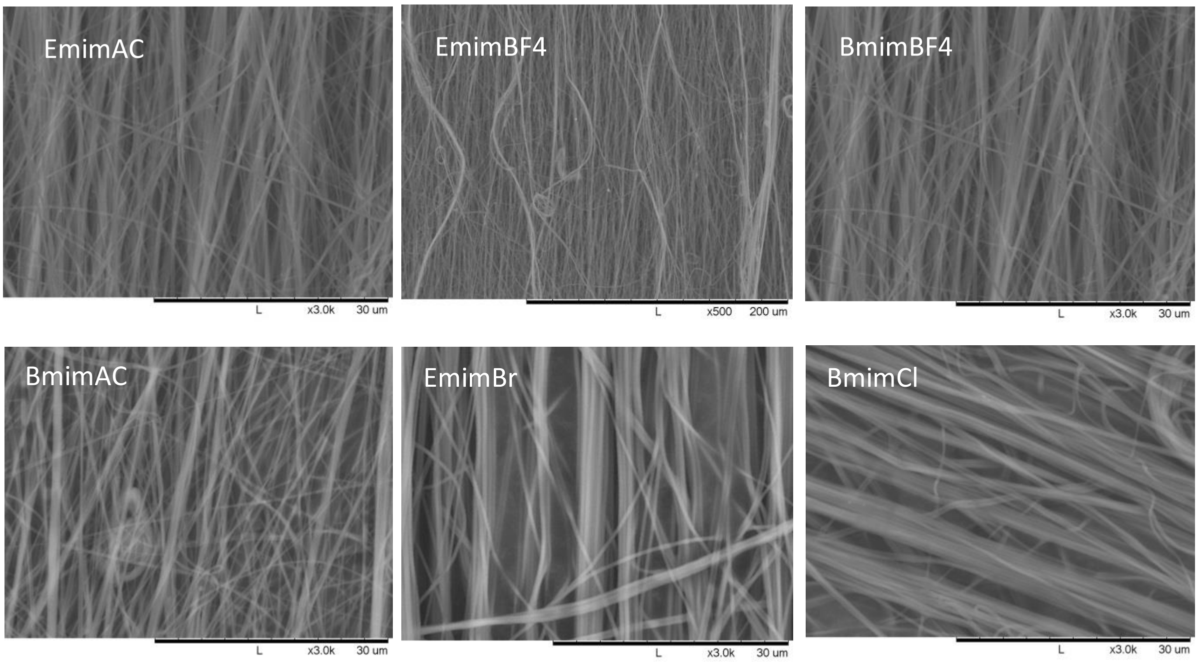


Figure 3.5 SEM images of PAN+IL electrospun membranes.

All PAN+ILs solutions could be easily electrospun. All the fibers irrespective of used ILs are beads-free, uniform in size and of submicron diameters. It is well known that the fiber diameter is affected generally by viscosity of electrospinning solution. Taken into account that both the concentrations of PAN in solution and PAN/IL ratios were the same for all tested systems, it is possible to evaluate the effect of IL viscosity on average fiber diameter of electrospun membrane, which is presented in Figure 3.6.

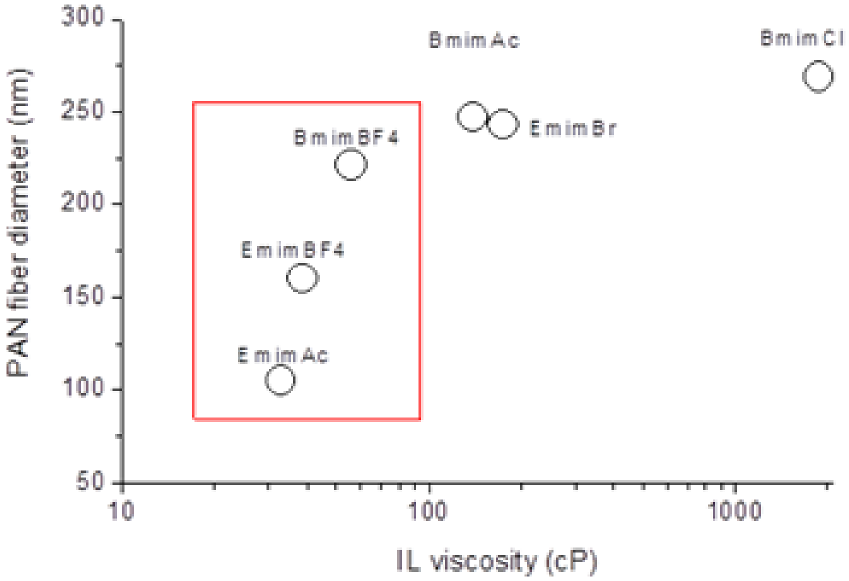


Figure 3.6 Effect of IL viscosity on average diameter of PAN+IL fibers

As seen from Figure 3.6, the thinnest fibers are observed for three ionic liquids: EmimAc, EmimBF4 and BmimBF4, which simultaneously have the higher conductivity and the lower viscosity comparing to other ones as it was shown above. The smaller the fiber diameter, the better is the mechanical properties of membranes. Therefore EmimBF4 and BmimBF4 are the best candidates to be used as impregnation material for carbons. EmimAc is a good candidate too, but is initially skipped due to the corrosive behavior.

From those 6 ionic liquids tested, EmimBF4 was chosen to continue working with. It was chosen due to highest conductivity of polymer/IL solution and lowest fiber diameters obtained by electrospinning.

3.3 Preparation of fibrous PAN/AC/CB electrodes by Method 1

3.3.1 Method of preparation

Preparation processes, which especially include strong shearing of the polymer/filler mixture, can affect the conductivity properties of the polymer composite. As it has been observed by several authors during mixing the composite, the mixing time, temperature and order of adding of the materials will strongly affect the conductivity of the composite [29-31]. Therefore, the process of composite preparation should be carefully studied and a well-balanced system with the homogeneous dispersion of carbons and a noticeable conductivity improvement should be achieved.

In this work two main preparation procedures have been applied and studied – Method 1 and Method 2. In both methods the combination of sonication and mechanical stirring is used. Sonication treatment offers a great potential in the processing of liquids and slurries to de-agglomerate and fragment of micrometer and nanometer-size materials, which can be both agglomerates of polymeric molecules and carbons aggregates. [32]

In this part Method 1 is mostly discussed and used. Prior to Method 1, the AC was mixed in different ways with PAN powder. Schematic representations of preparation ways are shown in Figure 3.7. Conductive CB has also been added to AC powder in ratio AC/CB=90/10. PAN/AC ratio was 50/50. Concentration of PAN in DMSO was kept the same 8 wt% to fulfill the requirements for continuous electrospinning process with formation of beads-free fibers. In some cases (Way 1 and Way 3) the sonication has not been applied at all, in other cases the carbons have been sonicated prior to addition of PAN to fragment the large aggregates of AC into smaller ones and achieve the best homogeneity of suspension.

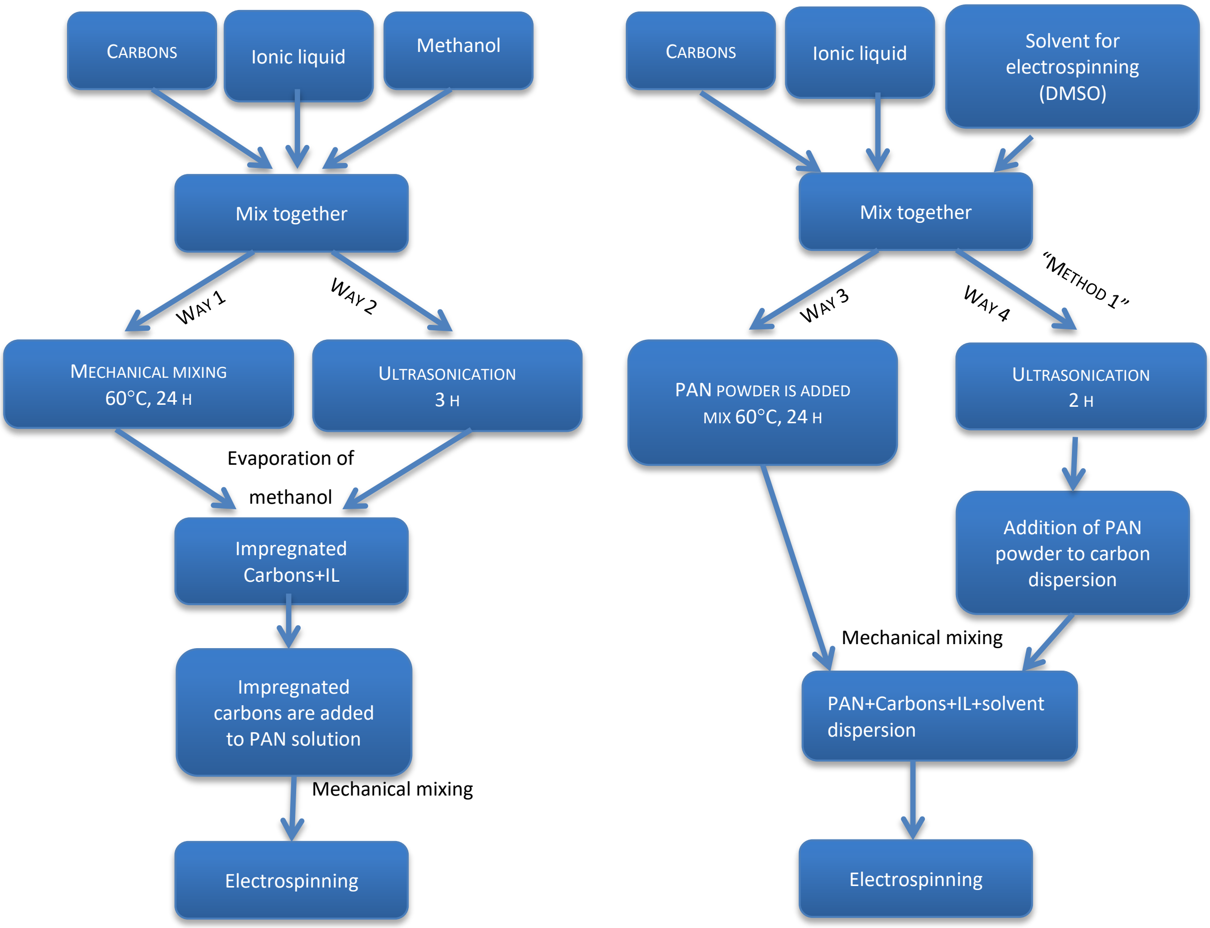


Figure 3.7. Different ways of preparation of PAN/AC/CB solutions. Method 1

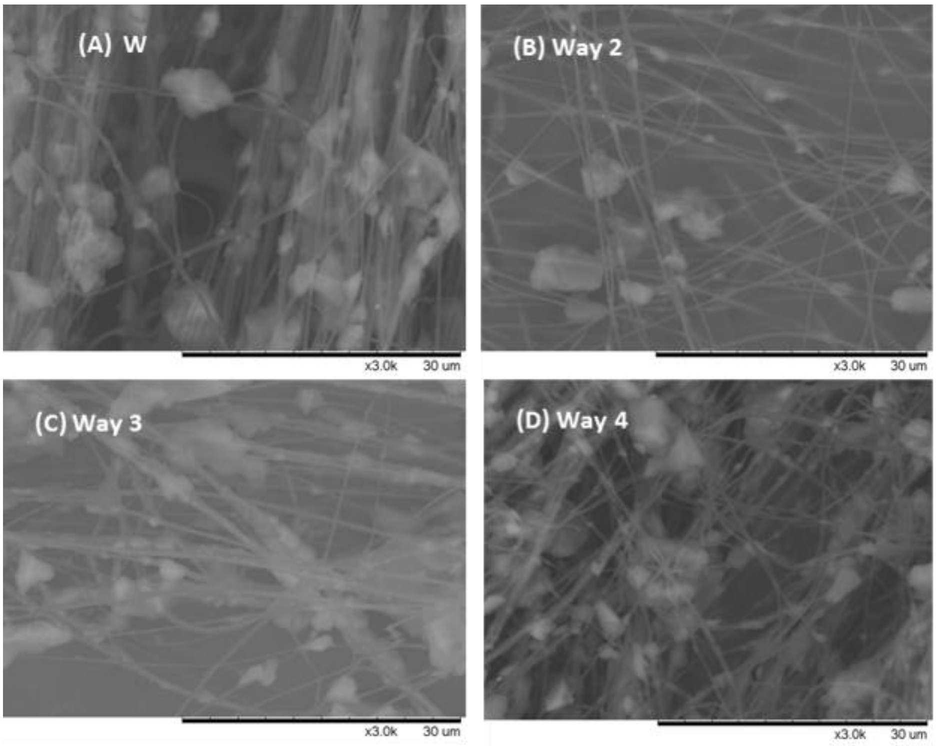


Figure 3.8. 3000x magnified SEM images of PAN/AC/CB samples prepared by different ways

Samples prepared by Way 1 shows the presence of high amount of large carbon aggregates comparing to the other ways, as can be seen from SEM images of fiber mats presented in Figure 3.8. Additionally, the average fiber diameter of this sample (irrespective of carbon aggregates) is the biggest from the other ones, as can be seen from the Table 3.3.

Table 3.3 Properties of PAN/AC/CB samples, prepared by different ways

Way	**IL content, wt%**	**PAN/AC**	**Fiber diameter , nm**	**Conductivity, μS/cm**
1	5	50/50	300	0,02
2	5	50/50	150	0,03
3	5	50/50	250	0,37
4	5	50/50	230	2,26

Due to the presence of large aggregates and bad connection between them, this sample shows the smallest electric conductivity compared to others, as can be seen from the Table 3.3.

Sample prepared by Way 2, has the best morphology, because the fibers seem to be uniform in size and there are the least agglomerates. From the Table 3.3 it can be seen that fibers have smallest diameters. However, this sample does not show any enhancement in conductivity value, and become only a little bit larger than that of the first method.

Sample prepared by Way 3 by their morphology is comparable with Way 4 (see Figure 3.8), but with the thinner fibers (see Table 3.3). It also shows a great improvement in conductivity values, becoming in 10 times higher than values for previous two methods.

However, as it is evident from Fig. 3.8, Way 4 with sonication of carbon dispersion helps to separate carbon agglomerates and makes more homogeneous suspension. Fiber diameter and morphology in this method are not drastically changed, but conductivity shows the highest value among all other ways of preparation. It can be concluded that the sonication of carbons in solvents for electrospinning is the best option both for impregnation of porous carbon materials with IL and their further dispersion in liquid media. Therefore, Way 4 has been chosen as general method for preparation of PAN/AC/CB solution for electrospinning and will be further named as Method 1.

Properties of PAN/AC/CB samples prepared by Method 1 are shown in Table 3.4.

Table 3.4 Parameters and properties of PAN/AC/CB samples, prepared by Method 1 (way 4)

Sample code	PAN/AC	AC/CB	EmimBF4 content, wt%	Electrospinnability	Fiber diameter, nm	Conductivity of mat, μS/cm
CB-1	50/50	99/1	5	Fibers	700	0,1
CB-2		90/10	5	Fibers	300	2,3
CB-3		97/3	10	Fibers	700	6,4
AC-1	40/60	100/0	10	No fibers	-	-
CB-4		90/10	10	Low amount of fibers	220	-
CB-5		80/20	10	Fibers	270	39,4
CB-6	35/65	90/10	10	No fibers	-	-
CB-7		80/20	10	No fibers	-	-
CB-8	30/70	90/10	10	No fibers	-	-

3.3.2 Effect of pressing conditions on electrode conductivity

Most of the mats produced via electrospinning are rather fluffy. It can lead to insufficient contact between the particles and as a result to low conductivity and capacitance values. To overcome this problem, two different pressing methods were tried and compared.

Before pressing the obtained nanofiber mat, namely CB-5, was divided into three parts:

1. First part is an initial sample without any actions on it
2. Second part has been pressed by roll press machine with minimal distance between rolls 0,1 mm. Rolls rotated in the opposite directions.
3. Third part has been pressed by flat plate press at 50 bars at room temperature. Pressing was done for 10 seconds.

After pressing, the conductivity of mat has been measured.

The conductivities of pressed mats can be seen in Figure 3.9. As seen from the results, there is a drastic difference between conductivities of differently pressed samples. The part of mat with no pressing exhibited very low conductivity. The best conductivity was achieved using flat pressing which means by using it, the fibers and particles are in better contact than with other methods.

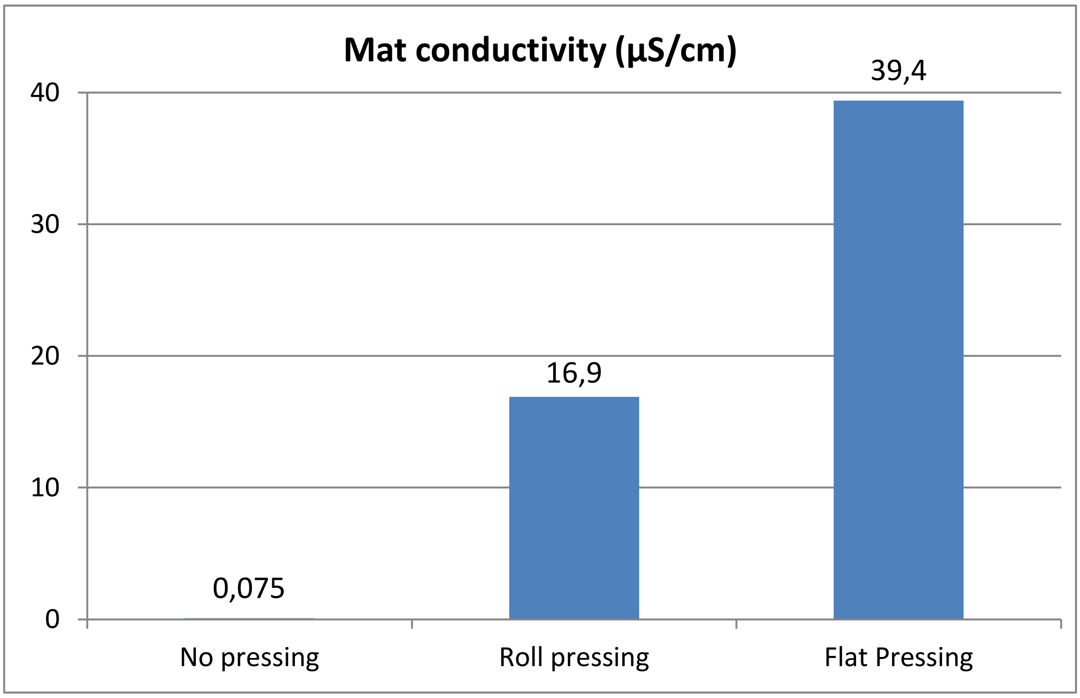


Figure 3.9 Conductivity of not pressed and pressed samples

Pressing of fibers can influence their fibrous morphology. To study the morphology, scanning electron microscopy was used and SEM images of samples can be seen in Figure 3.10. There are no any visible changes happened during pressing of the samples. All of them still have fibrous structures. It can be said, that pressing does not influence fiber structure, but just improve contact between carbon particles, making sample more compact and conductive.

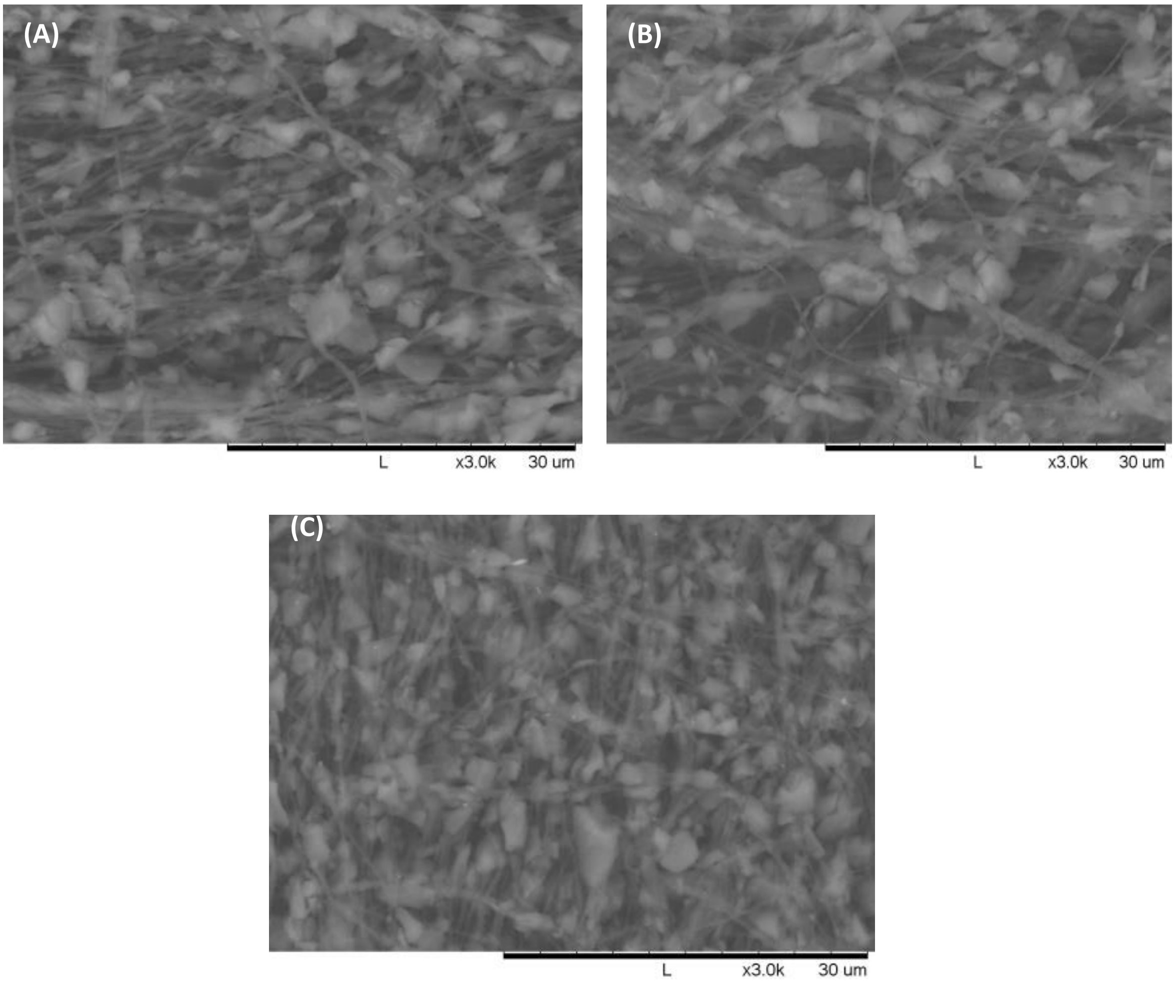


Figure 3.10 3000x magnified SEM images of (A) initial; (B) roll pressed; (C) flat pressed samples

In this work, all mats have been flat pressed using the conditions mentioned above before measuring the conductivity. The thickness of pressed samples has been taken into consideration.

3.3.3 Effect of AC loading

As it is known, the conductivity of polymer composites loaded with conducting filler depends largely on the content of fillers. As well, the capacitance of composite electrodes can also be affected by the amount of AC in composite electrode due to an increase in available surface area and micro-porosity. Therefore, to increase the conductivity and capacitance of PAN/AC/CB systems the content of carbon mix AC/CB in the composite was varied, so mixtures with PAN/(Carbon-mix)=50/50, 40/60, 35/65 and 30/70 were prepared by Method 1 (way 4) and compared, as can be seen from the Table 3.4 (above). Further this ratio PAN/(Carbon-mix) will be called just as PAN/AC. The ratio AC/CB has been fixed at 90/10 for all the samples.

Samples with 65% and 70% of active carbons were not possible to electrospin and powder-like product is produced (see Figure 3.11 (C), (D)). Samples with 50 and 60% of AC are electrospinnable and fibrous membranes have been obtained as can be seen from the Figure 3.11 (A) and (B), although sample with 60% AC had apparently bad mechanical properties.

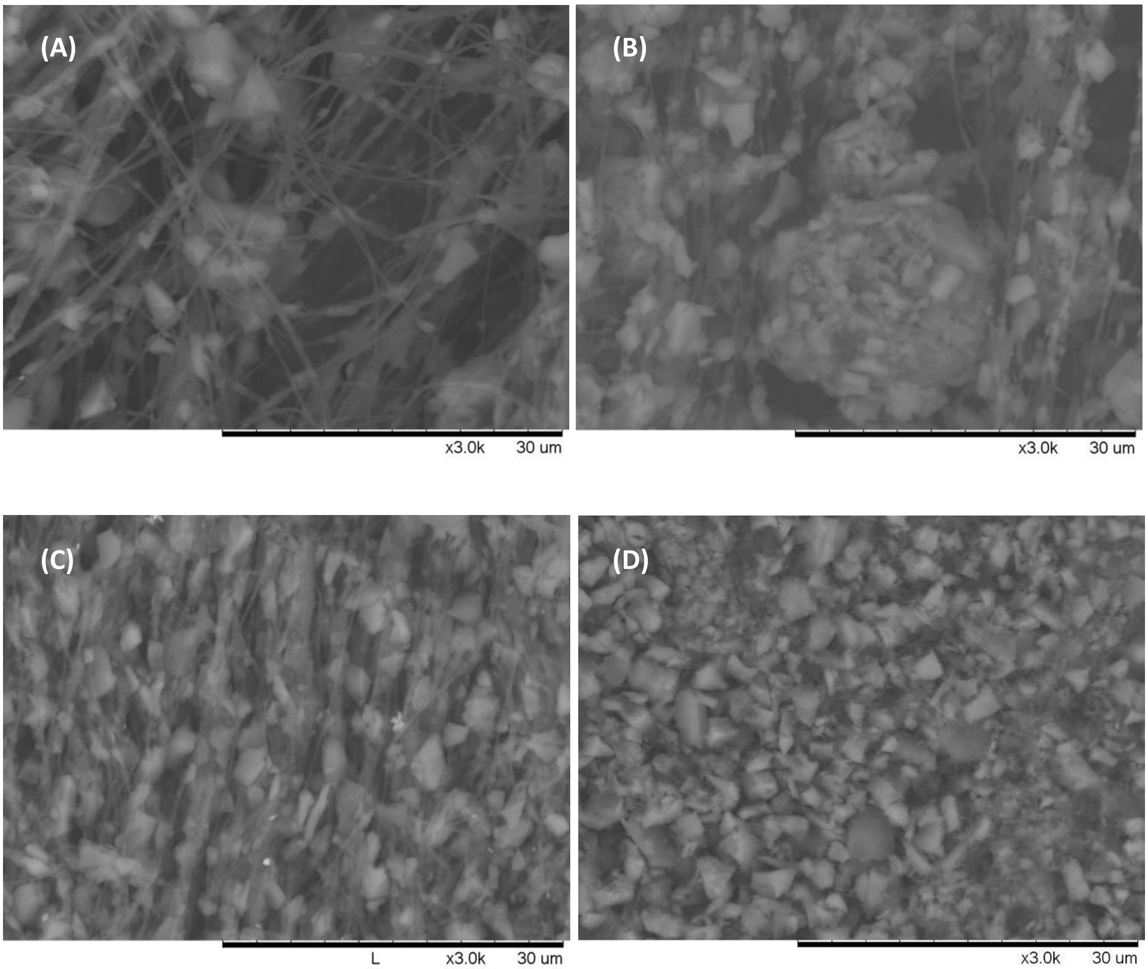


Figure 3.11 3000x magnified SEM images of samples containing PAN/AC: (A) 50/50; (B) 40/60;(C) 35/65; (D) 30/70

3.3.4 Effect of added conductive CB

To improve conductivity of AC-based electrodes, the special additive is used namely conductive carbon black (CB) Super C65. To study the effect of CB on morphology and conductivity of fibers, carbons mix of different ratios AC/CB have been added to PAN solution by Method 1 and electrospun. Composition of prepared samples is listed in Table 3.4. For this study the samples with the highest possible carbon content in final material (PAN/AC=40/60) were tested, namely samples AC-1, CB-4 and CB-5. The high AC content in final material is essential to fulfill the capacity requirements. The concentration of PAN in DMSO was 8% .

When the AC content is only 80% (and CB is 20%), see sample CB-5, the membranes with fibrous morphology are produced as can be seen from Fig. 3.12A. All the carbons are well distributed in the matrix.

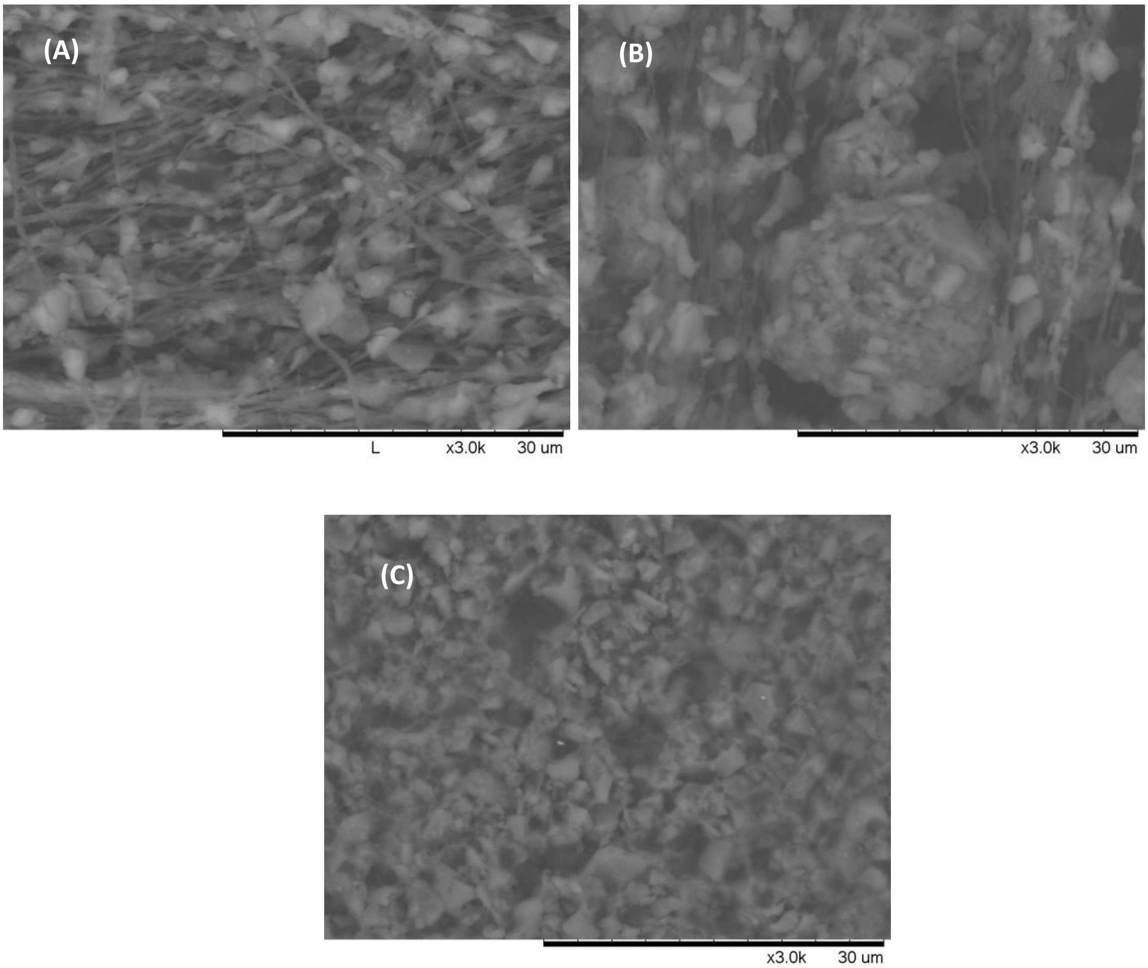


Figure 3.12 3000x magnified SEM images of membranes with various AC content. Ratio AC/CB: A) 80/20; B) 90/10; C) 100/0

With increasing AC content, the deterioration of fibrous morphology is detected − fewer fibers are produced. It is probably caused by attraction and entrapping of solvent molecules by carbon pores, less solvent amount is available for polymer dissolution. This in turn causes the creation of big “balls” of unsolved polymer molecules with AC as can be seen from Fig. 3.12 (B). That part of polymer which was able to be dissolved produces the fibers, but the amount of these fibers in membrane is negligible. With 100% of AC (no CB), sample AC-1, fibrous structure of membranes is disappeared totally (see Fig. 3.12 (C)). It results in deterioration of mechanical properties and fragile powder-like structure of obtained material. The prepared fiber mat was extremely fragile and it was not even possible to make any manipulations with it, including the conductivity measurements. Therefore, for samples CB-4 and CB-5 conductivity measurements have not been performed. Even if the conductivity of such samples were high enough, the poor mechanical performance would be an obstacle for its application elsewhere. So, it can be concluded that the presence of CB in amount more than 10% to the weight of porous ACs is compulsory to get fibrous structure of final product. However, it should be noticed that this amount (10% CB) can be the minimal only for materials having 40/60 PAN/AC ratio. For various PAN/AC ratios the minimal value of added CB (at which fibrous morphology is detected) can differ. Indeed, for 10% of CB by comparing Figure 3.11 (D) and Figure 3.12 (B), sample with 50/50 PAN/AC ratio (sample CB-2) shows much better fibrous morphology than 40/60 PAN/AC (sample CB-4).

3.4 Preparation of fibrous PAN/AC/CNT electrodes by Method 2

3.4.1 Method of preparation

To get high enough values of capacitance the content of AC in electrodes should be as high as possible. At the same time the level of conductivity should be preserved or even improved. As it was shown in previous sections to get PAN/AC/CB electrode with fibrous structure rather essential amount of CB (up to 20%) should be used in mixture with AC. This in turn will lower the relative content of active material (AC) in PAN/AC/CB electrode.

Therefore, in this work CNT has been tested as alternative to CB. It is expected that due to its tubular shape and high intrinsic conductivity CNT can be added in low enough amount (0,5–3%) to AC achieving the level of electrode conductivity identical to PAN/AC/CB samples or even higher.

PAN/AC/CNT samples with various CNT content have been tried to be prepared by Method 1 similar to PAN/AC/CB samples. However, as it turned out, Method 1 is not suitable for production defects-free fibrous PAN/AC electrodes based on CNT additives. Electrospinning process suffered from solution hardening at the top of the needle, bad deposition of the product onto collector and bad fibrous morphology of electrodes. As example, Figure 3.13 demonstrates the morphology of PAN/AC/CNT sample (CNT-M1), prepared by Method 1.

To achieve effective properties in nanofibers, the conditions for dispersing CNTs in polymer matrix need to be optimized. This is necessary for obtaining homogeneous fiber morphology and improving mechanical properties of nanofibers. Therefore, after different modifications and trials another preparation method has been elaborated and called Method 2. The description of the Method 2 is presented in Figure 3.14.

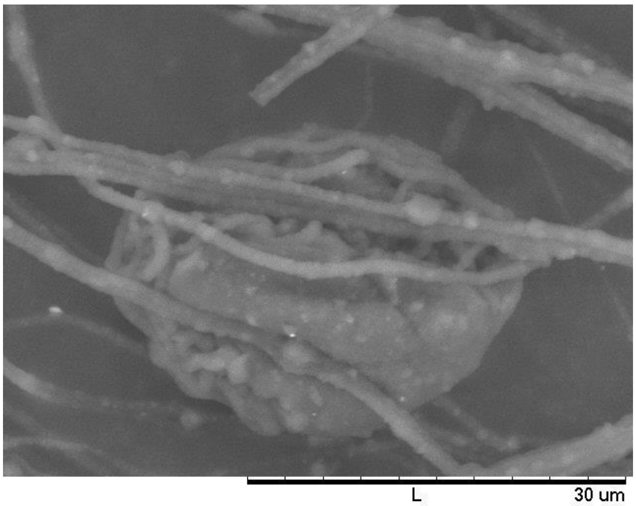


Figure 3.13 3000x magnified SEM image of sample CNT-M1 prepared by Method 1

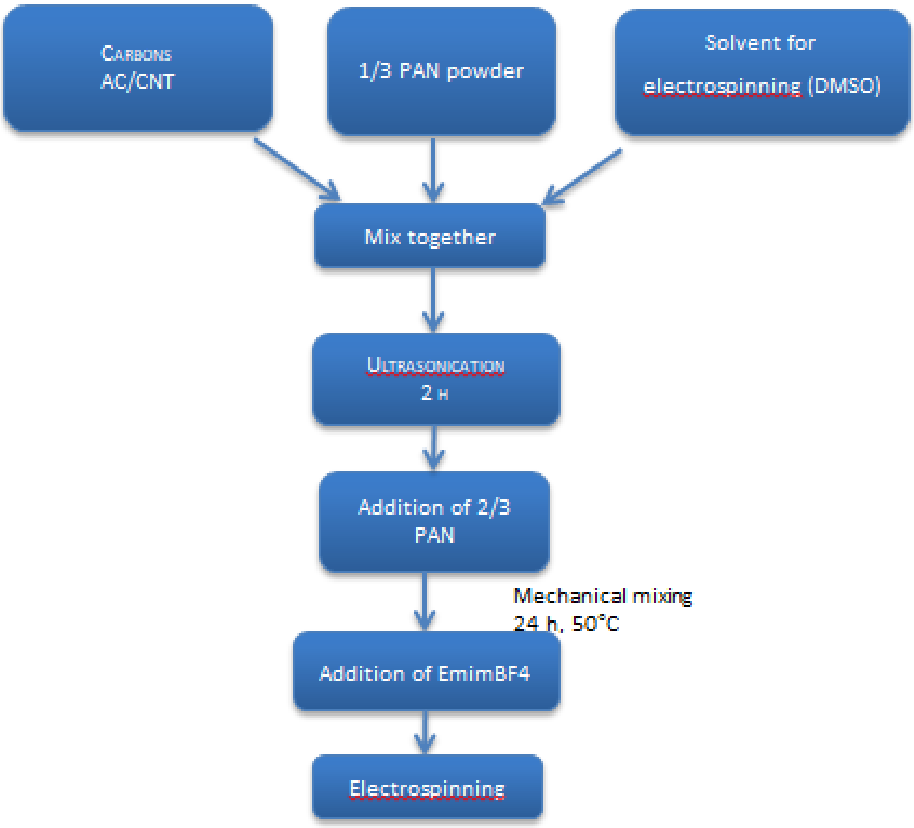


Figure 3.14. Description of solution preparation using Method 2

The main feature here is that 1/3 of PAN is added to carbon dispersion and sonicated. It was expected that it will improve the final homogeneity of PAN/AC/CNT suspension. Various PAN/AC/CNT electrodes have been prepared by Method 2 and electrospun. The composition of ectrodes along with their conductivity results are shown in Table 3.5.

Table 3.5 Parameters and properties of PAN/AC/CNT samples, prepared by Method 2.

Sample code	PAN/AC	Carbons: AC/CNT	EmimBF4 content, wt%	Electro-spinnability	Fiber diameter, nm	Conductivity of mat, μS/cm
CNT -M1 Method 1	50/50	97/3	10	fibers, some unsolved species	860	4,4
AC-2		100/0	10	Low amount of fibers, powder-like	-	-
CNT -1		99.5/0.5	10	fibers	415	5,4
CNT-2		99/1	10	fibers	690	9,0
CNT-3.1		97/3	5	fibers	240	2,6
CNT-3.2			10	fibers	570	13,5
CNT-3.3			15	fibers	1060	32,3
CNT-4	40/60	97/3	10	fibers	460	33,3
CNT-5	30/70	97/3	10	fibers, some unsolved species	660	43,5

3.4.2 Effect of IL content

Since it is known that ionic liquids have a great impact on conductivity, different amounts of it were added to solution and obtained electrospun mats were measured for their conductivity. In the compared samples, the solution used for electrospinning contained 8% PAN in DMSO and carbons mixture of 97/3 AC/CNT, see samples CNT-3.1 to CNT-3.3 in Table 3.5. The mass of carbons mixture was kept equal to the polymer one.

Solutions with different percentages of IL prepared by Method 2 were electrospinable. Obtained mats show fibrous structure (see Figure 3.15). It can also be seen, that with higher amounts of ionic liquid, the fibers tend to stick together more, so many bundles are present. The average fibers diameters (see Table 3.5) increase with the increase of the IL amount, which is probably due to sticking them together, so it is difficult to separate them from bundles.

The conductivities of mats can also be seen in Table 3.5. As it was expected, higher percentage of ionic liquid leads to an increase in the mat's conductivity. 15% of IL shows the best results regarding the conductivity, but this sample also has the largest fiber diameter and there are a lot of bundles observed in the SEM images.

For further research, 10% of ionic liquid to the weight of the whole solution was chosen. This amount showed a good increase in the conductivity with still nanoscale fibers. Also, it was easier to spin this solution than the one containing 15%.

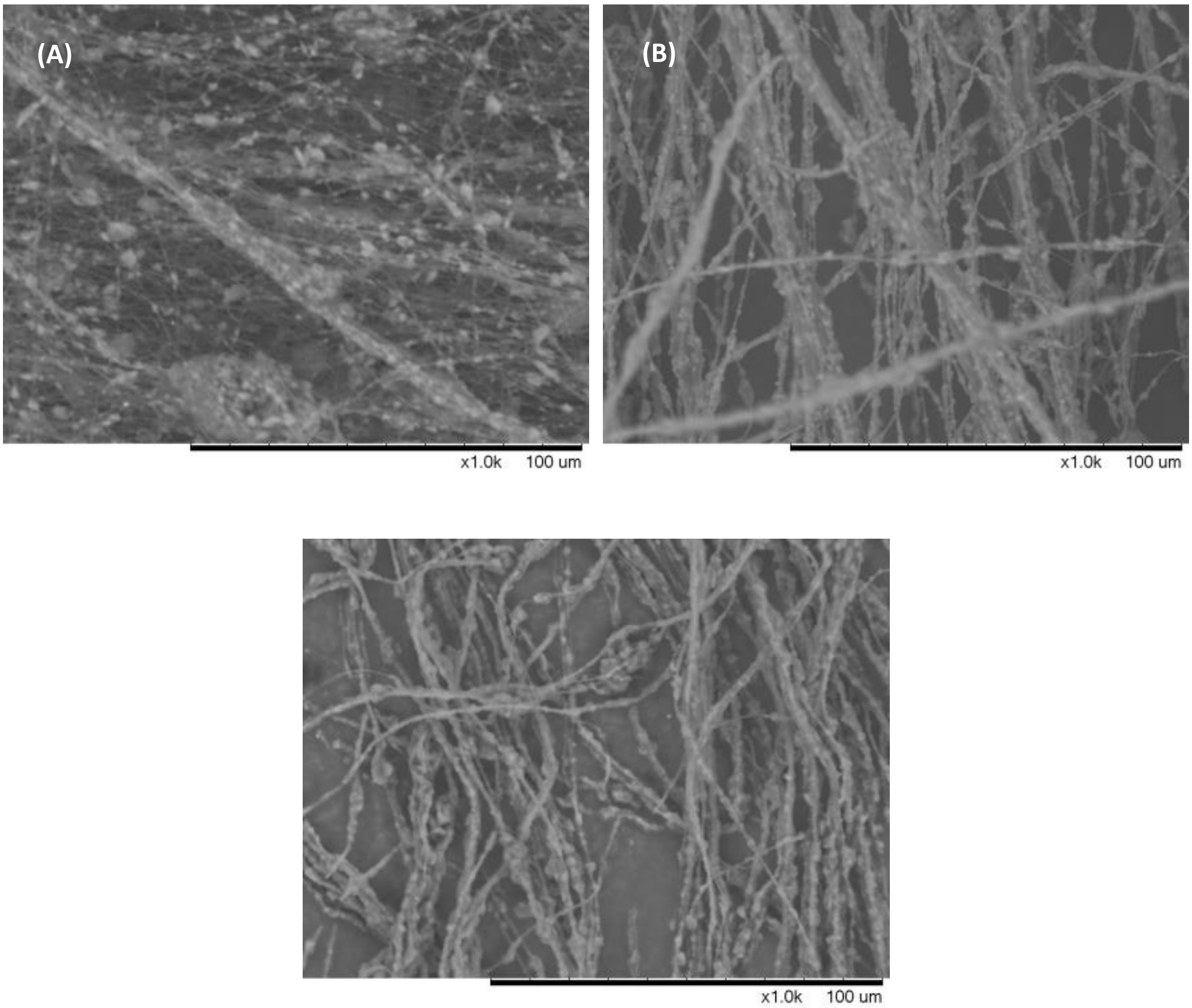


Figure 3.15. 1000x magnified SEM images. Solutions containing: A) 5%; B) 10%; C) 15% of ionic liquid.

3.4.3 Effect of added conductive CNT

The different amounts of CNT (see Table 3.5) has been mixed with PAN/AC, electrospun and analyzed. For this comparative study the samples with PAN/AC=50/50 has been chosen (see Table 3.5, samples AC-2, CNT-1 – CNT-3). IL content was fixed at 10%.

Figure 3.16 shows SEM micrographs of the electrospun Samples AC-2, CNT-1, CNT-2 and CNT-3.2. Polymer concentration and electrospinning parameters in all solutions were kept the same. As can be seen from Figure 3.16, Method 2, as expected, in contrast to Method 1, gives fibers with better morphology: they are more uniform in thickness and no big carbon aggregates can be observed. Moreover, sample AC-2 without any conductive additives shows better morphology than AC-1: if AC-1 does not show any fibrous structure (see Fig. 3.12 C), in sample AC-2 at least some imperfect fibrous morphology can be detected (see Fig. 3.16 A).

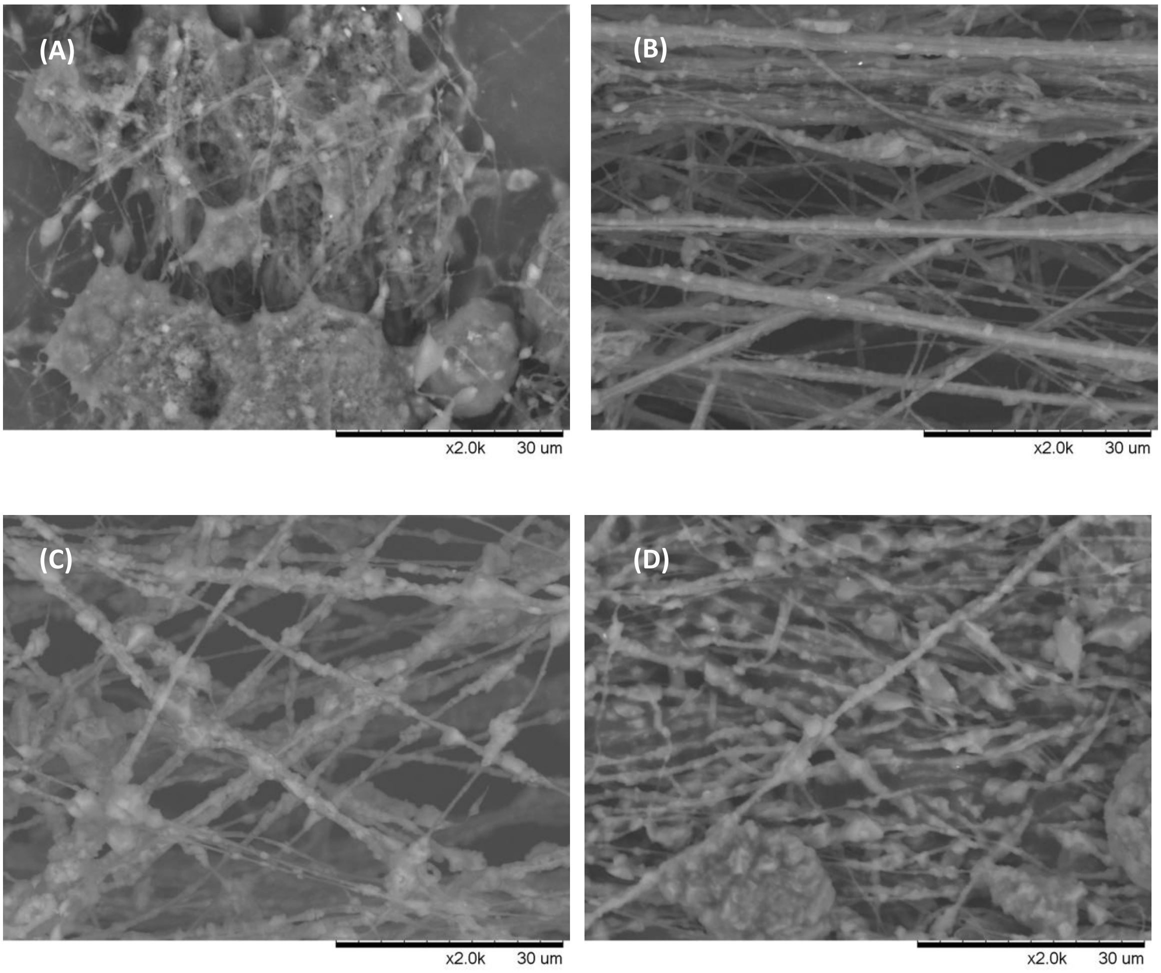


Figure 3.16 2000x magnified SEM images samples A) AC-2; B) CBT-1; C) CNT-2; D) CNT-3.2

The fiber diameters of samples PAN/AC/CNT prepared by Method 2 are thinner than those for Method 1 comparing the samples CNT-3.2 and CNT-M1, as example.

Due to beads-free morphology and homogeneity of thickness of fibers prepared by Method 2, the fiber mats have a good toughness and could be easily operated with. For such samples the conductivity measurements were conducted, the results are listed in Table 3.5. It is seen that conductivity of the samples has reached the high conductivity in Micro Siemens range if to compare with PAN/AC/CB samples prepared by Method 1. Samples CB-3 and CNT-3.2 both had 3% additive added and 10% IL. CB-3, prepared by Method 1, has twice lower conductivity than CNT-3.2, prepared by Method 2 (see Tables 3.4 and 3.5). This means that at the same amount of conductive additive, higher conductivity can be obtained when using solution preparation Method 2 and CNTs as conductivity enhancers. However, it should be noticed that fiber diameters of samples PAN/AC/CNT are thicker than those of PAN/AC/CB, see Tables 3.4 and 3.5.

By comparing samples CNT-1, CNT-2 and CNT-3.2, it is seen that the higher the amount of conductive additive, the higher is the conductivity of final fibrous PAN/AC/CNT electrodes. Like it was expected, the highest value of 3% of CNTs led to the best conductivity regarding the PAN/AC ratio of 50/50. Therefore, the ratio of AC/CNT of 97/3 was chosen for further testing.

3.4.4 Effect of AC loading

The effect of AC loading in PAN/AC/CNT composites has been studied. For this purpose three samples, CNT-3.2, CNT-4 and CNT-5, with various PAN/AC ratios were prepared by Method 2 and analyzed.

Figures 3.17 show the morphology and fiber diameters of studied samples. As can be seen, all samples have fibrous structure. However, sample CNT-5 with 30/70 PAN/AC shows non-uniform fibrous structure with lots of carbon agglomerates and low amount of fibers, which are also thin and weak - this mat did not have much elasticity and it was difficult to do any manipulation with it. The fibers of CNT-3.2 and CNT-4 seem to be uniform in size and no large agglomerates are present.

As can be seen from the Table 3.5, with increasing AC content, the electric conductivity of the electrodes is also increasing. The sample CNT-4 is comparable with the best CB sample CB-5 (Table 3.4) having conductivity over 30 µS/cm. It should be noted that the amount of conductivity enhancers is totally different regarding these two samples − CB-5 has 20% of CB, but CNT-4 has only 3%. Sample CNT-5 with 70% of AC shows the best conductivity at over 40 µS/cm, but the mechanical properties of this sample are not feasible.

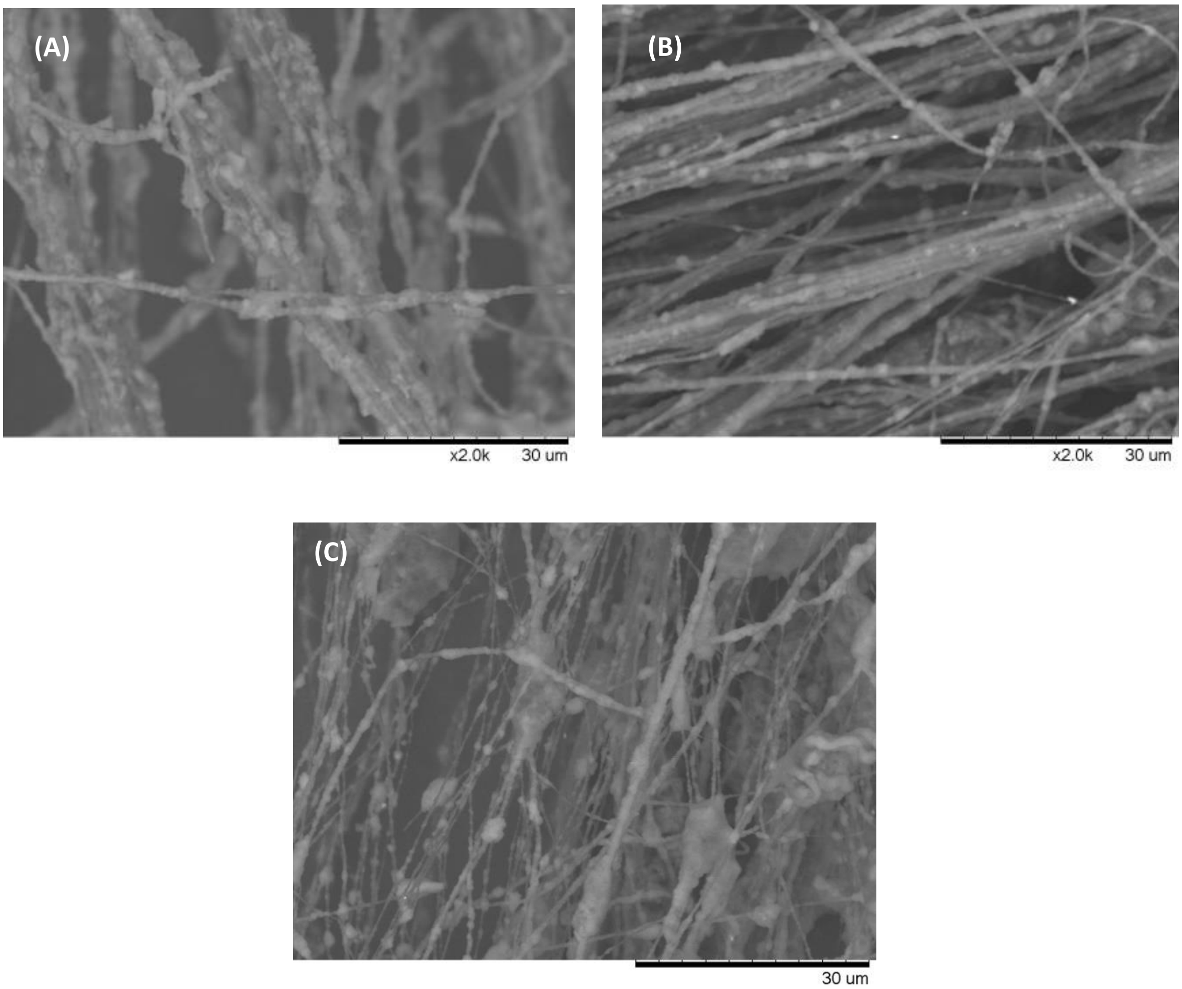


Figure 3.17. 2000x magnified SEM images of mats containing CNTs as enhancer with ratio of PAN/AC: A) 50/50; B) 40/60; C) 30/70

3.4.5 Effect of added conductive CB by Method 2

The difference in morphology and conductivity between PAN/AC/CNT and PAN/AC/CB electrodes can be the result of different methods of solution preparation. Therefore, several PAN/AC/CB samples have been prepared by Method 2 for comparative analysis with PAN/AC/CNT samples. The composition and results for such samples are shown in Table 3.6.

Table 3.6 Parameters of PAN/AC/CB samples, prepared by Method 2

Sample code	PAN/AC	Carbons: AC/CB	EmimBF4 content, wt%	Electrospinnability	Fiber diameter, nm	Conductivity of mat, μS/cm
CB-9	50/50	99/1	10	fibers	710	19,2
CB-10		97/3	10	fibers	720	20,8
CB-11		90/10	10	No Fibers	-	-
CB-12	40/60	97/3	10	fibers	770	57,8
CB-13	30/70	97/3	10	No fibers	-	-

The sample CB-13 was not possible to electrospun and no fibers were obtained. Figure 3.18 shows the SEM micrographs of samples CB-9 – CB-12. As can be seen, with addition of only 1% of CB (Fig. 3.18A) the fibrous morphology is rather imperfect − there are lots of agglomerates, fibers are not homogeneous in size. However, by comparing with Method 1 which give possibility to get fibers only with CB content higher than 3−10% (see Fig. 3.11), Method 2 gives fibers even without conductive additives (see AC-2). Comparing AC-2 (Fig. 3.16A) and CB-9 (Fig. 3.18A) the large improvement in fiber morphology can be observed. Addition of 3% of CB leads to rather good fiber structure with evenly distributed CB within fibers (see Figure 3.18B and D). Surprisingly, high amount of CB (10%) deteriorate the fiber morphology and the wetting of the membranes is observed.

Comparing the values of solutions conductivity, it was detected that Method 2 gives approximately the same or a little bit higher values than Method 1. Solution containing 97/3 AC/CB prepared by Method 2 had a conductivity of 7 mS/cm versus 6 mS/cm prepared by Method 1.

By comparison of samples CB-9 and CB-10, it is evident that the membrane conductivities are almost the same at around 20 μS cm^{-1}, which means that small difference in the amount of additive added into the carbons mix does not affect the conductivity.

The effect of varied PAN/AC ratio in PAN/AC/CB samples was tested too.

The ratio of AC/CB was fixed at 97/3. If sample CNT-5 with 30/70 PAN/AC ratio was electrospinnable, Sample CB-13 with the same PAN/AC ratio was not possible to electrospin and no fibers were obtained. Comparison of samples CB-10 and CB-12 shows that higher content of ACs leads to an increase in the conductivity of final membrane.

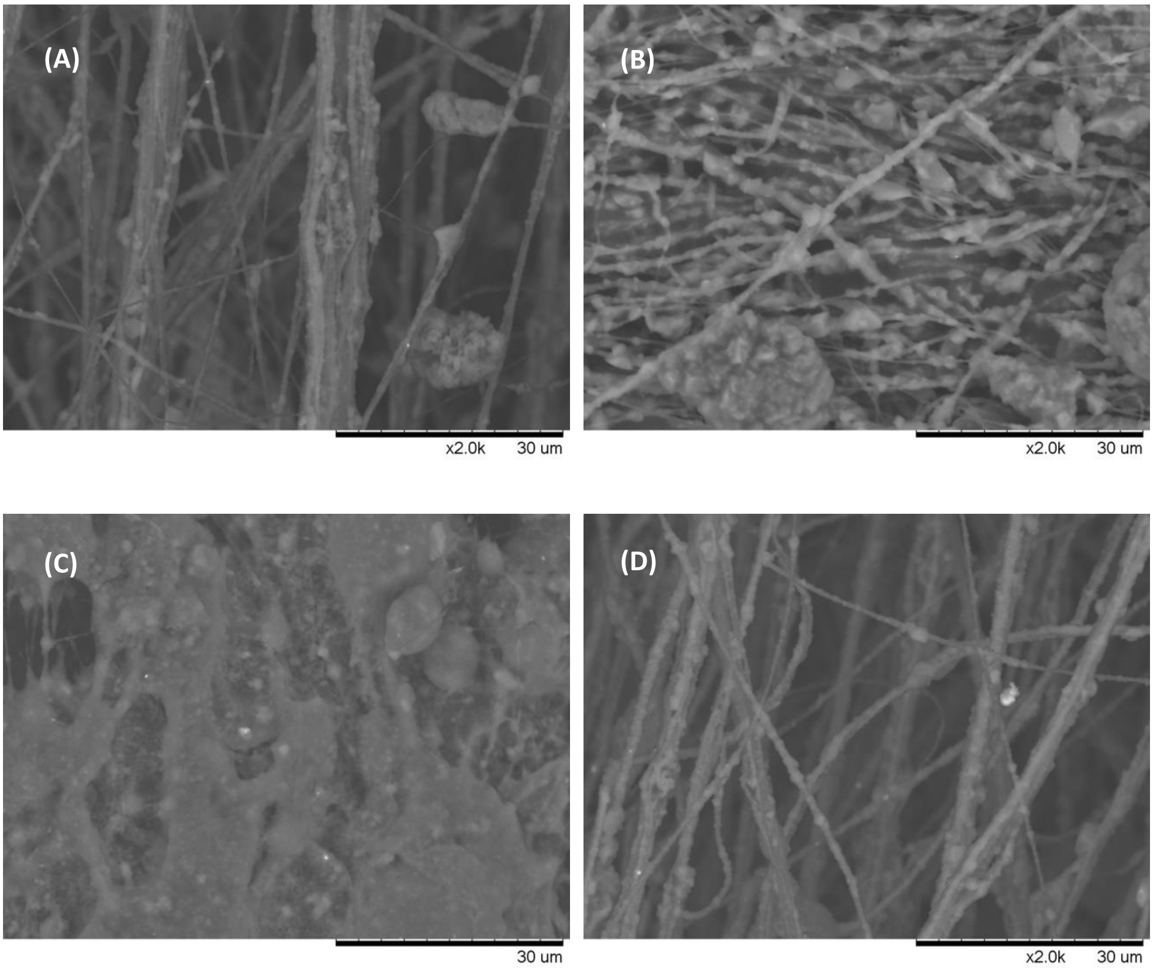


Figure 3.18 2000x magnified SEM image: A) sample CB-9; B) sample CB-10; C) sample CB-11; D) sample CB-12

By comparing PAN/AC/CB with PAN/AC/CNT samples prepared by the same Method 2, it is seen that an addition of CB leads to a better conductivity than CNTs and the difference is more than two times if compare samples CNT-2 and CB-9 (see Tables 3.5 and 3.6), where the same amount of additive was used. From morphological point of view samples with CB and CNT show rather similar fibrous structure with evenly distributed carbons within the fiber.

Finally, it can be concluded that Method 2 provides samples with better morphology, higher solution and electrode conductivities comparing with Method 1. The open question now how these two preparation methods and two types of composites (PAN/AC/CB and PAN/AC/CNT) will behave in EDLC cell. This will be discussed in next section.

3.5 Cyclic voltammetry and capacitive behavior of electrospun PAN/AC/CB and PAN/AC/CNT electrodes

For several electrospun electrode membranes the cyclic voltammetry (CV) has been conducted and electrochemical parameters like electrochemical stability window (V) and cell capacitance (F) have been evaluated. Considering that the mass of electrospun electrodes differ from cell to cell, and the mass of active material (AC) in electrodes are also varied, it is wiser to take the mass of AC in each electrode into consideration and calculate the specific capacitance of the cell (in F/g) by formula (2.3) presented in Experimental section. This formula uses integrated area under the CV curve, so the shape of the curve is taken into consideration. Note, that mass of PAN, conductive additive and IL have been skipped from calculation and only mass of active material, namely AC, has been taken into consideration. The results of these calculations are shown in Table 3.7.

Table 3.7. Composition and specific capacitance of the studied samples

Sample	Method	PAN/AC	Conductive additive (CA)	AC/CA	Specific capacitance to the weight of AC (±6%), F/g
AC/CB					
AC-0	casted	no PAN	CB	97/3	78
PAN/AC					
AC-2	2	50/50	no	100/0	20
PAN/AC/CB					
CB-1	1	50/50	CB	97/3	9
CB-10	2	50/50	CB	97/3	64
CB-11	2	50/50	CB	90/10	19
CB-12	2	40/60	CB	97/3	45
PAN/AC/CNT					
CNT-M1	1	50/50	CNT	97/3	6
CNT-3.2	2	50/50	CNT	97/3	61
CNT-4	2	40/60	CNT	97/3	44
CNT-5	2	30/70	CNT	97/3	35

To have the reference material with almost 100% porous coconut shell activated carbons (AC) the electrode AC-0 (see Table 3.7) has been prepared by standard conventional procedure of electrode preparation [33]. By this procedure, AC have been mixed with polymer binder PTFE (6% to the weight of carbons) and roll-pressed into thin flat film electrode. Activated carbons are poured over the PTFE/ethanol solution, constantly stirring to evaporate the solvent and mix the components. Then dough is placed into vacuum oven and baked under vacuum during several hours at temperature 105°C. After that dough is passed through roller gaps of roll press from 5 mm to 0,1 mm to reduce thickness to 0,12–0,13 mm. It is then baked at 150°C for 72 h to evaporate the residual solvent and moisture. This electrode AC-0 has been tested by cyclic voltammetry. The cyclic voltammetry curve for it can be seen in Figure 3.23. Specific capacitance was found to be 78 F/g (see Table 3.7). This value will be the reference which should be achieved by electrospun electrodes.

3.5.1 Effect of preparation method

First, samples CB-1 and CNT-M1 prepared by Method 1 have been tested and analyzed. All studied samples have been pressed at 85 bars and 75°C during 1 min before being assembled into EDLC cell. It should be notice here that fibrous electrospun electrodes have thicknesses around 0,012-0,030 mm after pressing, which are in 10 times thinner that casted electrodes and it is one of the advantages of electrospun electrodes. As can be seen from the Figure 3.19 the shape of CV curves is far from rectangular, which indicates non-EDLC behavior of the electrodes. It can be a result of both low electric conductivity and bad morphology of such type of electrodes. Therefore, this preparation method cannot be considered as successful.

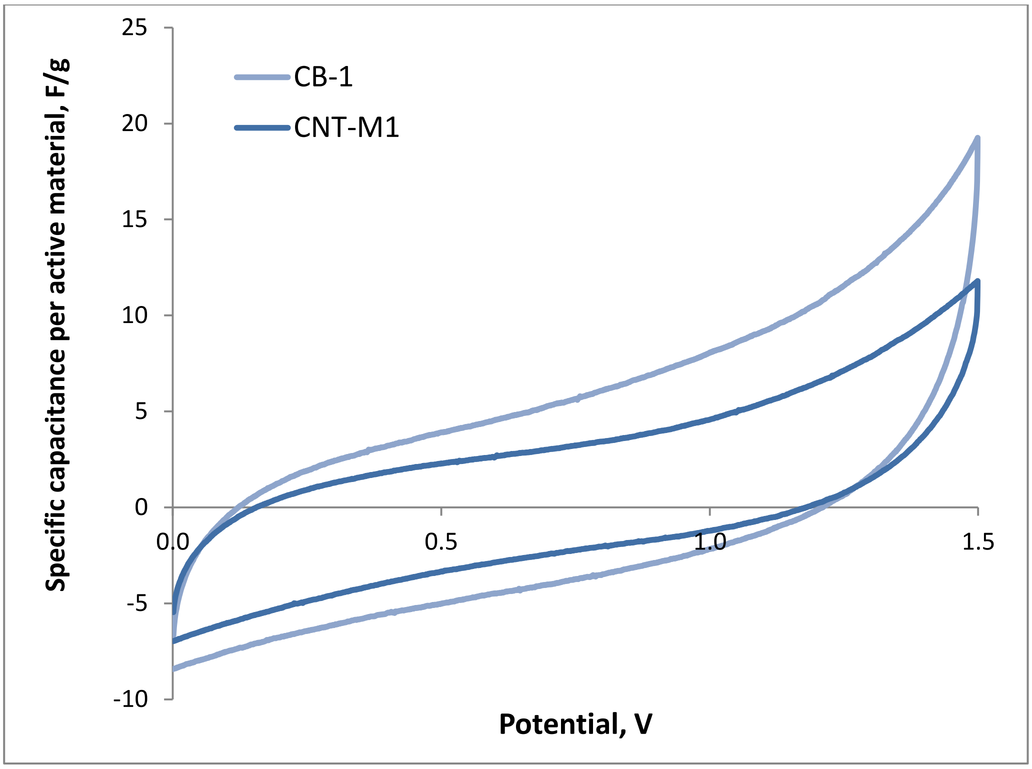


Figure 3.19. Specific capacitance (F/g) for electrospun electrodes CB-1 and CNT-3, prepared by Method 1. Sweep rate is 2 mV/s

Surprisingly, Method 2 has shown much better and promising results.

First of all, sample AC-2 with no added CB or CNT has been prepared by Method 2 and tested. The ratio of PAN/AC was 50/50. Figure 3.20 shows the cyclic voltammetry curve recalculated in terms of specific capacitance by formula (2.4). After normalization by sweep rate and recalculation in terms of specific capacitance, the Y-axis unit is F/g. Therefore, the Y-axis of a CV plot will be called as "apparent specific capacitance". Testing cells show an almost rectangular shape of the CV curve for different studied sweep rates. This indicates the capacitive behavior of the cell with a double-layer formation at the interfaces. However, during charge and discharge real capacitors can lose its power. This loss is formed by resistances in electrical contacts, electrolyte, and electrodes. This resistance leads to the slight increase in the current and two corners of the CV rectangle at the beginning of the charge and discharge process are smoothed. Therefore, the deviation from ideal rectangular behavior of the sample AC-2 can indicate increased resistances associated with PAN/AC electrodes due to presence of polymeric constituents and insufficient conductivity of electrodes due to improper fibrous morphology of this material. The obtained value of specific capacitance for this sample is only 20 F/g.

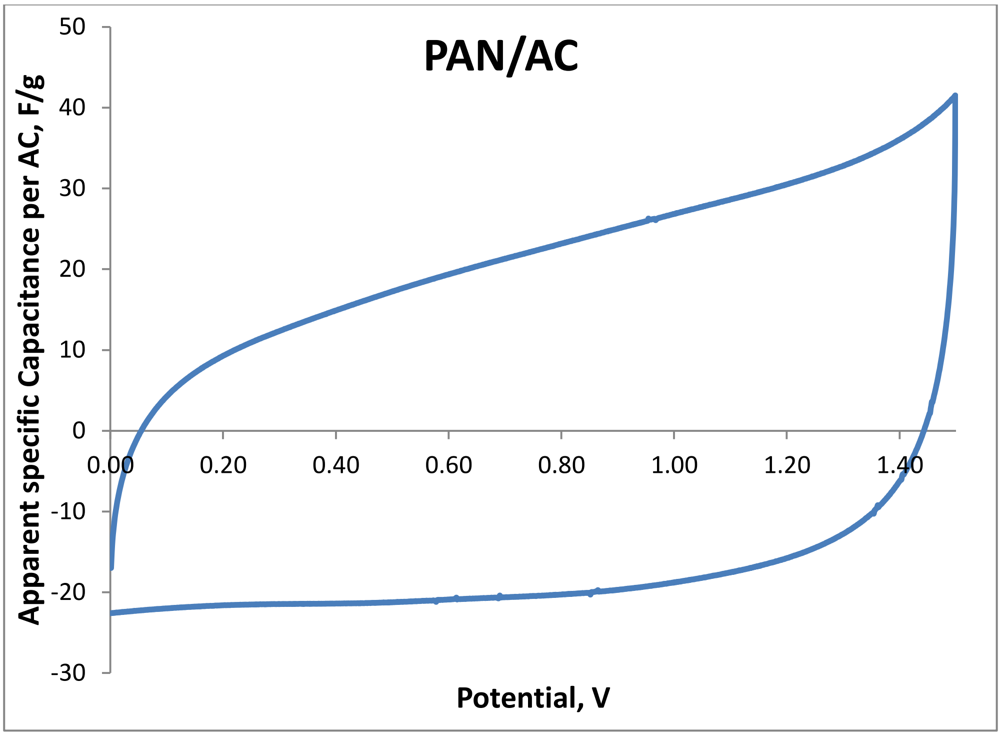


Figure 3.20. Specific capacitance (F/g) for electrospun electrode AC-2, prepared by Method 2. Sweep rate is 2 mV/s

Taking this into account the samples with conductive additives CB and CNT prepared by Method 2 have also been tested. The results are presented in Table 3.7. When conductive additives are added to PAN/AC composites the shape of cyclic voltammetry curves is significantly improved and close to rectangle as can be seen from the Figure 3.21 where PAN/AC/CNT electrodes are used. The same shape of the curves is observed for all studied PAN/AC/CNT and PAN/AC/CB electrodes prepared by Method 2. It can be a result of both improved conductivity and morphology of the samples compared to Method 1.

The effect of sweep rate on capacitance has been investigated. Sweep rates of 2, 5, 10 and 50 mV/s were used. The capacitor was held at 0 V for 10 minutes between the scans. The scan limits were set to 0 V and 1,5 V.

Differences occur in the current that increases with increasing sweep rate as can be seen from the Figure 3.21. As it is known, for ideal capacitors, CV curves normalized by sweep rate superimpose, and capacitance does not depend on the sweep rate.

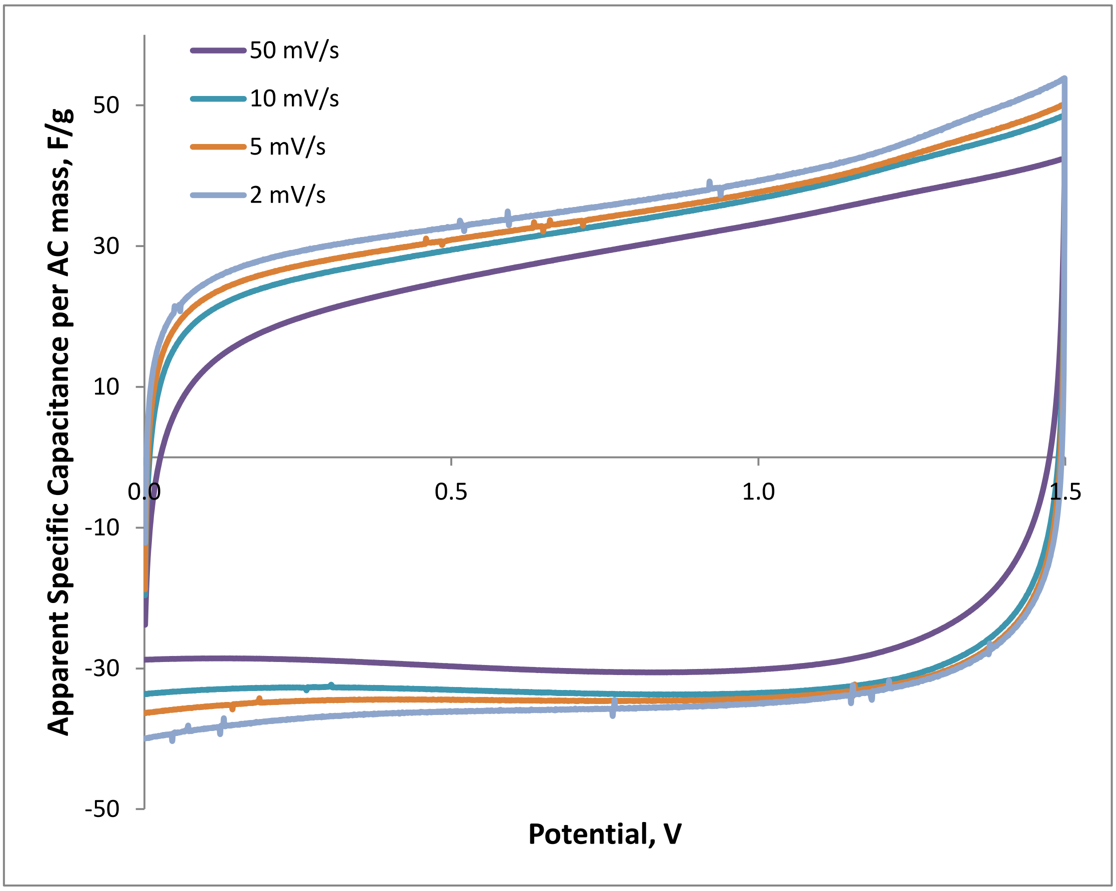


Figure 3.21 Cyclic voltammetry of the CNT-5 cell at various sweep rates. Method 2.

However, EDLCs are not ideal and normalized CV curves do not superimpose usually. In Figure 3.21, apparent specific capacitance with the highest sweep rate (50 mV/s) resembles the CV curve of an ideal capacitor with accounted resistance of electrodes. As sweep rate decreases (up to 2 mV/s), capacitance rises and shows stronger voltage dependence. This phenomenon is usually observed for voltage-driven chemical reactions.

The increase in apparent capacitance with decreasing sweep rate can be described by kinetically slow Faradaic reactions on the surface of electrode. Faradaic current has enough time to flow if sweep rates are slower, leading to an increase in total current and capacitance. An electrode surface having high resistance to electrolyte will not have time to reply to changes in voltage during a fast sweep. The similar sweep rate dependence has been observed for all studied PAN/AC/CNT and PAN/AC/CB fibrous electrodes.

It is known that capacitors can only operate within a “voltage window” with both an upper and lower voltage limit. Voltages exceeding this window can lead to electrolyte decomposition damaging the device. Commercial single-cell ECs currently have an upper voltage limit below 3,5 V. Therefore, in given study the range of the voltage window was also studied for all electrodes. As example, Figure 3.22 shows the CV response of the sample CNT-6 with a gradual increase in the voltage range from 1,5 to 2,7 V at the constant sweep rate of 50 mV/s.

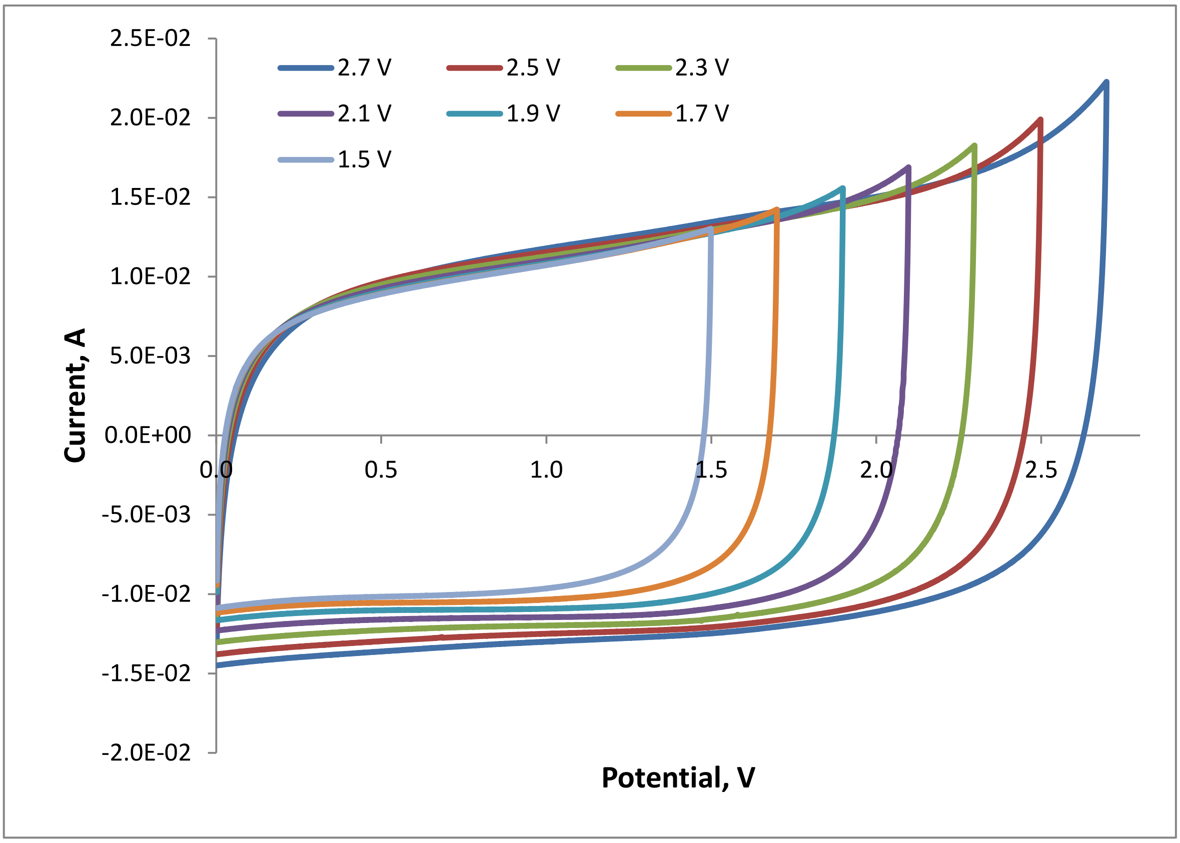


Figure 3.22 Cyclic voltammetry of the CNT-6 cells at various operating voltage windows. Sweep rate is 50 mV/s

With the increasing voltage limit applied to cell, the shape of the voltammetry curves remains the same at least until 2,3−2,5 V. At 2,7 V increasing current which indicates the beginning of electrolyte decomposition starts to be observed. The same behavior is observed for all other PAN/AC/CNT and PAN/AC/CB samples. This observation is attributed to the wide enough electrochemical potential windows of studied electrodes.

3.5.2 Effect of conductive additives and AC loading on capacitance

By comparing capacitance values obtained for PAN/AC/CNT and PAN/AC/CB with those of PAN/AC (sample AC-2) presented in Table 3.7 for the same 50/50 PAN/AC ratio, it is evident that an addition of even 3% of conductive additives (CNT or CB) to AC improves the capacitance in 3 times. The obtained value of ≈63 F/g for samples CB-10 and CNT-3.2 is comparable to the capacitance of conventional AC-0 electrode which is 78 F/g (see Table 3.7).

It is interesting that CB shows a little bit higher capacitance values than those of CNT. It can be explained by the fact that CB-based electrodes demonstrate the higher electric conductivities than

CNT-based as can be seen from Tables 3.4 and 3.6. The morphology of CB- and CNT-based samples is mostly identical. However, to be honest, this difference in capacitance between CB- and CNT-based electrodes is within experimental errors (6%).

The influence of PAN/AC ratio on capacitive behavior of electrospun electrodes has also been studied. Figure 3.23 shows the voltammetry curves in terms of apparent specific capacitance for samples CNT-3.2, CNT-4 and CNT-5 with PAN/AC ratios 50/50, 40/60 and 30/70, respectively. The ratio AC/CNT in these samples was fixed at 97/3.

As can be seen from the figure, increase in AC content does not improve specific capacitance; however, the shape of the curve is significantly improved. The higher the AC content, the lower the PAN content in electrodes and as a result the Equivalent Series Resistance decreases that leads to improving CV shape close to ideal rectangular. However, imperfect morphology of such samples and insufficient conductivity level are the reasons for low values of capacitance.

As can be seen from the Table 3.7, the same trend in capacitive behavior is observed for PAN/AC/CB samples: with increasing AC content the specific capacitance decreases, see samples CB-10 and CB-12. Perhaps, the fiber morphology of electrodes plays the main role here. It is confirmed by the fact that an addition of higher amount of conductive CB to the sample in order to improve conductivity does not enhance the capacitance at all: indeed, the capacitance of CB-11 with AC/CB=90/10 thrice lower than that for CB-10 with AC/CB=97/3 (50/50 PAN/AC ratio was fixed; see Table 3.7). The only the reason is that CB-10 has much worse fiber morphology and mechanical properties than CB-10 (see Fig. 3.18 B and C).

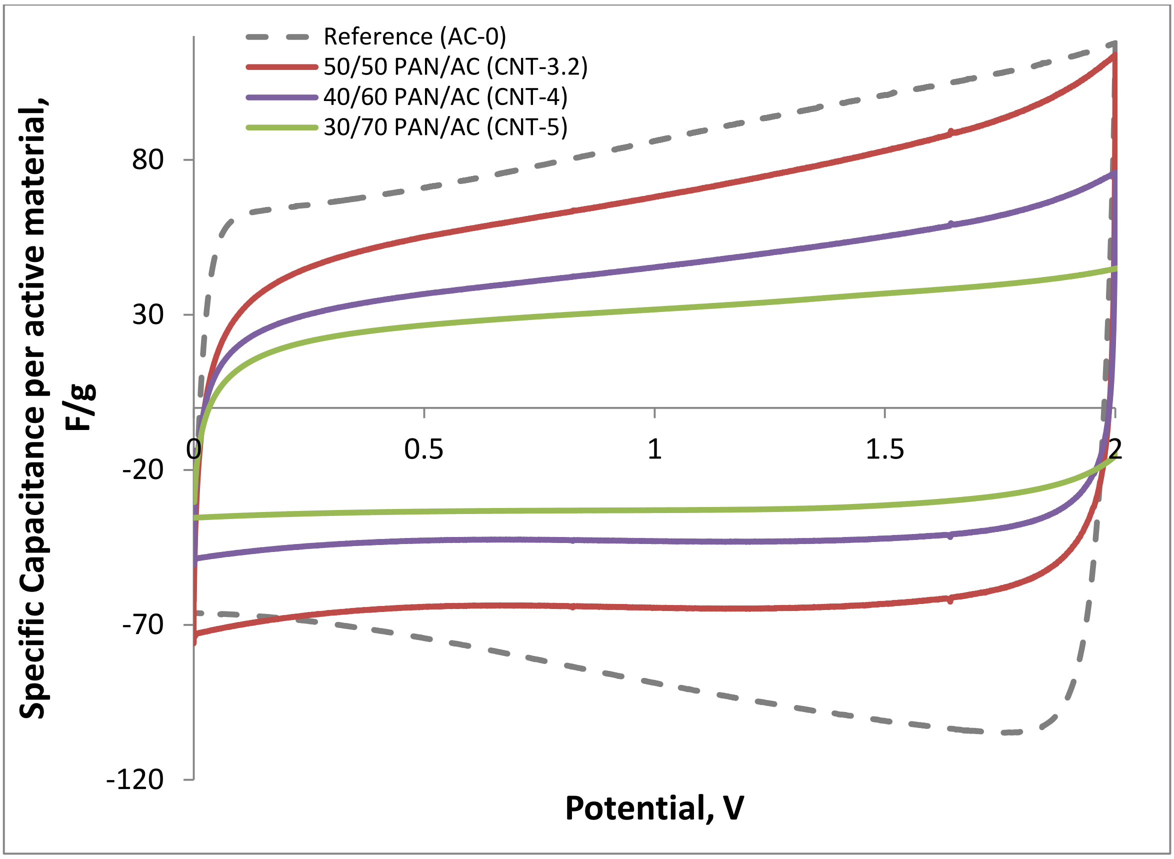


Figure 3.23. Effect of AC loading on voltammetry curves. Sweep rate is 2 mV/s.

Finally, up to now based on existing data it can be concluded that PAN/AC/CB and PAN/AC/CNT electrodes with 50/50 PAN/AC ratio and 3% of added conductive additive gives the best capacitance value of 63 F/g in average which is rather close to 78 F/g of reference AC electrode. It is believed that this value of capacitance can be further enhanced by finding the suitable compacting conditions of electrodes like applied pressure, temperature and time of pressing, drying of electrode before pressing or vice versa etc.

3.6 Conclusions

1. Comparing all methods, it has been concluded that the preparation of a stable AC/solvent suspension in presence of PAN under sonication is a very important initial step in producing homogeneous defects-free conductive fibers. Such method additionally allows producing strong enough fiber electrodes where all AC particles are bound to the polymer constituents and no free particles are present. In this case prepared electrodes show high enough electric conductivity and EDLC capacitive behavior with almost rectangular shape of cyclic voltammetry curves.
2. Addition of conductive additives (CB or CNT) improves the electric conductivity and general fibrous morphology. As a result, the specific capacitance of electrodes increases twice or thrice (up to 64 F/g) compared to the electrode with no conductive additives (20 F/g).
3. Increase in AC content does not improve specific capacitance; however, the shape of the curve is significantly improved due to the decrease in polymer content and as a result Equivalent Series Resistance caused by presence of polymer constituents in electrodes decreases as well.
4. Studied electrodes show wide enough operating electrochemical potential window (up to 2,5 V).

SUMMARY

In this work fibrous electrodes were prepared for supercapacitor's application. These were done using electrospinning process, which involves formation of fibers from a solution using high voltage. The electrodes for supercapacitors need to have high specific surface area and the electrospun membranes show great promise regarding that. As the polymer matrix for fibers, polyacrylonitrile (PAN) was used and the solvent was dimethylsulfoxide (DMSO). To give the electrodes capacitance, porous carbons were added to the electrospinning mixture, namely activated carbon (AC) made from coconut shell, which was preliminarily grinded to ensure the particles to be in nanoscale. For the purpose of increasing the conductivity of membranes conductive carbon conductivity enhancers were added together with AC. In this work commercially available carbon black (CB) and conductive carbon nanotubes composite (CNTs) were tested and compared. To prevent the AC pores from blockage by polymer and to increase the conductivity of solution ionic liquid was added to the electrospinning solution. Mainly two different solution preparation methods were used in this work. Both of them used ultrasonication technique, which helps to disperse carbon materials in the mixture. Obtained electrospun nanofiber membranes were measured for their conductivity, analyzed by scanning electron microscopy (SEM) and the most promising ones were tested in the electrochemical double-layer capacitors (EDLC) cells.

SEM analysis showed that almost all samples prepared via electrospinning had fibrous structure with fibers being in nanoscale. The carbon materials were also well dispersed. From the two methods tested, the one where 1/3 of PAN was added to the mixture prior ultrasonication gave the better results regarding the conductivity of membrane and also capacitance, so this method was further used. The addition of conductive additives (CB or CNTs) increases the electric conductivity and improves general fibrous morphology of the membrane. As a result, the specific capacitance of electrodes improves twice or thrice (up to 64 F/g) compared to the electrode with no conductive additives (20 F/g). Comparison of two additives shows that CB work better − both the capacitance and conductivity of membranes is bigger.

In this work the capacitance of fibrous electrode has reached the value (64 F/g) that is comparable with capacitance of conventional EDLC electrode material (78 F/g).

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