FULLY ELECTROSPUN DURABLE ELECTRODE AND ELECTROCHEMICAL DOUBLE-LAYER CAPACITOR FOR HIGH FREQUENCY APPLICATIONS

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ABSTRACT

Present work focuses on developing the method of producing carbon rich nanofibrous electrodes by electrospinning for supercapacitor electrodes. The influence of different polymer/carbon ratio to solution viscosity and conductivity were observed. Electrochemical behavior of produced electrodes was evaluated in triethylmethylammonium tetrafluoroborate ($TEMABF_4$) in acetonitrile (ACN) electrolyte by cyclic voltammetry method. The effects of various contents of polymer/ carbons to capacitance and mechanical properties are discussed. Results of experimental work showed that with electrospun fibrous mats in thickness below 20 µm, capacitance up to 121 F/g was achieved.

INTRODUCTION

Electrochemical capacitors are energy storage devices with long cycle life and fast charge-discharge capability [1]. Supercapacitors store energy using either ion adsorption (electrochemical double layer capacitors, EDLC) or fast surface redox reactions (pseudocapacitors). Traditional capacitor electrodes are produced in the form of film, activated carbon paste or carbon fabric. However, in recent years electrochemical capacitor electrodes have been also produced from electrospun nanofibers. Electrospinning as fiber forming process has found to be one of alternative methods to produce durable supercapacitor electrodes [2]. The advantage of the electrospinning method comes from the high specific surface area of the fibrous material, which is directly related to supercapacitor performance at higher frequencies. In addition, electrospun fibers have good mechanical properties including resistance to cyclic loading and vibrations [3]. Another advantage of the electrospinning is the inequality of the composition of fibers, which can be produced from the large variety of different polymers and polymer composites.

Therefore, the goal of this study is to develop electrospun fibrous flexible EDLC electrodes, which are suitable for high frequency applications with stable capacitance under specific environmental conditions.

EXPERIMENTAL

First, to achieve the aim of the study the polyacrylonitrile (PAN, Mw 150 000 g/mol, by Sigma Aldrich) was chosen as a binder. For the solutions and dispersions preparations dimethylformamide (DMF, Sigma Aldrich) was used as a solvent and ionic liquid (IL), 1-ethyl-3-methylimidazoliumtetrfluoroborate ($EMIMBF_4$) (produced by IoLiTec) as carbon dispersive and electric conductivity enhancing agents. The properties and electrospinnability of all solutions and dispersions have been studied. For developing the method of preparation of the carbide derived carbon (CDC) containing fibrous electrodes, titanium carbide derived carbon was used, with particle size 5 µm. Used CDC was produced by Skeleton Technologies OÜ. As the initial particle size of CDC was too large, grinding process was applied to reduce their size down to ~0.5µm. Retsch PM 100 planetary ball mills was used to grind the carbon particles by zirconium oxide balls. Then, to electrospin fibrous electrodes from polymer/carbon dispersions, two dispersion

preparation methods have been elaborated and tested. In both methods, the Node ultrasonic homogenizer Bandelin Sonoplus (Germany) was used with a 1 cm diameter nozzle to disperse the carbon particles in the solvent. Finally, mechanical strength and electrochemical behavior was studied for electrospun membranes. The electrochemical evaluation was done by cyclic voltammetry (VMP3, EC-lab software) mostly. Mechanical testing and vibration tests of the membranes/electrodes were also conducted.

1. Evaluation of the properties of electrospinning solutions and dispersions

The flow curves of all the solutions and dispersions were measured to study their shear viscosity. The rheology measurements were conducted with the Physica MCR 501 rheometer (Anton Paar, Austria) using the cone and plate method in continuous rotation mode. The measuring cone CP25-2 with a diameter of 25 mm and 2° angle was used for the measurements and the shear viscosity was measured at shear rates from 0,01 to 100 s^{-1}. The tests were conducted at room temperature.
The electric conductivity was measured for all the prepared solutions and dispersions using a conductivity meter (Metler Toledo Seven Compact) at room temperature.

2. Electrospinning setup and conditions

Samples were electrospun at room temperature and humidity, at the voltage of 10 kV, the distance between spinneret and collector of 10 cm and the pumping rate of 0.2 ml/h. The membranes were electrospun to the drum collector with dimensions of 10 cm in diameter and 5 cm in width. As a spinneret the stainless steel needle with inner diameter of 0.1 mm was used, which connected to 1 ml plastic syringe.

Fig. 1. Electrospinning setup: spinneret with syringe pump (right), collector drum (left)

3. Electrochemical evaluation of EDLC cell

The capacitance of electrospun electrodes was studied in EDLC test cell. Cellulose based ion-permeable separator paper Nippon Kodashi with thickness of 2*25 μm (TF44-25) was used in measuring EDLC cell.

From electrospun mats, electrodes of size 2×3 cm and 3×4 cm were cut out. Each electrode was then pressed under flat plate pressing machine at 25 bars (per surface area 1.77 cm^2) and 75°C. After that, electrodes were dried under vacuum at 110°C for 72 h to get rid of any excess moisture before assembling into the cell. To provide better electric connection with cell, double side carbon coated aluminum foil (Toyal foil with thickness 22 μm) was used as a collector. The assembled cell firstly was dried under vacuum at 110°C during 72 h and then filled with 1.8 M $TEMABF_4$/ACN electrolyte.

The electrochemical properties of fully assembled cells were determined using cyclic voltammetry (two-electrode experiment). In cyclic voltammetry (CV), the current at the working electrode versus the applied voltage is plotted to give the cyclic voltammogram. The measuring of current was done using different sweep rates (1, 2, 5, 10 and 50 mV/s). From the CV curves, the cell capacitance in Farads (F) was firstly calculated and next, specific capacitance in F/g per mass of active carbonous material has been calculated.

The cell capacitance was calculated using formula:

$$C_{cell} = \frac{I}{v} \quad (1)$$

where C_{cell} – cell capacitance (F), I – current (A), v – sweep rate (V s^{-1}).

Specific capacitance from CV curve was calculated by formula:

$$C_{sc} = \frac{2\times(q_a+q_c)}{m_t\times v\times \Delta V} \quad (2)$$

where C_{sc} – specific capacitance (F/g), q_a, q_c – anodic and cathodic charge (C), found by integrating 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:

$$C_{cs} = \frac{4\times C_{cell}}{m_t} = \frac{4\times I_{disc}}{v\times m_t} \quad (3)$$

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

RESULTS AND DISCUSSION

1. Preparation of electrospinning dispersions filled with carbons

Electrospinning process needs homogeneous solutions or dispersions of proper viscosity and electric conductivity to produce membranes of uniform fibrous structure in nanoscale size. The viscosity of the solution can be controlled by polymer concentration and the amount of added carbonous fillers. The electric conductivity can be tuned by both, addition of the IL and amount of dispersed carbonous filler.

In this work, two main dispersion preparation methods have been studied - Method 1 and Method 2 (see Fig. 1.1). The ratio of PAN/Carbon was 50/50 and Carbon/IL=7/10. As a Carbon in this section the mixture of CDC and carbon black (CB) was used in the ratio of CDC/CB=80/20. In both methods the combination of sonication and mechanical stirring was used.

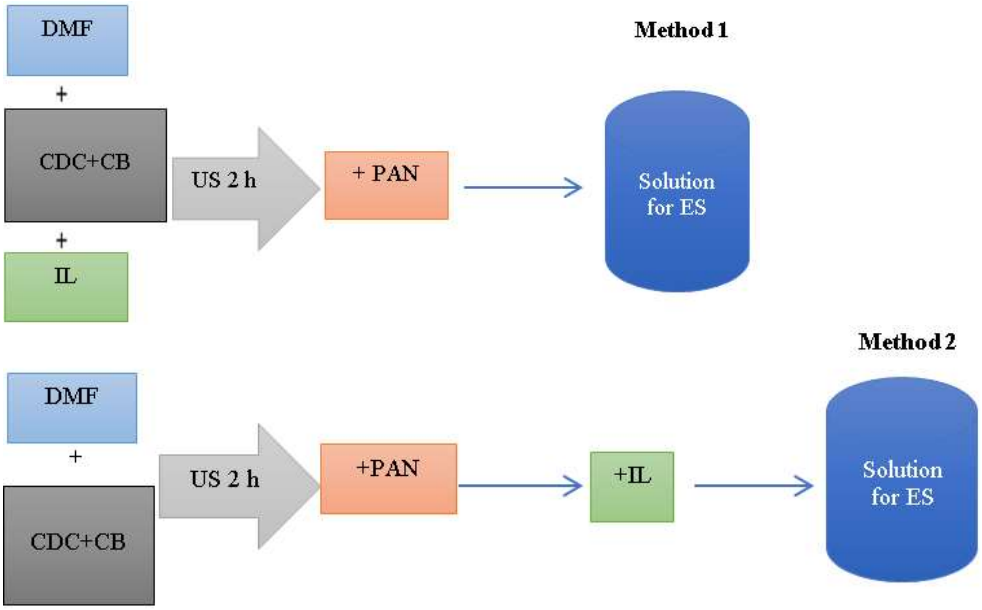

Fig. 1.1. Schematic representation of two methods used for the preparation of carbon-based dispersions.

In both solution preparation methods carbonous additives (CDC and CB) were dispersed in DMF by means of ultra-sonication (US). In Method 1 IL has been added to carbon dispersion prior to sonication to provide impregnation of carbons with IL and protect pores from potential blockage by polymers. However, ultrasonic treatment of solutions with ionic liquids could cause the degradation of IL [4]. Therefore, in method 2 IL has been added at the end of solution preparation.

Morphology of electrospun samples have been studied by scanning electron microscopy (SEM, see Fig. 1.2).The evident difference observed in the morphology of membranes. Method 2 gives more uniform and dense packaging of fibers in membrane. Additionally, carbons are more evenly distributed along the fibers, which gives better contact between carbon particles and as a result the electric conductivity of such membranes (20.8 μS/cm) are thrice higher

in comparison to Method 1 (6.4 μS/cm). Therefore, the dispersion preparation Method 2 has been chosen for further experiments.

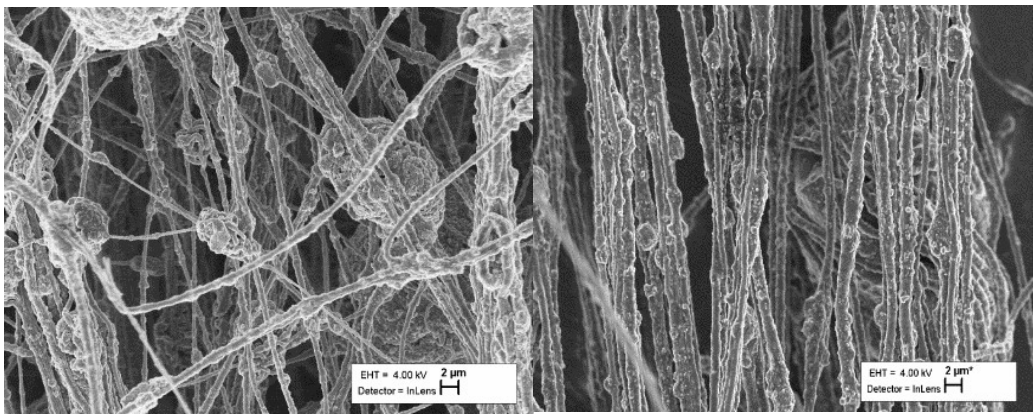

Fig. 1.2. SEM images membranes prepared by method 1 (left) and 2 (right).

2. Effect of PAN/TiC ratio in electrospun electrodes

One of the most important parameters affecting capacitive properties is the content of TiC in electrospun electrodes. Logically the higher TiC content, the higher should be capacity of the electrodes. Therefore, electrodes with PAN/Carbon=50/50, 40/60, 35/65 and 30/70 have been prepared and tested. As a Carbon in this section the mixture of TiC and CB was used in the ratio of TiC/CB=80/20. Ratio of Carbon/EmimBF$_4$=7/10 was fixed for all the samples. The concentration of PAN in DMF was kept constant as 7%.

With increase of the carbon content the viscosity of solution increases. Higher amount of TiC/CB absorbs more solvent and viscosity increases as a result (see Fig.2.2). The same with the electric conductivity: decrease of the content of the carbon results in the electric conductivity decrease (see Tab.1).

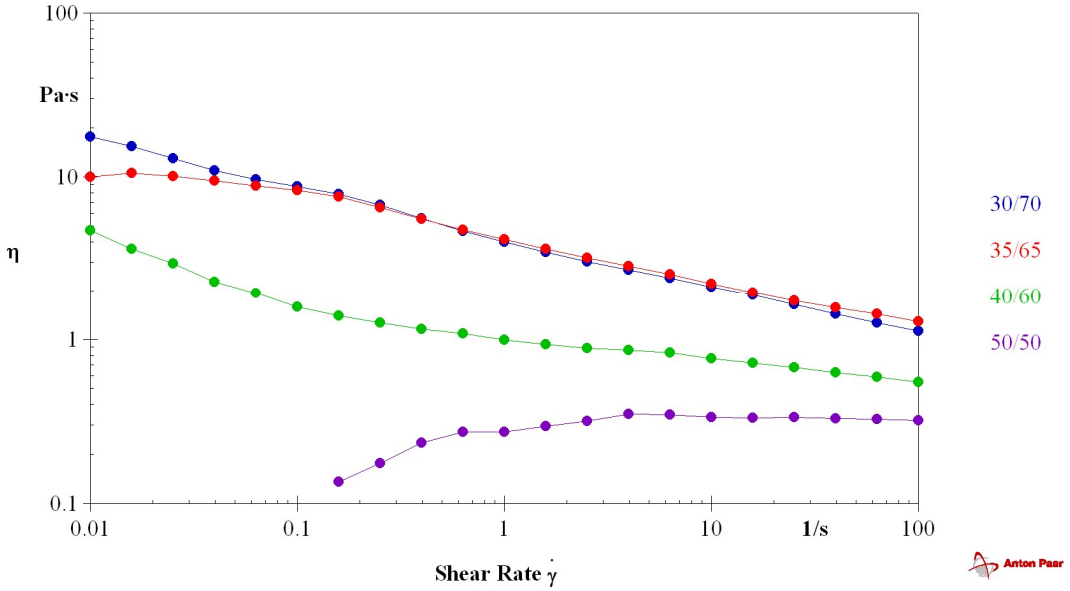

Fig. 2.2 Viscosity and conductivity results for PAN/TiC/CB samples with different PAN-to-TiC ratios.

Table 1. Electric conductivity of electrospinning solutions.

PAN-to-TiC ratio	30/70	35/65	40/60	50/50
	Electric conductivity values (mS/cm)			
	12,41	12,16	8,45	9,2

Fig. 2.3 demonstrates the morphology of fibers according to TiC content in electrospun electrodes. As could be seen from SEM images increase of TiC content significantly influences electrospinning and electrospun fibrous mat morphology. In content range between 50/50 and 40/60 fibers are uniform and TiC particles are distributed evenly. Process of electrospinning is normal.

A) B)

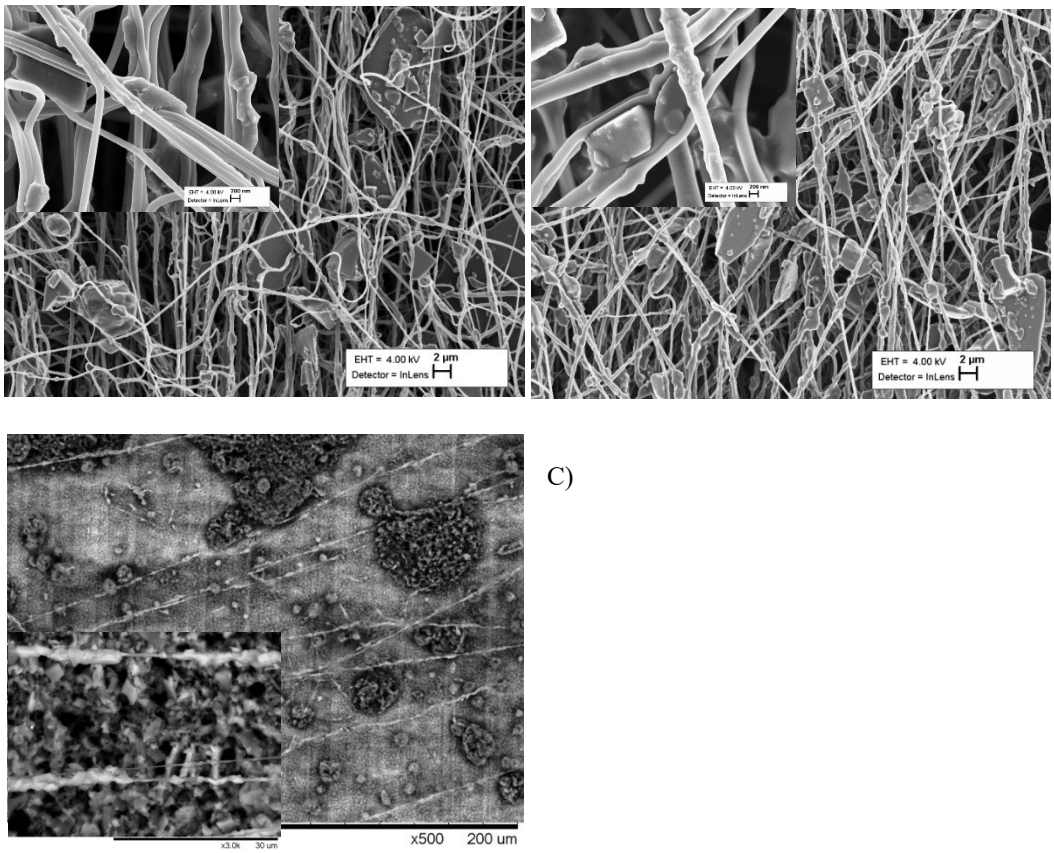

Fig. 2.3. SEM images of electrospun mats A) PAN/TiC = 50/50, B) PAN/TiC=40/60 with solution concentration 7% and C) PAN/TiC= 30/70 with solution concentration 6%

At 35/65 and higher ratio discharge of jet during electrospinning is observed, what makes fibers depositing not only on collector, but on every surface. Fibers became thinner with limited length. However, at 30/70 ratio electrospinning process disrupts, fiber generation is hindered, mostly droplets are formed (see Fig. 2.3 C).

Therefore, it has not been possible to get any electrodes from 35/65 and 30/70 PAN/TiC samples at PAN concentration 7 wt%. To initiate the electrospinning process it is necessary to decrease the viscosity of solution (dispersion). One of the routes is to prepare the electrospinning solution with lower polymer concentration. For this purpose, the 35/65

PAN/TiC sample has been chosen and electrospun from solutions with various PAN concentrations: 7%, 6%, 5% and 3.9%. A PAN was added in respective concentrations.

At the same time as can be seen from the Table 2 the polymer concentration in solution does not have any effect on the electric conductivity of the dispersion. This is due to the fact, that the ratio of PAN/TiC and TiC/EmimBF$_4$ was kept constant for all dispersions. Slightly lower value of the electric conductivity at 3.9% of PAN is related to the temperature of the dispersion. With increase of the temperature of the solution during measurement, the value of the electric conductivity decreases.

Table 2. Influence of PAN concentration in electrospinning dispersion on various parameters of 35/65 PAN/TiC sample.

PAN/TiC	Concentration of PAN in DMF, wt%	Electrical conductivity of the solution (mS/cm)	Spinning distance, cm	Fiber diameter, nm	Gravimetric capacitance (F/g)
35/65	3.9	10.95	10	201	28
35/65	5.0	12.08	7	195	60
35/65	6.0	12.32	7	249	121
35/65	7.0	12.60	7	a few fibers, 389	Poor spinnability

Decrease in viscosity with lowering of concentration helped to initiate the electrospinning process. If at the concentration of 7% the spinning process resembled the sputtering of dense dispersion, so at the concentration of 6% the true electrospinning process with formation of fibers has started.

The capacity properties of electrodes have been also evaluated by formula 2. Capacitance is affected by concentration of polymer in dispersion. It increases with increasing the concentration of polymer in dispersion as seen from Table 2. It can be explained by improving of fibrous morphology of samples electrospun at higher PAN concentration which is confirmed by Fig. 2.4.

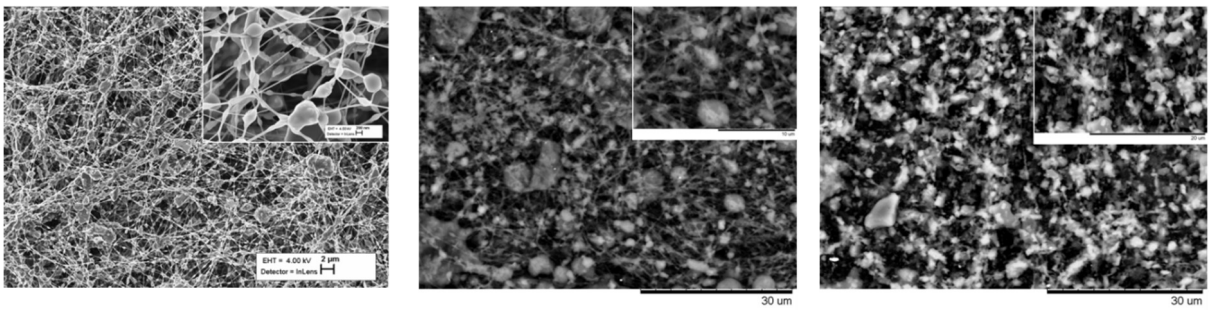

Fig. 2.4. SEM images of electrospun mats with PAN concentrations 6% (left), 5% (middle) and 3.9% (right).

Fig. 2.5 shows the cyclic voltammetry curves recalculated in terms of specific capacitance by formula 3 for samples with 50/50 and 35/65 PAN/TiC. The achieved specific capacitance for 50/50 PAN/TiC was 112-114 F/g, with higher TiC content (35/65 PAN/TiC), the specific capacitance is increasing, and 121 F/g can be achieved. However, increasing content of carbons in fibrous membranes results in deterioration of mechanical properties of electrodes which was even visually observed.

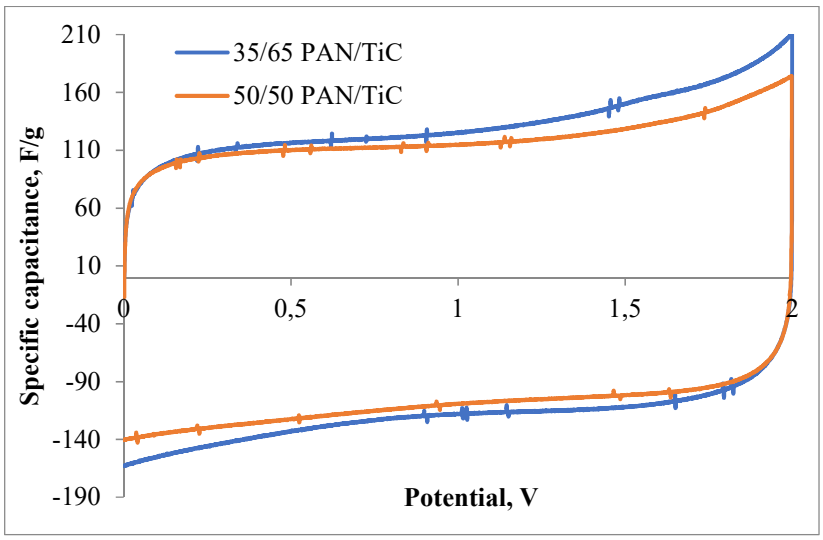

Fig. 2.5. Specific (gravimetric) capacitance (F/g) for PAN/TiC/CB electrodes: PAN/TiC=50/50 (orange) and PAN/TiC=35/65 (blue)

Therefore, the 50/50 PAN/TiC ratio gives the highest specific capacitance of 112-114 F/g. Capacitance can be enhanced up to 121 F/g by increasing TiC content in final electrospun electrode, but mechanical properties will be deteriorated.

3. Properties of electrospun electrodes

3.1 Evaluation of mechanical properties of fibrous electrodes

Two types of electrospun membranes were tested for mechanical properties. Electrospun mat was made of PAN+TiC/CB+EmimBF$_4$, with ratios of components: 50/50 PAN/Carbon, 80/20 TiC/CB, 7/10 Carbon/EmimBF$_4$. Second electrode - conventional roll-milled casted electrode made of PTFE+TiC+EmimBF$_4$ in ratios: 94/6 TiC/PTFE. Electrospun mat of fibrous electrode was compressed to achieve higher density, mats thickness decreases approximately 3 times from 80 to 25-30 micrometers, fibers correspondingly flattens and average size change from 284 nm to 389 nm.

Table 3 Properties of the electrodes

Sample	Tensile stress S, MPa	Specific stress σ_{sp}, N/tex	Fiber diameter, nm
Cell 1	1.08	$4.9 \cdot 10^{-3}$	284±31
Cell 1 compressed	2.33	$3.8 \cdot 10^{-3}$	389±44
Cell 2	0.23	$2.7 \cdot 10^{-4}$	-

For mechanical tests ribbons of 5 mm thick were cut from mat and tested at 100 mm/min on extension. As could be seen from Fig. 3.1 (left) electrospun mats has specific stress almost 20 times higher than roll casted mats. Compression of electrospun mats decrease specific stress for 22%, probably during hot-pressing the crystallization rate of fibers increases and thus make mat more fragile.

At Fig. 3.1 (right) tensile stress is represented, as could be seen difference between samples is a bit smaller. Tensile stress recalculates the breaking force over cross-section area but cased electrodes are solid, whereas electrospun mats are fibrous with approx. 80% macro porosity, thus it cannot be used to compare these two types of materials. Specific stress is recalculated from real density and thus could describe fibrous materials better.

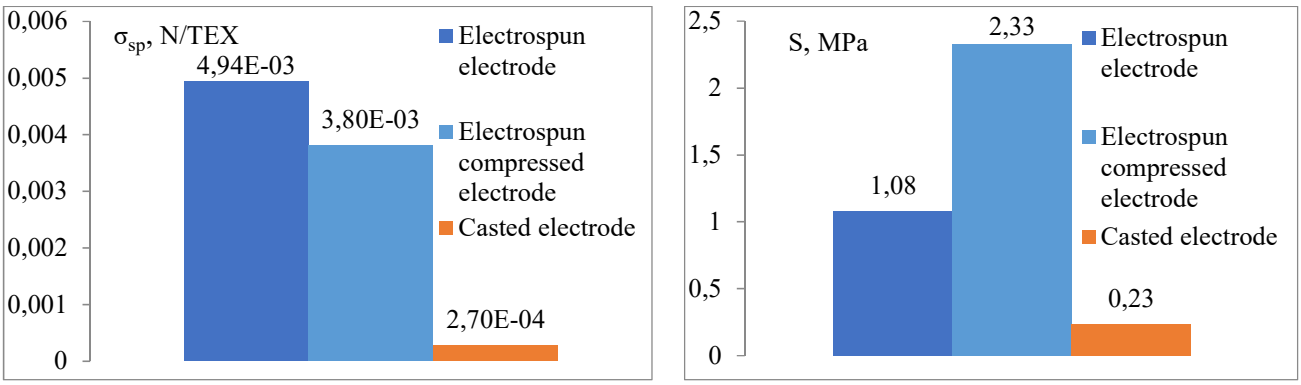

Fig. 3.1. Specific stress σ_{sp} (left) and tensile stress S (right) of electrodes

When extension is applied to mats electrode composed of PAN+TiC/CB+EmimBF$_4$ breaks through breaking the fibers. This fact is proven by microscopy, SEM images are represented in Fig. 3.2.

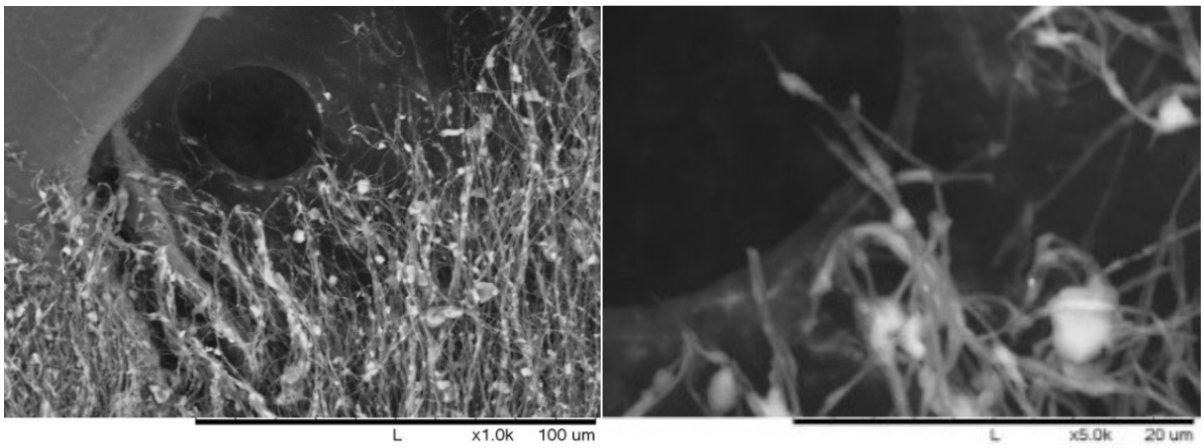

Fig. 3.2. SEM images of electrospun mat of Cell 1 zoom 1000x (left), 5000x (right).

3.2. Behavior under vibration

Vibrational test: One TiC based electrode containing cell, has been tested under applied vibrations. Cell were composed from electrode of PAN/TiC=50/50, TiC/CB=80/20, TiC/EmimBF$_4$=7/10. The program of vibration test is presented in Table 4.

Table 4. Vibration test: Sine sweep (High Abort 6 dB, High Alarm 3 dB, Low Alarm -3 dB, Low Abort -6 dB)

Frequency	Acceleration	Velocity	Displacement
5 Hz	1 g	0,3 m/s	20,0 mm
10 Hz	4 g	0,6 m/s	20,0 mm
11 Hz	5 g	0,7 m/s	20,5 mm
30 Hz	5 g	0,3 m/s	2,7 mm
31 Hz	22,5 g	1,1 m/s	11,6 mm
71 Hz	22,5 g	0,5 m/s	2,2 mm
200 Hz	22,5 g	0,2 m/s	0,3 mm
201 Hz	10 g	0,1 m/s	0,1 mm
2000 Hz	10 g	0,008 m/s	0,001 mm

Frequency range	Sweep Rate	Total duration
(5…70) Hz	0,3 Oct/min	00:12:41
(71…2000) Hz	2,0 Oct/min	00:02:25

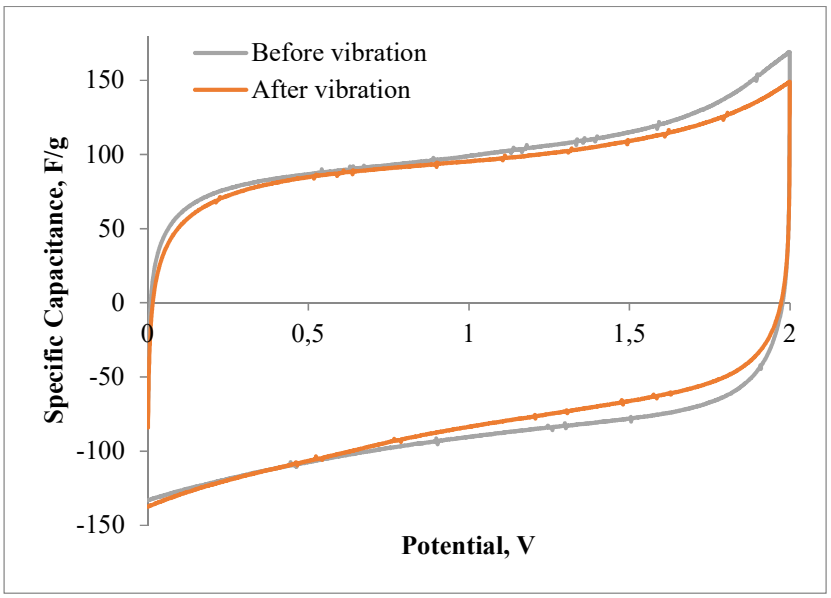

Fig. 3.3. Specific (gravimetric) capacitance (F/g) for PAN/TiC/CB electrodes in $TEMABF_4$/ACN electrolyte. PAN/TiC=50/50. Scan rate is 1 mV/s.

As it is seen from Fig. 3.3, specific capacitance drops after vigorous vibration by 5% only. It means that electrospun electrodes can withstand rather high loads (vibrations) with minimal lose in power.

CONCLUSION

In present study electrospun fibrous flexible EDLC electrodes have been developed. This material is suitable for higher frequency applications without significant loss of capacitance under specific environmental conditions. The developed flexible fibrous electrode PAN+ TiC/CB + $EMIMBF_4$ showed the specific capacitance up to 121 F/g with CDC and CB ratio 80/ 20 respectively.

Produced electrode showed good mechanical properties as specific stress for fibrous electrodes were almost 20 times higher compared to the roll casted mats. Furthermore, fibrous electrodes can be easily folded or twisted without inducing any visual damage. This combination of flexibility, folding and twisting possibility is desirable for supercapacitor electrodes.

Developed fibrous electrodes were tested in EDLC cells under vibration, the specific capacitance dropped after vigorous vibration by only 5%, which indicates that electrospun electrodes can withstand rather high loads (vibrations) with minimal lose in energy.

Acknowledgements

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