Fully electrospun durable electrode for electrochemical double-layer capacitor

Tallinn University of Technology

Elvira Tarasova

Viktoria Vassiljeva

Illia Krasnou

Natalja Savest

Andres Krumme

Skeleton Technologies OÜ

Siret Malmberg

Mati Arulepp

Jaan Leis

ESTEC

Léo Farhat

Denis Lacombe

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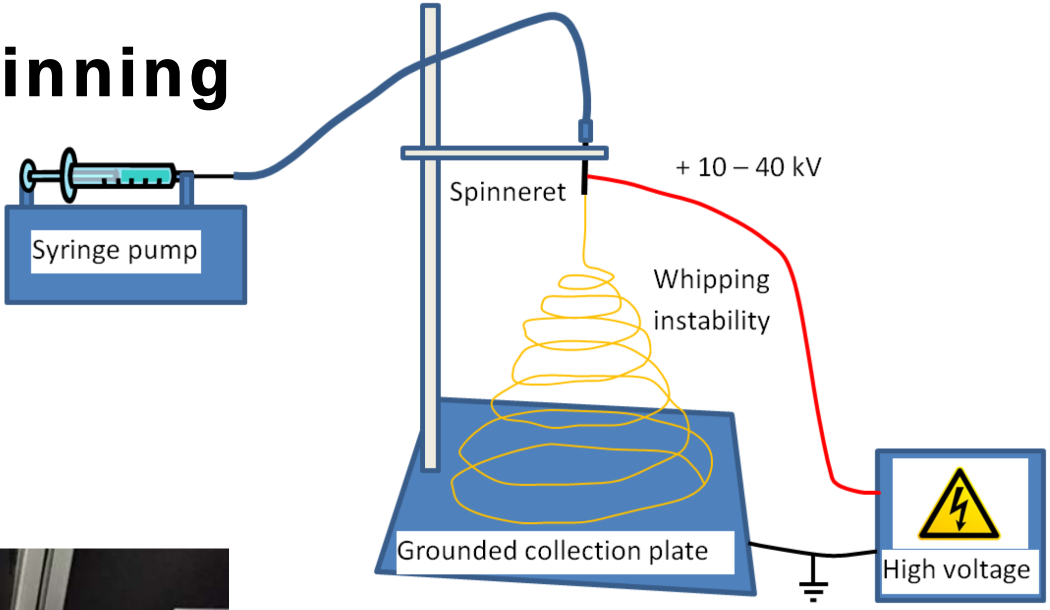
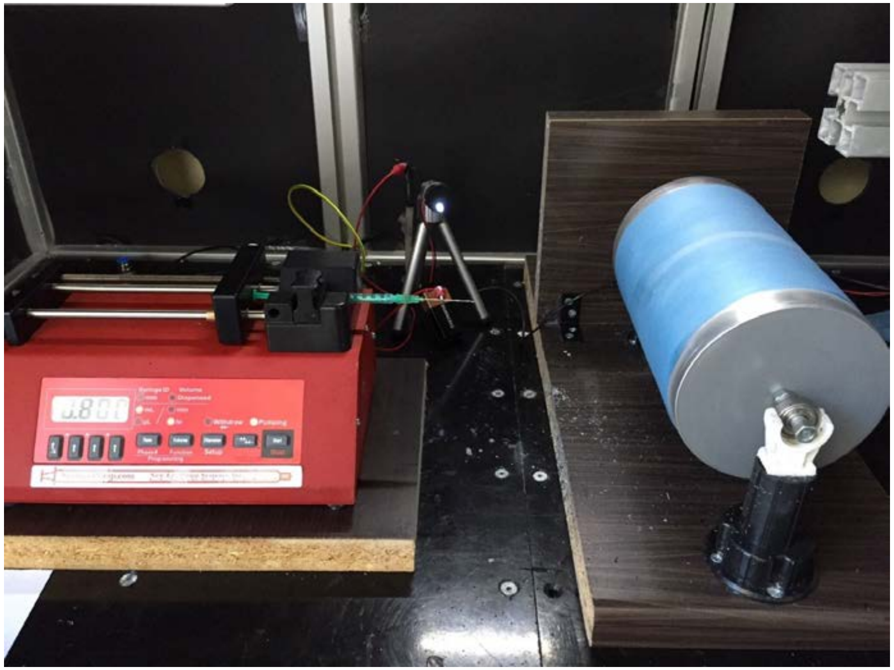
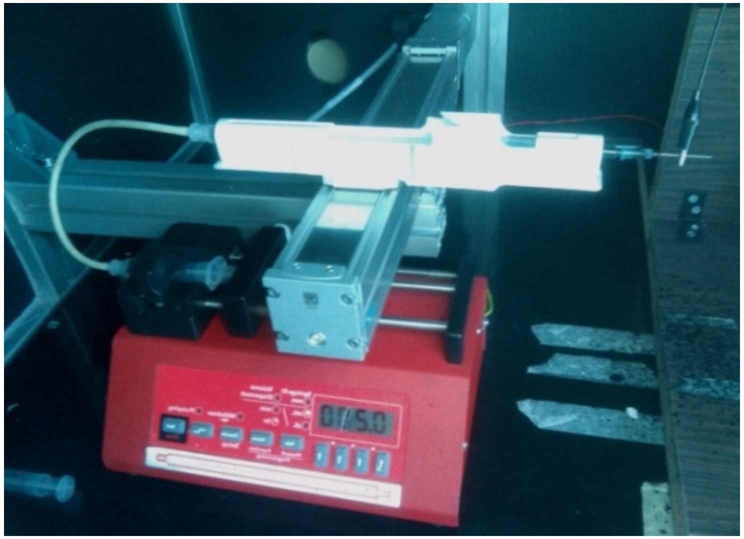
Motivation and content

- Present work focuses on developing a method of producing carbon rich nanofibrous electrodes of EDLC supercapacitors by electrospinning method. Influence of properties of electrospinning solutions and polymer/carbon ratio to several physical and morphological properties of the electrodes was examined.
- Content:
  - Introduction to electrospinning technology
  - Components of the electrodes
  - Properties of the electrospinning solutions
  - Effect of carbon ratio to electrochemical properties
  - Effect of carbon ratio to mechanical properties

Electrospinning

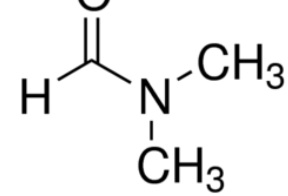


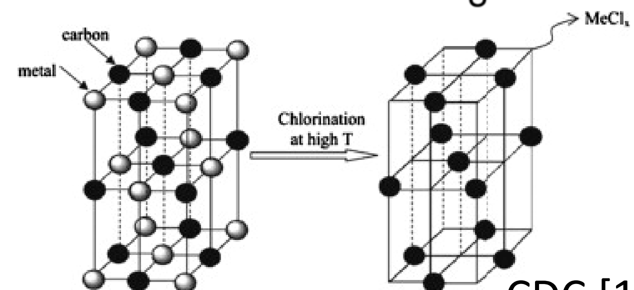




Components of the electrodes

DMF

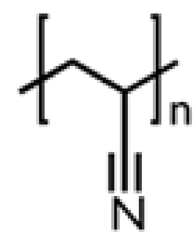


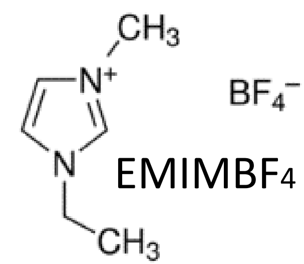


CDC [1]

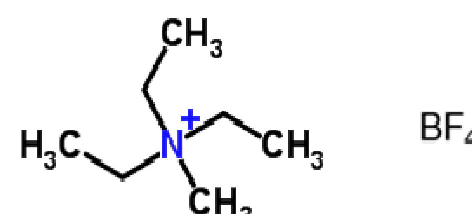
- Solvent for electrospinning solutions:dimethylformamide (DMF)
- Matrix polymer: polyacrylonitrile (PAN)
- Filler for capacitance: TiC based carbide derived carbon (CDC)
- Filler for improved conductivity: carbon black (CB)
  - CDC/CB ratio was 80/20 wt-%
  - PAN/Carbon (CDC + CB) ratio was 50/50, 60/40, 65/35 and 70/30 wt-%
- Additive for improved dispersion of carbon and conductivity: 1-ethyl-3-methylimidazoliumtetrfluoroborate ($EMIMBF_4$) ionic liquid (IL)
  - Carbon/EMIMBF4 ratio was 7/10 wt-%
- Electrolyte: triethylmethylammonium tetrafluoroborate ($TEMABF_4$) in acetonitrile (ACN)

PAN





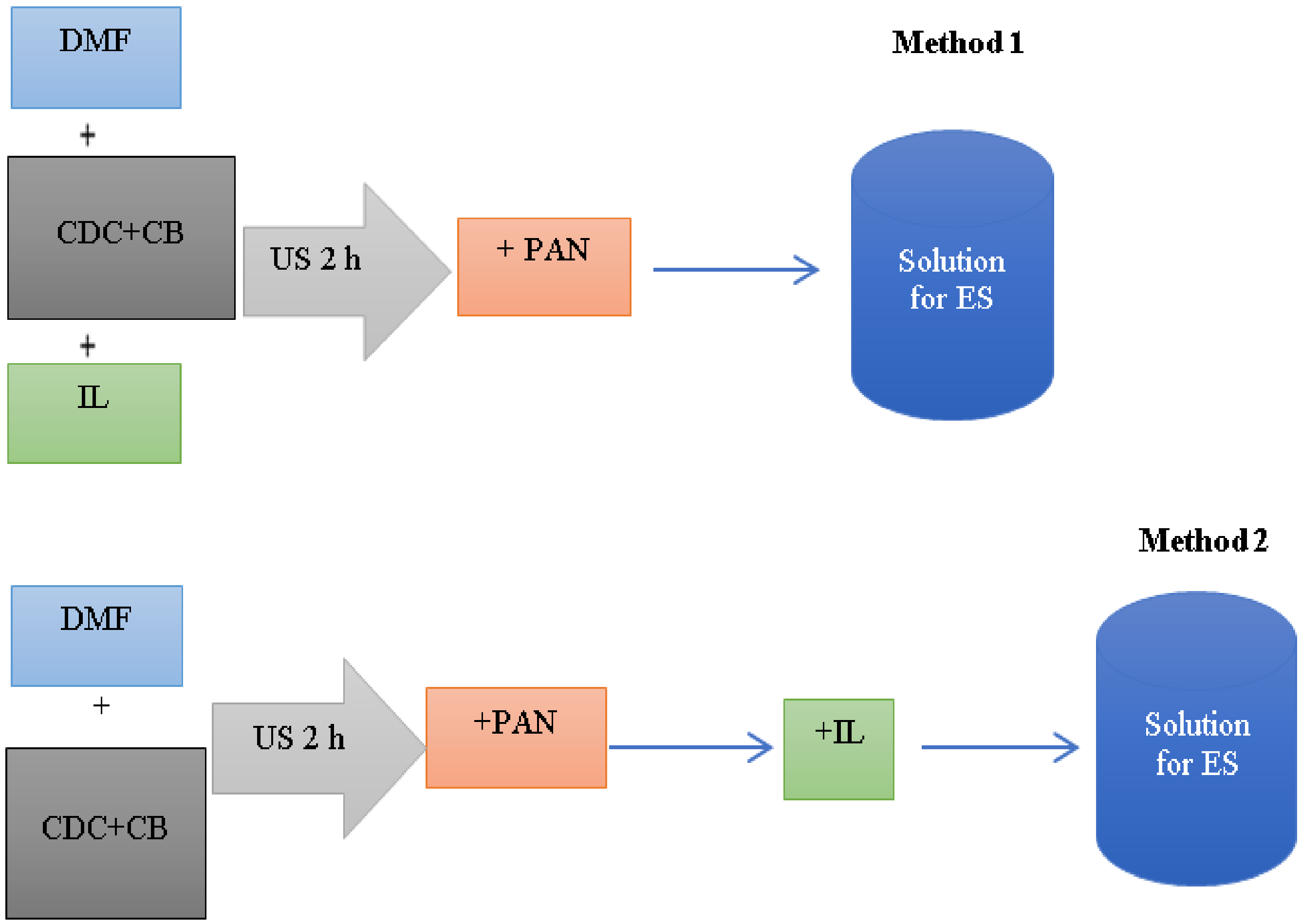
$EMIMBF_4$



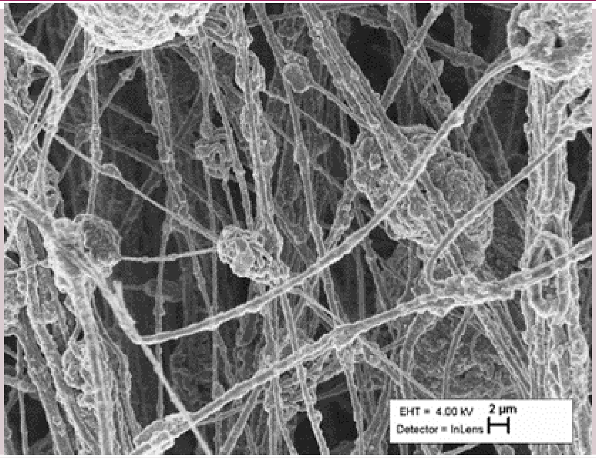
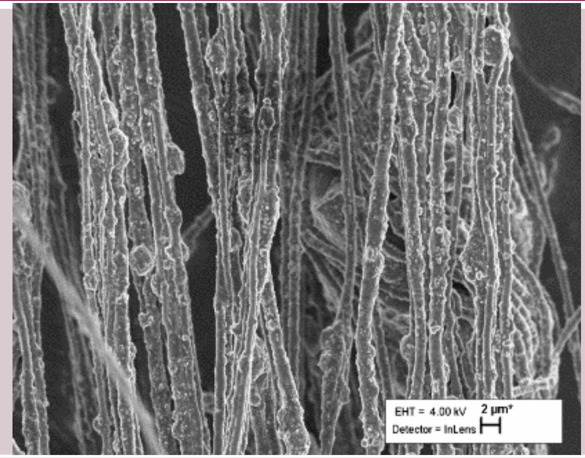
$TEMABF_4$

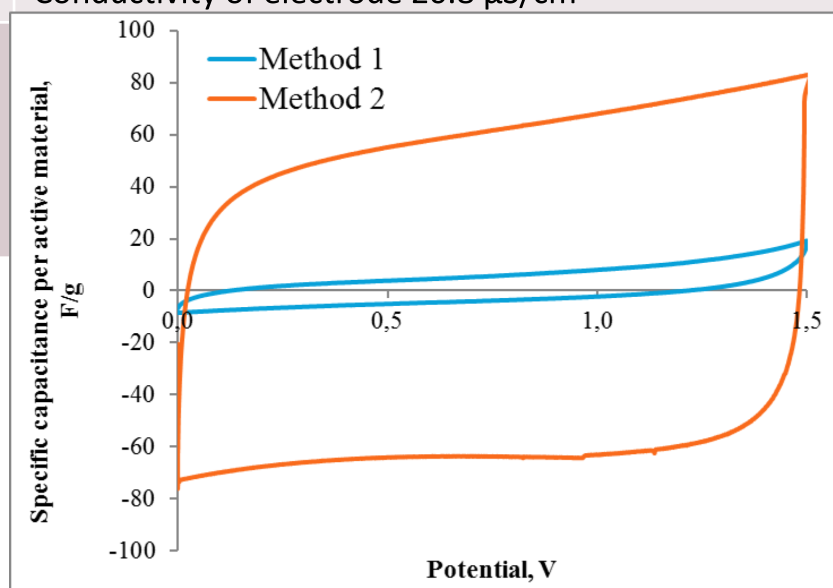
[1] M. Sevilla, R. Mokaya, Activation of carbide-derived carbons: aroute to materials with enhanced gas and energy storage proper-ties, Journal of Materials Chemistry 21 (2011) 4727–4732

Electrospinning solutions



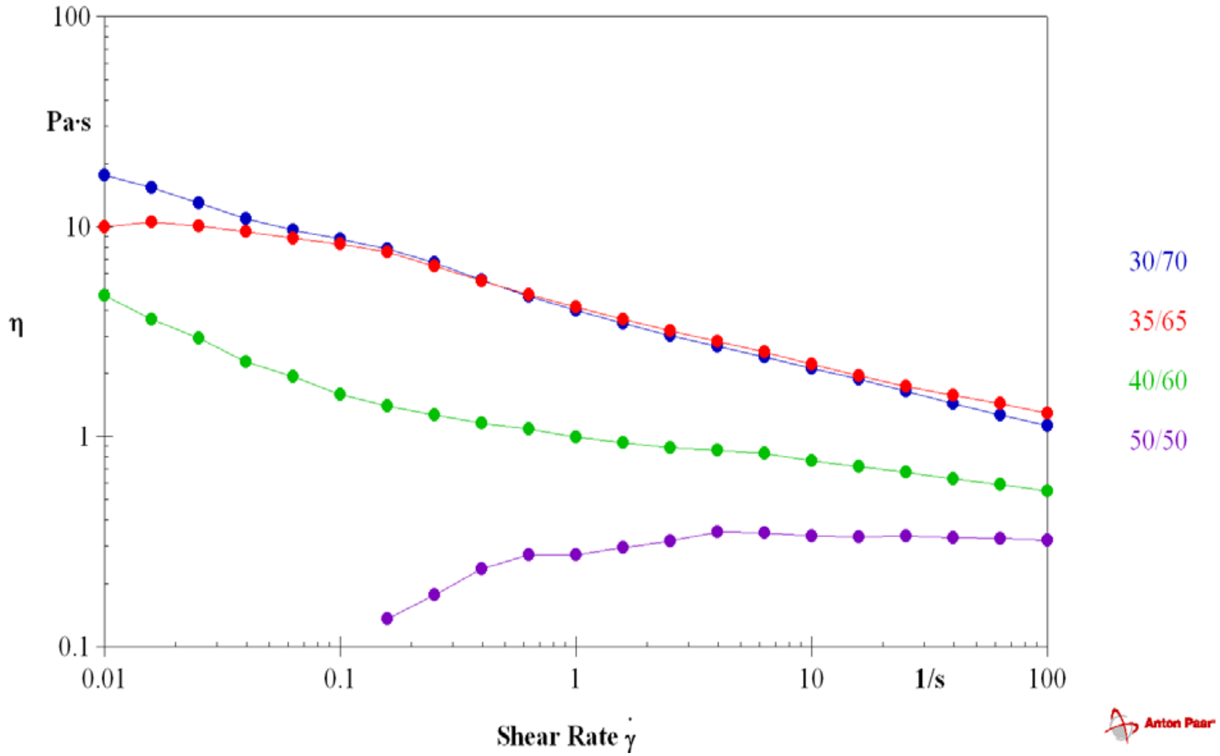
Electrospinning solutions

Method 1	Method 2
	
Pros: IL can protect pores from blocking	Pros: Uniform morphology and even distribution of carbon Conductivity of electrode 20.8 µS/cm
Con: Degradation of IL due to US treatment [2] Agglomeration of carbon particles Conductivity of electrode 6.4 µS/cm Low capacitance	



[2] G. Chatel and D. R. MacFarlane, Ionic liquids and ultrasound in combination: synergies and challenges, Chem. Soc. Rev., 2014, 43, 8132

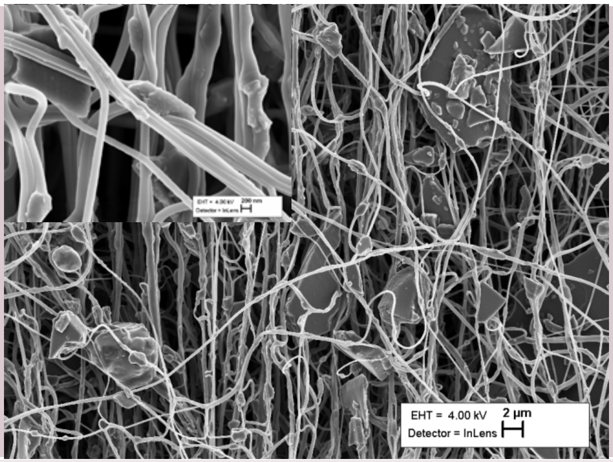
Effect of PAN/carbon ratio: solution properties



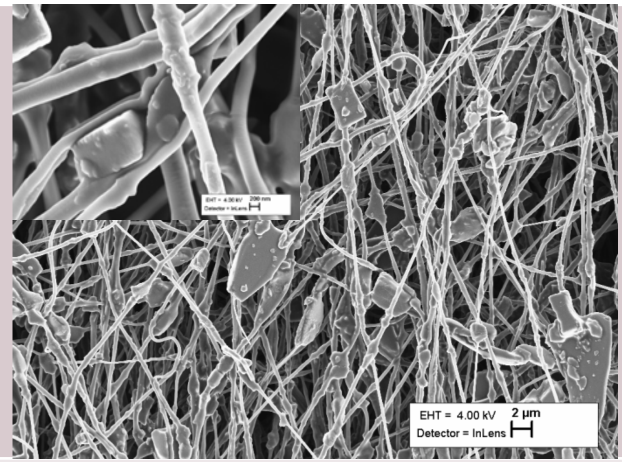
PAN/carbon ratio	30/70	35/65	40/60	50/50
	Electric conductivity values (mS/cm)			
	12.41	12.16	8.45	9.2

Effect of PAN/carbon ratio: morphology

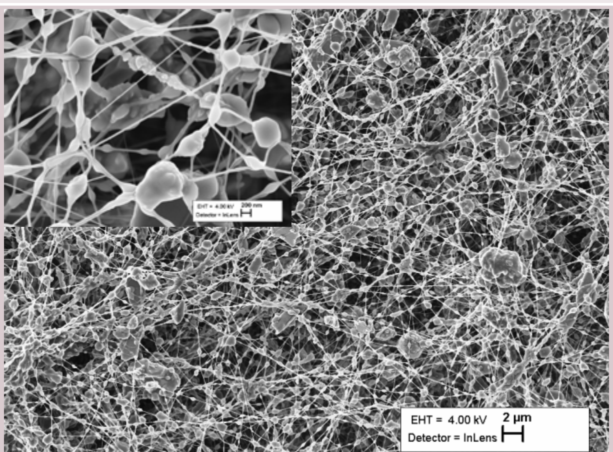
50/50 (PAN/carbon) (PAN conc. 7 wt-% in DMF)



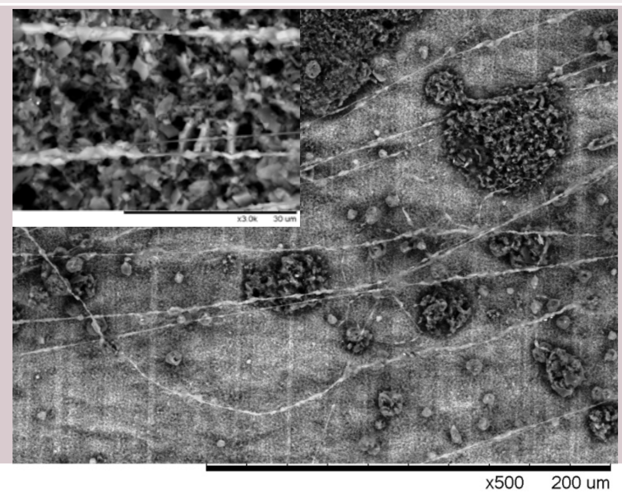
40/60 (PAN conc. 7 wt-% in DMF)



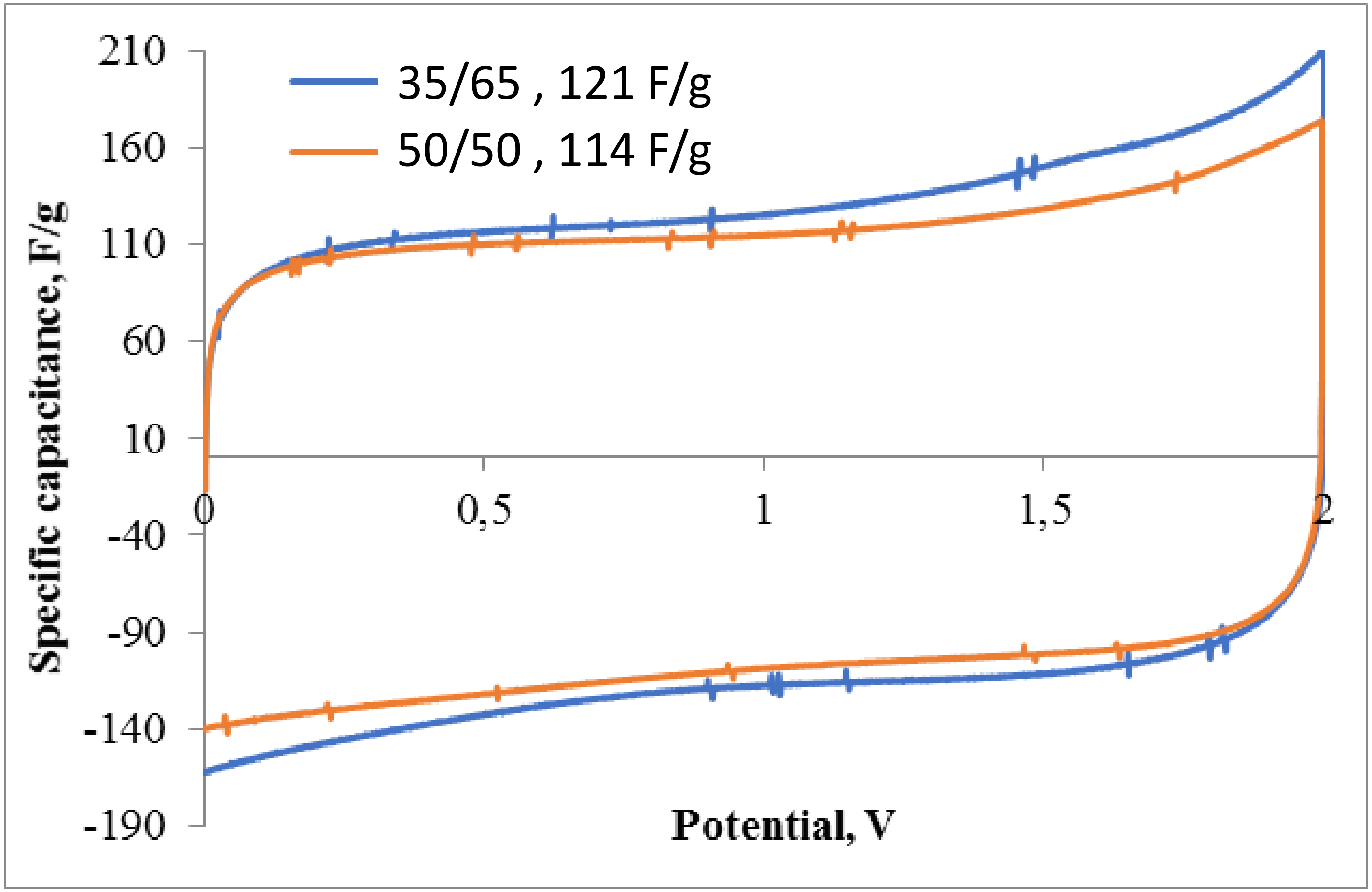
35/65 (PAN conc. 6 wt-% in DMF)



30/70 (PAN conc. 7 wt-% in DMF)



Effect of PAN/carbon ratio: specific capacitance



Effect of PAN/DMF ratio (PAN/carbon ratio 35/65)

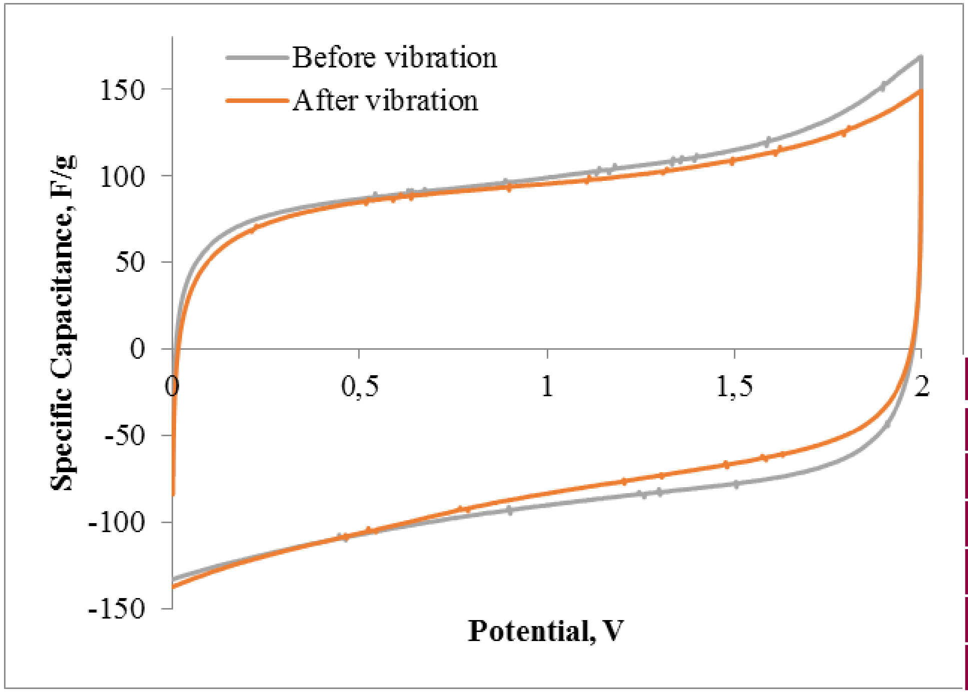
Concentration of PAN in DMF, wt-%	Electrical conductivity of the solution (mS/cm)	Fiber diameter, nm	Specific capacitance (F/g)
3.9	10.95	201	28
5.0	12.08	195	60
6.0	12.32	249	121
7.0	12.60	a few fibers, 389	N/A

Mechanical properties

Sample	Tensile stress S, MPa	Electrode thickness, µm
50/50 PAN/Carbon, 80/20 TiC/CB, 7/10 Carbon/$EmimBF_4$	1.08	80
50/50 PAN/Carbon, 80/20 TiC/CB, 7/10 Carbon/$EmimBF_4$ compacted in hydraulic press between flat plates at 25 bars and 75°C.	2.33	25 - 30
conventional roll-milled casted electrode made of PTFE+TiC+$EmimBF_4$ in ratios: 94/6 TiC/PTFE	0.23	180

TTÜ100

Vibration test (PAN/carbon ratio 50/50, loss of capacitance ~5%)

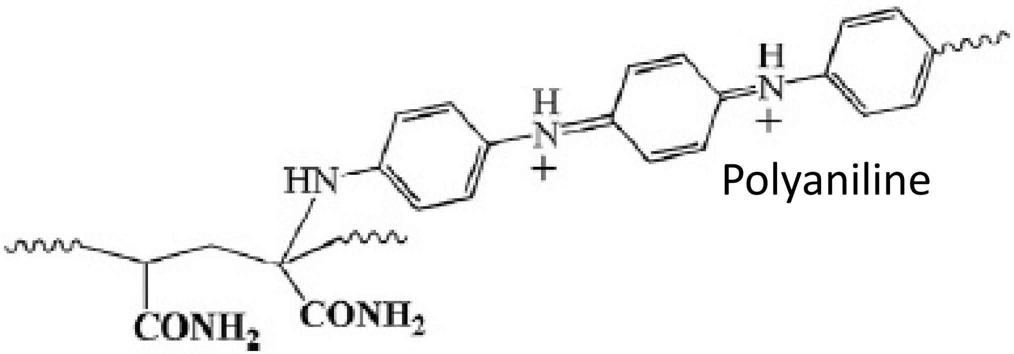


Frequency	Acceleration	Velocity	Displacement
5 Hz	1 g	0,3 m/s	20,0 mm
10 Hz	4 g	0,6 m/s	20,0 mm
11 Hz	5 g	0,7 m/s	20,5 mm
30 Hz	5 g	0,3 m/s	2,7 mm
31 Hz	22,5 g	1,1 m/s	11,6 mm
71 Hz	22,5 g	0,5 m/s	2,2 mm
200 Hz	22,5 g	0,2 m/s	0,3 mm
201 Hz	10 g	0,1 m/s	0,1 mm
2000 Hz	10 g	0,008 m/s	0,001 mm
Frequency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

Conclusions

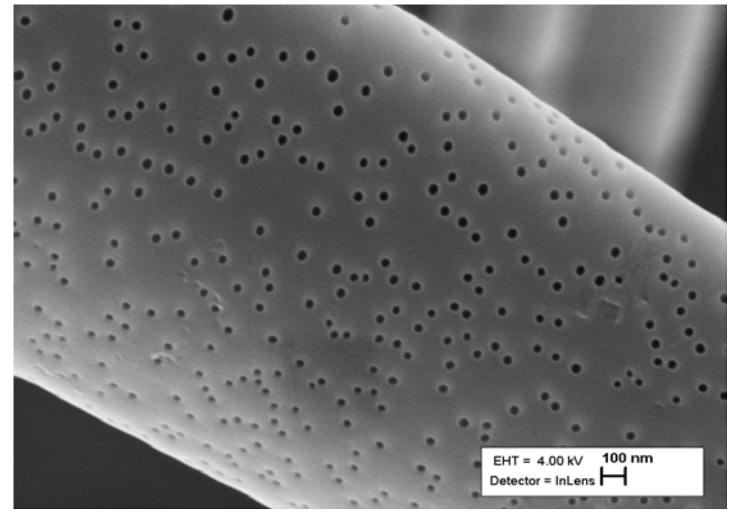
- Electrospun fibrous flexible EDLC electrodes have been successfully developed and corresponding technological procedures/conditions established.
- The developed flexible fibrous electrode PAN+ TiC/CB + $EMIMBF_4$ showed the specific capacitance up to 121 F/g.
- Optimal (regarding capacitance and mechanical properties) PAN/carbon ratio is 50/50 wt-%.
- Produced electrode showed good mechanical properties as tensile stress for fibrous electrodes were almost 10 times higher compared to the roll casted mats.
- Fibrous electrodes can be easily folded or twisted without inducing any visual damage.
- Specific capacitance of the electrode dropped after vigorous vibration only by 5%.

Further steps: conductive / porous / binded matrix

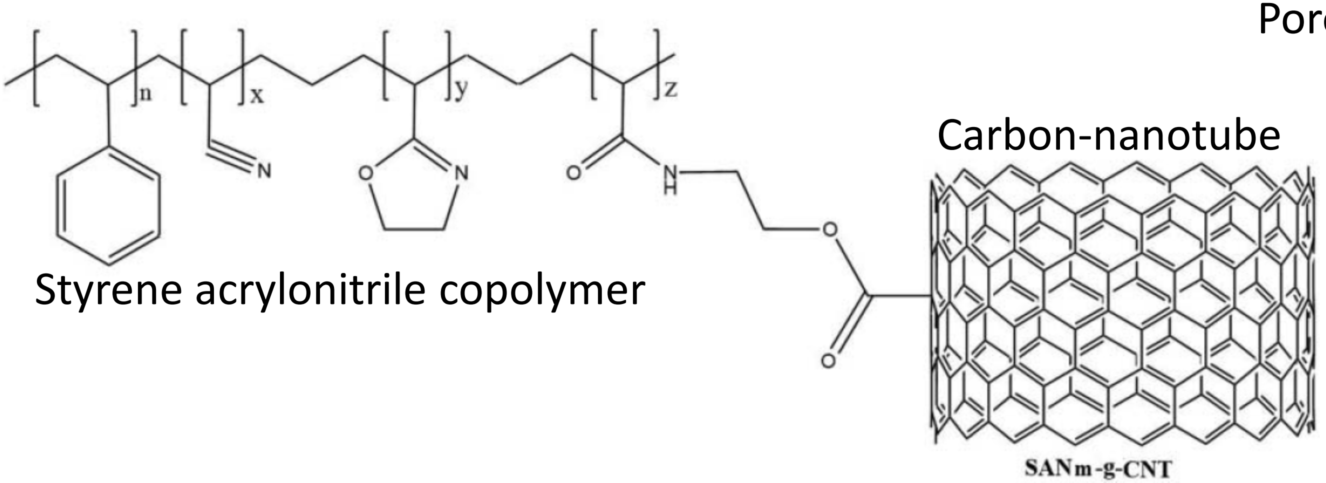


Polyaniline

Polyacrylamide



Porous SAN fibre



Styrene acrylonitrile copolymer

Carbon-nanotube

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- ESA (Contract No. 4000119258/16/NL/CBi, Fully electrospun durable electrode and electrochemical double-layer capacitor for high frequency applications)
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Mati, Siret, Tiia, Illia, Mihkel, Elvira, Viktoria, Andres

Prof. Andres Krumme

Tallinn University of Technology
Department of Materials- and Environmental Technology
Laboratory of Polymers and Textile Technology

Ehitajate tee 5
19086 Tallinn
Estonia

andres.Krumme@ttu.ee

Tel. +372 620 2907