Supercapacitors utilizing electrodes derived from polyacrylonitrile fibers incorporating tetramethylammonium oxalate as a porogen

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Thermally sensitive tetramethylammonium oxalate (TMAO) is incorporated as an in situ porogen into freestanding nonwoven nanofibers of polyacrylonitrile (PAN) produced by electrospinning. Supercapacitor electrode materials are prepared by a series of thermal treatments on these fibers, including stabilization followed by a single step carbonization and CO₂ activation. The specific surface areas of the resultant carbon nanofibers (CNFs) are controlled by varying the amounts of TMAO in the precursor fibers. The electrochemical properties of the carbon nanofibers are characterized by cyclic voltammetry and galvanostatic charge–discharge tests. The highest surface area (2663 m² g⁻¹) and best electrochemical performance are obtained from PAN containing 0.1 wt% of TMAO (T10), which gives a maximum specific capacitance of 140 F g⁻¹ at a scan rate of 10 mV s⁻¹ in comparison to CNFs from PAN alone, which yielded only 90 F g⁻¹. At a discharge current density of 1 A g⁻¹, the obtained energy and power densities are 68 Wh kg⁻¹ and 1.7 W kg⁻¹, respectively, with capacitance retention of 80% after 1000 cycles.

1. Introduction:

Electrochemical double layer capacitors (EDLC), also known as supercapacitors or ultracapacitors, are energy storage devices that store energy as a charge separation at the electrode-electrolyte interface. They have drawn considerable interest due to their higher power density than batteries and higher energy density than conventional capacitors. They also have excellent cycling stabilities due to their non-faradic and highly reversible energy storage mechanism [1]. EDLCs are seeing use as back-up systems in consumer electronics and hybrid

electric vehicles, where high power is needed. Compared to batteries, however, EDLCs have lower energy densities, which limit their applications [2,3].

Much research has been directed to increasing energy density while maintaining high power density in supercapacitors. The energy (E) stored in an electrochemical capacitor is dependent on capacitance (C) and voltage (V) by the equation $E = \frac{1}{2} CV^2$. Capacitance is dependent on the surface area of the electrode [4, 5]. Various studies have been done to efficiently use the surface area by tuning electrode pore size to match with the size of the electrolyte ions [6, 7]. Since the energy density of supercapacitors varies quadratically with voltage, electrolytes that can withstand high operating voltage (3V or higher), such as ionic liquids, offer some advantages [8, 9].

Carbon nanofibers from electrospun polymer precursors are attractive electrode materials for supercapacitors because they have high surface area, good electrical conductivity and do not require binding agents or conductive additives. Electrospinning is a well known and efficient technique to produce continuous nonwoven nanofiber mats with fiber diameters mostly in the submicron range [10]. A simple lab-scale electrospinning setup comprises a syringe pump with the syringe loaded with polymer solution, a (rotating) grounded collector, and a high voltage power supply. A high voltage difference is applied between the needle and the collector, which causes the solution to be drawn as continuous fibers onto the collector [11-13]. The nonwoven nanofiber mat is subsequently thermally treated and activated to afford freestanding high surface area carbon electrode (nano) fibers [14].

Polyacrylonitrile (PAN) has been widely studied and recognized as a promising material for EDLCs due to its spinnability, stability during the thermal treatments, including stabilization and carbonization, and high carbon yield [15-17]. An oxidative stabilization treatment is used to convert PAN into a stable ladder structure, which helps to increase the mechanical stability of the final product [18]. The carbonization process removes noncarbon functionality and increases electrical conductivity [19, 20]. Carbonized PAN fibers typically require activation with KOH or gases including steam, CO₂, or NH₃ to increase porosity [14, 21-23]. Modification of PAN-based carbon materials has also been accomplished by using different porogens or sacrificial polymers. These porogens decompose during the subsequent thermal treatments to leave pores that further increase the surface area [24].

PAN/ZnCl₂ composite nanofibers have been reported where the addition of ZnCl₂ increased the conductivity of the spinning solution, which resulted in a decrease in fiber diameter, and thus increased the surface area. Also ZnCl₂ acted as a pore creating agent and helped to produce pores during the pyrolysis [25]. Porous materials from PAN and polymethylhydrosiloxane (PMHS) blends have been prepared and their electrochemical performance was measured. PMHS used as a porogen produce micropores in the fibers during the pyrolysis [26]. Blends of PAN and a sacrificial polymer (Nafion®) with varying PAN to Nafion ratio have also been reported. The decomposition of Nafion during the thermal treatment produced intra-fiber pores that led to high surface area carbon nanofibers (CNFs) without any chemical or physical activation process [27]. Interconnected nanofibers have been generated using different ratios of poly (acrylonitrile-co-butadiene (PAN-co-PB) copolymer and PAN. Polybutadiene in the copolymer decomposes during the thermal treatment and causes fiber fusion to form porous interconnected carbon nanofibers thus increasing electrical conductivity and better electrochemical performance [28]. Nataraj *et al.* incorporated iron oxide particles into PAN-derived carbon nanofibers, which were then activated with NaOH to increase the surface area of fibers but no electrochemical performance was reported [29]. Recently, Abeykoon *et al.* incorporated PMMA as a sacrificial polymer with PAN to tune the porosity and to produce high surface area materials. [30].

The use of an additive or porogen that completely decompose during the thermal treatment is advantageous since it does not need an extra step to remove the porogen. Also small molecules as a porogen need only small amount to make micropores therefore reduce the cost. Tetramethylammonium oxalate (TMAO) was selected as a porogen for PAN-based carbon nanofibers. TMAO also increases the conductivity of the spinning solution, which could lead to reduction of fiber diameter thus increase the surface area. TMAO undergoes a two-stage decomposition at 260 °C and 294 °C into gaseous products including CO, CO₂ and dimethyl ether. The release of gaseous products during the thermal treatments generates pores in the fiber [31, 32]. The higher decomposition temperature of TMAO compared to the stabilization temperature of PAN (240 °C) used in this experiment allowed the formation of the more stable ladder structure of PAN prior to the creation of pores, preventing shrinkage or loss of the fiber morphology. We have also shown that the surface area of carbon nanofibers derived from PAN was increased by 33% with only a small amount of (0.1 wt %) TMAO.

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93 **2. Experimental**

94 *2.1. Materials*

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96 Polyacrylonitrile (PAN) (MW = 150,000 Da) was obtained from Pfaltz & Bauer, Inc.
97 Anhydrous DMF, oxalic acid, ethanol and tetramethylammonium hydroxide were purchased
98 from EMChemicals USA. The CR2032 coin cell blanks and the associated crimper were
99 obtained from Shenzhen Yongxingye Precision Machinery Mould Co. Ltd., China. Gore™
100 polytetrafluoroethylene (PTFE) separator and electrochemical grade ethylmethyimidazolium bis
101 (trifluoromethylsulfonyl) imide (EMITFSI) (99.5% purity) were obtained from W.L. Gore &
102 Associates, Inc. and IoLiTec, Inc., respectively. All the chemicals were used without further
103 purifications.

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105 *2.2. Preparation of spinning solution and carbon nanofibers*

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107 Tetramethylammonium oxalate (TMAO) was prepared using tetramethylammonium
108 hydroxide and oxalic acid by following a reported procedure [32]. Different amounts of TMAO
109 were dissolved in same amount of water (0.04 wt%) and dispersed in DMF by ultrasonication for
110 1 hr followed by mechanical stirring overnight. Polyacrylonitrile (PAN, 1.00 g, 10 wt%) was
111 dissolved in the dispersion at 50 °C for an hour and stirred overnight at room temperature. PAN
112 (10 wt%) solution was prepared without TMAO as a control. We refer the 0.05 wt% and 0.1 wt%
113 TMAO incorporated samples as T5 and T10, respectively, and the neat PAN as T0. The solutions
114 were electrospun through a 20G spinneret under an applied voltage of 15 kV (Gamma High
115 Voltage Research, Inc., power supply). The fibers were deposited on a grounded collector
116 rotating at a speed of 300 rpm. The applied voltage, distance between the needle tip and
117 collector drum (15 cm) and the speed of the collector drum were kept constant for all the
118 samples.

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120 *2.3. Thermal treatments of carbon nanofibers*

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The as-spun nanofibers were stabilized at 240 °C under airflow (200 mL min⁻¹) for 6 hr. The carbonization and CO₂ activation were done in a single step in an inert environment at 1 atm using He (200 mL min⁻¹) at a heating rate of 5 °C min⁻¹ to a final temperature of 1000 °C. Then CO₂ (50 mL min⁻¹) was introduced while maintaining the temperature for 1 hr to obtain porous carbonized nanofibers.

2.4. Characterization

The conductivity of electrospinning solutions was measured using an Oakton CON 11 conductivity meter. The surface morphology of as-spun and carbonized nanofibers was observed by scanning electron microscopy (Zeiss SUPRA 40 SEM) after sputter coating with gold/palladium. The ratio of disordered to graphitic carbon was obtained by Raman spectroscopy using a HORIBA Jobin Yvon high-resolution LabRam Raman microscope system with a 633 nm helium-neon laser. Surface area and pore volume of the carbon nanofibers were obtained using Quantachrome Instruments Autosorb-1 at 77 K after degassing for 12 hours at 200 °C.

2.5. Supercapacitor device assembly and electrochemical measurements

Two electrodes (1.5 mg each) were punched out from carbonized and activated carbon nanofiber mats and transferred into a nitrogen filled glove box. They were soaked in EMITFSI electrolyte. Electrodes were separated by a GORE™ polytetrafluoroethylene separator. The symmetrical supercapacitors were assembled using CR2032 coin cells as the current collectors. Cyclic voltammetry (CV) and galvanostatic charge-discharge tests were carried out at different current densities using an Arbin Supercapacitor Testing Systems (SCTS) to evaluate the performance of the device.

3. Results and discussion

The SEM images and average fiber diameter of the electrospun samples, T0, T5 and T10 are shown in Fig. 1. The nanofibers are uniform and smooth and the average fiber diameter decreased with increasing amount of TMAO. The fiber diameters of the electrospun, and

carbonized and activated nanofibers were measured from the SEM images using ImageJ software (<http://rsb.info.nih.gov/ij/>). Average fiber diameter values for 150 individual measurements are summarized in Table 1. The average fiber diameter of the electrospun T0 sample was 970±120 nm, which decreased to 660±70 nm upon addition of only 0.05 wt% of TMAO and further decreased to 500±65 nm when the amount of TMAO is doubled. This can be explained by the increase in conductivity of the spinning solution from 12.1 mS m⁻¹ for T0 to 17.9 and 25.3 mS m⁻¹ for T5 and T10, respectively. The addition of TMAO increases the charge density of the spinning solution, which leads to an increase in repulsive force that overcomes the formation of spheres, thus decreasing the fiber diameter [33]. SEM images and average fiber diameter distributions of carbonized and activated nanofibers are illustrated in Fig.2. The images show that the morphology is conserved for all the samples after carbonization and activation with reduced fiber diameters of 525±75 nm, 260±50 nm and 245±40 nm for T0, T5 and T10, respectively.

Insert Figure 1 here.

Insert Figure 2 here.

Table 1. Average fiber diameters all samples

Samples	Average fiber diameter of electrospun fibers (nm)	Average fiber diameter of carbonized and activated fibers (nm)
PAN (T0)	970±120	525±75
PAN-TMAO (T5)	660±70	260±50
PAN-TMAO (T10)	500±65	245±40

We carried out TGA-MS on TMAO, electrospun PAN and electrospun PAN–TMAO (T10) to better understand the pore development in the fibers. TMAO thermally decomposes according to the following equation [31].

Fig. 3 shows plots of ion current vs temperature for selected ions with mass numbers of 28, 44, 46, 59, 118, which correspond to CO, CO₂, dimethyl ether, trimethylamine and dimethyl oxalate, respectively. The peaks around 300 °C in Fig. 3.a confirmed that TMAO is totally decomposed and produced all the gaseous products according to reported literature [31]. Fig 3.b does not show any peaks except the one that corresponds to CO₂, which is a product of carbonization of PAN. The presence of peaks for mass number 59 in the T10 sample in Fig. 3.c indicates that TMAO was successfully incorporated into PAN. The peak for dimethyl oxalate ($m/z=118$) shifted to a higher temperature region in the T10 sample, which suggest that this solid decomposition product might have been trapped in the fiber and decomposed into gaseous products (CO, etc.) beyond the stabilization temperature.

Insert Figure 3 here.

Raman spectra of all the samples were shown in Fig. 4. Raman spectroscopy is one of the most sensitive techniques used to study the structural properties of carbonaceous materials [34]. Fig. 4 shows the Raman spectra of carbon nanofibers derived from different samples. There are two broad overlapping peaks centered around 1360 cm⁻¹, known as the D band, which corresponds to disordered sp³ carbon, and 1590 cm⁻¹, which is identified as the G band, which is due to graphitic crystallites or sp² bonded carbons [34]. Peaks were fitted using a Lorentzian equation and the ratios of the integrated intensity of D band to G band (I_D/I_G) were calculated [35]. The I_D/I_G ratio increased slightly from 3.31 to 3.46 with 0.1 wt% addition of TMAO, which suggests that the addition of TMAO did not significantly increase the amount of disordered carbon.

Insert Figure 4 here

Nitrogen adsorption/desorption isotherms for T0, T5 and T10 samples shown in Fig. 5. The specific surface area was calculated using Brunauer-Emmett-Teller (BET) equation [36]. DFT pore size distribution illustrated in Fig. 5.b is calculated by applying DFT calculation to the nitrogen adsorption isotherms using the Quantachrome Instruments Autosorb-1 software. Table 2 summarizes the data for all three samples. The T0 sample possesses a specific surface area of 1963 m² g⁻¹ with a total pore volume of 1.229 cm³ g⁻¹, 43% of which are mesoporous (2-50 nm).

Addition of only 0.05 wt% of TMAO increased the specific surface area of the T5 sample to 2295 m² g⁻¹ without a significant change in the mesoporosity percentage. A further increase of TMAO increased the specific surface area to 2663 m² g⁻¹ (36% greater than T0) with a decrease in mesoporosity (29%). We consider only the pores with at least the same size or greater than the electrolyte ions. Ion sizes of cation (EMI⁺) and anion (TFSI⁻) are 4.3 x 7.6 Å and 2.9 x 7.9 Å respectively. For all three samples, more than 95% of the pore volume is accessible to cations and 100% are accessible to anions (by considering the shortest dimension of ions) [37].

Insert Figure 5 here

Table 2. BET surface area, pore volumes obtained from N₂ sorption isotherms of carbonized and activated nanofibers

	BET SSA (m ² g ⁻¹)	DFT TPV (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)
PAN (T0)	1963	1.229	0.703 (57%)	0.526 (43%)
PAN-TMAO (T5)	2295	1.260	0.690 (55%)	0.570 (45%)
PAN-TMAO (T10)	2663	1.487	1.060 (73%)	0.427 (29%)

The capacitance, C, of a two electrode coin cell was calculated from CV using the equation

$$C = \int I/U \, dt \quad (1)$$

where I is the integrated discharge current over the potential range U is the scan rate. Specific capacitance, C_{sp}, was calculated from

$$C_{sp} = 4C/m \quad (2)$$

Where m is mass of both electrodes. In Fig.6. (a), the CV curve of activated PAN showed a slightly skewed rectangular shape. On the other hand, T5 and T10 in (Fig. 6b-c) showed more rectangular cyclic voltammograms. The Specific capacitance values of T0, T5 and T10 samples calculated from the CV curves are 90 F g⁻¹, 129 F g⁻¹ and 140 F g⁻¹, respectively. There is a 30% increase in specific capacitance for T10 sample compared to the PAN at the scan rate of 10 mV

s⁻¹. This improvement can be attributed to its high surface area and higher amount of mesopores that allow better pore accessibility and faster diffusion of bulky ions of ionic liquid electrolytes [38].

Insert Figure 6 here

Table 3 Specific capacitance, energy density and power density of carbonized and activated nanofibers

Samples	Specific capacitance at 10 mV s ⁻¹ (F g ⁻¹)	Energy density (Wh kg ⁻¹) at 1 kW kg ⁻¹	Energy density (Wh kg ⁻¹) at 10 kW kg ⁻¹
T0	92	40	17
T5	129	63	62
T10	140	69	65

Galvanostatic charge-discharge tests were carried out from 0-3.5 V at different current densities. Fig.7. (a) shows the discharge plots of all samples at constant current density of 1 A g⁻¹. Linear discharge plots for T5 and T10 samples illustrate the capacitive behavior. The IR drop for neat PAN was 0.3 V, which is higher than that of T5 and T10 samples (0.02 V). Also, the discharge time increased with the addition TMAO. Energy densities (E_d) and power densities (P_d) were calculated using following equations 3 and 4, respectively.

$$E_d = \frac{1}{2} C(\Delta V)^2 \quad (3)$$

$$P_d = E_d/t \quad (4)$$

where I is the discharge current and t is the time it takes to discharge to 0 V from the initial voltage (ΔV), considering the IR drop at the beginning of discharge. Energy and power densities of all the samples are shown in the Ragone plot in Fig.7.(b) and summarized in Table 3. Energy densities of T0 and T5 were 40 and 63 Wh kg⁻¹, respectively at 1 kW kg⁻¹ power density. The

highest energy density of 69 Wh kg^{-1} was obtained for T10 sample containing highest amount of TMAO. The energy density of T0 dropped to less than 50% of its initial value when the power density was increased to 10 kW kg^{-1} .

Insert Figure 7 here

High surface area and the high amount of mesoporosity facilitated faster ion diffusion allowing the T5 and T10 samples to hold a very good energy retention ($>95\%$) at the higher discharge rate. Cycle stability is an important characteristic to evaluate the performance of supercapacitors. Figure.8. shows the plot of specific capacitance retention of T10 against cycle number. Although the specific capacitance faded upon cycling, it retained 80% of its initial value after 1000 cycles at 1 A g^{-1} .

Insert Figure 8 here

4.0 Conclusion

In this study, different amounts of a porogen, TMAO were incorporated into PAN to produce carbon nanofibers with reduced fiber diameter because of the increased conductivity of electrospinning solution. A high surface area of $2663 \text{ m}^2 \text{ g}^{-1}$ for sample T10 was obtained, which is comparable to theoretical surface area of graphene ($2600 \text{ m}^2 \text{ g}^{-1}$). A specific capacitance of 140 F g^{-1} and an energy density of 69 Wh kg^{-1} at 1 kW kg^{-1} at 3.5V in coin cells utilizing the ionic liquid electrolyte, EMITFSI, were observed. These values are about 60% higher than those for devices utilizing electrodes from electrospun PAN *without porogen* in the same electrolyte. The carbon nanofiber derived from neat PAN dropped from 40 Wh kg^{-1} to 17 Wh kg^{-1} when the power density increased from 1 kW kg^{-1} to 10 kW kg^{-1} whereas T10 retained 94% of its original value.

References

- [1] B.E. Conway, Transition from “Supercapacitor” to “Battery” Behavior in Electrochemical Energy Storage, J. Electrochem. Soc 183 (1990) 1539-1548.

- 294 [2] Martin Winter, Ralph J. Brodd, What Are Batteries , Fuel Cells , and
295 Supercapacitors ?, Chem. Rev. 104 (2004) 4245–4269.
- 296 [3] A. Burke, Ultracapacitors: why, how, and where is the technology, Journal of Power
297 Sources. 91 (2000) 37–50.
- 298 [4] R. Ko, M. Carlen, Principles and applications of electrochemical capacitors,
299 Electrochimica Acta. 45 (2000) 2483–2498.
- 300 [5] J. Chmiola, G. Yushin, R.K. Dash, E.N. Hoffman, J.E. Fischer, M.W. Barsoum, et al.,
301 Double-Layer Capacitance of Carbide Derived Carbons in Sulfuric Acid, Electrochem.
302 Solid-State Lett. 8 (2005) A357.
- 303 [6] M. Zhi, F. Yang, F. Meng, M. Li, A. Manivannan, N. Wu, Effects of pore structure on
304 performance of an activated-carbon supercapacitor electrode recycled from scrap waste
305 tires, ACS Sustain. Chem. Eng. 2 (2014) 1592–1598.
- 306 [7] M. Galiński, A. Lewandowski, I. Stepniak, Ionic liquids as electrolytes, Electrochim.
307 Acta. 51 (2006) 5567–5580.
- 308 [8] Hybrid Supercapacitors With Ionic Liquid Electrolytes, ECS Transactions. 1 (2006) 55–
309 59.
- 310 [9] D.H. Reneker, I. Chun, Nanometre diameter fibres of polymer, produced by
311 electrospinning, Nanotechnology. 7 (1999) 216–223.
- 312 [10] N. Bhardwaj, S.C. Kundu, Electrospinning: A fascinating fiber fabrication technique,
313 Biotechnol. Adv. 28 (2010) 325–347.
- 314 [11] W.E. Teo, S. Ramakrishna, A review on electrospinning design and nanofibre assemblies.,
315 Nanotechnology. 17 (2006) R89–R106.
- 316 [12] J. Doshi, D.H. Reneker, Electrospinning process and applications of electrospun fibers,
317 Conf. Rec. 1993 IEEE Ind. Appl. Conf. Twenty-Eighth IAS Annu. Meet. 35 (1993) 151–
318 160.
- 319 [13] H.M. Lee, H.G. Kim, K.-H. An, B.-J. Kim, Effects of pore structures on electrochemical
320 behaviors of polyacrylonitrile-based activated carbon nanofibers by carbon dioxide
321 activation, Carbon Lett. 15 (2014) 71–76.
- 322 [14] B. Kim, N. Bui, K. Yang, M.E. Cruz, J.P. Ferraris, Electrochemical Properties of
323 Activated Polyacrylonitrile / pitch Carbon Fibers Produced Using Electrospinning, Bull.
324 Korean Chem. Soc. 30 (2009) 1967–1972.
- 325 [15] L. M. Manocha, O. P. Bahl, and G. C. Jain , Length Changes in PAN Fibers During Their
326 Pyrolysis to Carbon Fibers, Die Angewandte Makromolekulare Chemie. 67 (1978) 11–29.

- 327 [16] S. Dalton, F. Heatley, P.M. Budd, Thermal stabilization of polyacrylonitrile fibres,
328 Polymer (Guildf). 40 (1999) 5531–5543.
- 329 [17] M.S. a. Rahaman, a. F. Ismail, a. Mustafa, A review of heat treatment on polyacrylonitrile
330 fiber, Polym. Degrad. Stab. 92 (2007) 1421–1432.
- 331 [18] Y. Wang, J.J. Santiago-aviles, R. Furlan, I. Ramos, Pyrolysis temperature and time
332 dependence of electrical conductivity evolution for electrostatically generated carbon
333 nanofibers, IEEE Trans. Nanotechnol. 2 (2003) 39–43.
- 334 [19] H. Teoh, P.D. Metz, W.G. Wilhelm, Electrical conductivity of pyrolyzed
335 polyacrylonitrile, Mol. Cryst. Liq. Cryst. 83 (1982) 297–306.
- 336 [20] G.K. Nieh, D.T. Grow, Activation of carbon fibers by steam, J. Colloid Interface Sci. 119
337 (1987) 280–285.
- 338 [21] H. Tavanai, R. Jalili, M. Morshed, Effects of fiber diameter and CO₂ activation
339 temperature on the pore characteristics of polyacrylonitrile based activated carbon
340 nanofibers, Surf. Interface Anal. 41 (2009) 814–819.
- 341 [22] X. Yu, H. Xiang, Y. Long, N. Zhao, X. Zhang, J. Xu, Preparation of porous
342 polyacrylonitrile fibers by electrospinning a ternary system of PAN/DMF/H₂O, Mater.
343 Lett. 64 (2010) 2407–2409.
- 344 [23] M. Mehraban, A. Zadhoush, S. Abdolkarim Hosseini Ravandi, R. Bagheri, A. Heidarkhan
345 Tehrani, Preparation of porous nanofibers from electrospun polyacrylonitrile/calcium
346 carbonate composite nanofibers using porogen leaching technique, J. Appl. Polym. Sci.
347 128 (2013) 926–933.
- 348 [24] X. Wang, H. Ma, H. Zhang, M. Yu, X. He, Y. Wang, Interconnected mesoporous carbon
349 sheet for supercapacitors from low-cost resources, Mater. Lett. 158 (2015) 237–240
- 350 [25] C. Kim, B.T.N. Ngoc, K.S. Yang, M. Kojima, Y. a. Kim, Y.J. Kim, et al., Self-Sustained
351 Thin Webs Consisting of Porous Carbon Nanofibers for Supercapacitors via the
352 Electrospinning of Polyacrylonitrile Solutions Containing Zinc Chloride, Adv. Mater. 19
353 (2007) 2341–2346.
- 354 [26] B.H. Kim, K.S. Yang, H.G. Woo, K. Oshida, Supercapacitor performance of porous
355 carbon nanofiber composites prepared by electrospinning polymethylhydrosiloxane
356 (PMHS)/polyacrylonitrile (PAN) blend solutions, Synth. Met. 161 (2011) 1211–1216.
- 357 [27] C. Tran, V. Kalra, Fabrication of porous carbon nanofibers with adjustable pore sizes as
358 electrodes for supercapacitors, J. Power Sources. 235 (2013) 289–296.
- 359 [28] Y.-H. Hsu, C.-C. Lai, C.-L. Ho, C.-T. Lo, Preparation of interconnected carbon nanofibers
360 as electrodes for supercapacitors, Electrochim. Acta. 127 (2014) 369–376.

- [29] S.K. Nataraj, B.H. Kim, M. dela Cruz, J. Ferraris, T.M. Aminabhavi, K.S. Yang, Free standing thin webs of porous carbon nanofibers of polyacrylonitrile containing iron-oxide by electrospinning, *Mater. Lett.* 63 (2009) 218–220..
- [30] N. Abeykoon, J.S. Bonso, J.P. Ferraris, Supercapacitor performance of carbon nanofiber electrodes derived from immiscible PAN/ PMMA polymer blends, *RSC Adv.* 5 (2015) 19865–19873.
- [31] B. Albert, M. Jansen, Why does tetramethylammonium oxalate exhibit sublimation?, *J. Chem. Soc. Chem. Commun.* (1993) 965.
- [32] A. T. Lawson and Norman Collie, Ph.D., F.R.S.E., The action of heat on the salts of tetramethylammonium, *J. Chem. Soc., Trans.*, 53 (1888), 624-636.
- [33] L. Ji, A.J. Medford, X. Zhang, Electrospun polyacrylonitrile/zinc chloride composite nanofibers and their response to hydrogen sulfide, *Polymer (Guildf)*. 50 (2009) 605–612.
- [34] T. Jawhari, a. Roid, J. Casado, Raman spectroscopic characterization of some commercially available carbon black materials, *Carbon N. Y.* 33 (1995) 1561–1565.
- [35] M. Endo, C. Kim, T. Karaki, T. Kasai, M.. Matthews, S.D.. Brown, et al., Structural characterization of milled mesophase pitch-based carbon fibers, *Carbon N. Y.* 36 (1998) 1633–1641.
- [36] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of Gases in Multimolecular Layers, *J. Am. Chem. Soc.* 60 (1938) 309–319.
- [37] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors., *Nat. Mater.* 7 (2008) 845–854.
- [38] A. Vu, X. Li, J. Phillips, A. Han, W.H. Smyrl, P. Bühlmann, et al., Three-dimensionally ordered mesoporous (3DOm) carbon materials as electrodes for electrochemical double-layer capacitors with ionic liquid electrolytes, *Chem. Mater.* 25 (2013) 4137–4148.

References

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