Supporting Information

Atmospheric Pressure Plasma-Jet Treatment of PAN-Nonwovens—Carbonization of Nanofiber Electrodes

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Materials: Acrylonitrile Polymer (DralonX) with a molar mass of $\sim M_w = 85.000$ g/mol was obtained from Dralon GmbH, Dimethysulfoxide (DMSO) was obtained from Fisher Scientific, Acetone was obtained from Sigma-Aldrich and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI; 99.5%) was obtained from Iolitec GmbH.

Nonwoven: We utilize PAN-nonwoven, that has been fabricated in an electric-field assisted rotational spinning apparatus, obtained from DIENES Apparatebau GmbH, in which we spin PAN-based solutions with mass concentrations of $W_{PAN} = 10$ wt% in a mixture of DMSO and Acetone of a volumetric ratio $X_{DMSO:Acetone} = 4:1$ onto a stationary wide-meshed metal grid collector, at a voltage $V = 70$ kV (300 µA), rotational speed of the spinneret $\omega = 15$ krpm, dope pump-speed $V_{pump} = 9$ mL/min, air-pressure from the top $p_{air} = 0.75$ bar and humidity $H = \sim60$ rh%. The obtained fiber diameters of the nonwovens average at f = 776 nm ± 164 nm for an
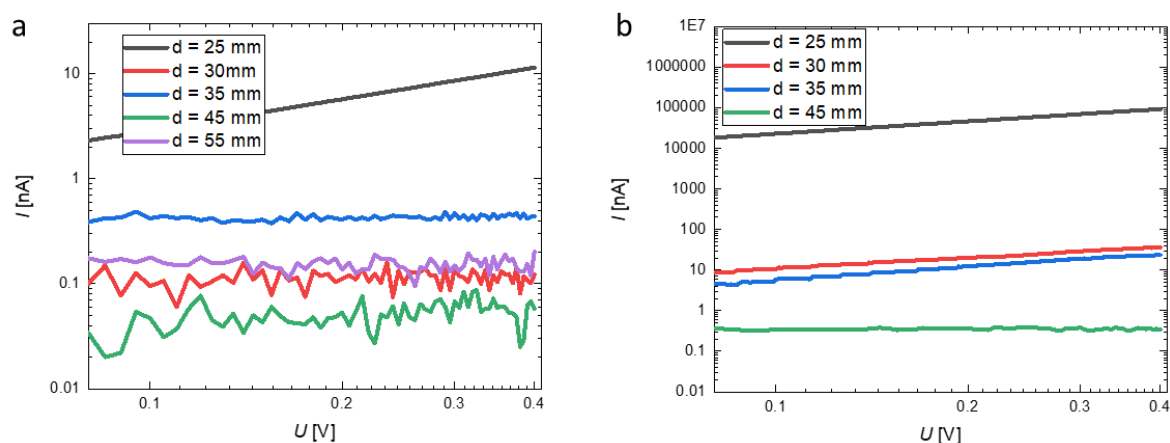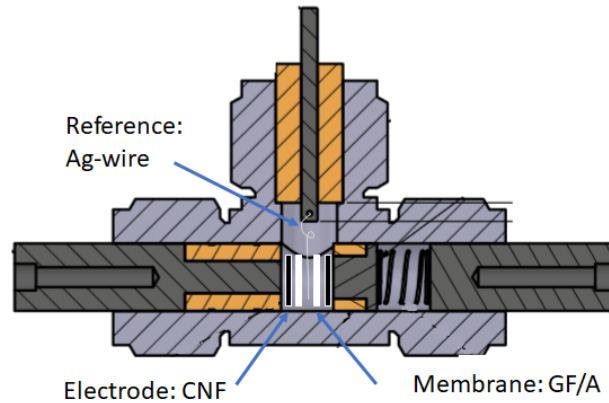

Figure S1. Logarithmic current-voltage curves of a) the center and b) edge of plasma-jet carbonized nanofiber nonwoven, at various distances *d*.

AN-copolymer (DralonX from Dralon GmbH). We dry those nonwoven for one day in a fumehood and stabilize them afterwards in a heat convective furnace at a Temperature of 230°C for 30 min. and 280°C for another 30 min. ($\Delta T = 5$ K/min.).

Current-voltage curves: The resistance was calculated from the slope of current (I) voltage (U) curves in Figure S1. The curves were recorded in a two point setup, with a distance of 4 mm between the measuring points and a constant contact pressure.

Electrochemical measurements: Electrochemical measurements were conducted in 3-electrode Swagelog-cells, which were connected to an Iviumsat.h potentiostat (Ivium technologies) via banana clips. The cells contain two circular carbon nanofiber (CNF) electrodes, sandwiching two layers of whatman GF/A membranes and a silver-wire as pseudo-reference electrode. The cells were assembled in a glovebox. EMIM TFSI was used as an electrolyte.

Scheme S1. Cell-setup for electrochemical measurements.

After 12 h of swelling, cyclic voltammograms were recorded at scanrates from 5 – 100 mV/s between -1 V and +1 V, with at least 10 cycles. The specific capacitance C_{sp} was calculated by

$$C_{sp} = \frac{\int_{E_{max.}}^{E_{min.}} I \, dE}{2 \cdot v \cdot \Delta E \cdot m}$$

with the scanrate (v), the electric potential difference vs. Ag-wire (E), the potential window (ΔE) and the electrode weight (m). Galvanostatic charge discharge curves were recorded between -1 V and +1 V. Impedance spectra were recorded from 0.01 Hz 5.0 MHz at a voltage of 0.05 V. The circuit in Figure 4a was used as an equivalent circuit with the inductivity (L), resistance (R), capacitance (C) and constant phase element (CPE). The fit-results are displayed

in Table S3 with CPE2(Q) being the corresponding capacitive value, CPE2(n) the corresponding exponent in the CPE and f_{val} describing the goodness of the fit.

Instruments: SEM images were recorded on a Hitachi S-5200.

XPS was performed on a PHI 5800 ESCA system (Physical Electronics), using monochromatized Al Kα radiation (1486 eV). The pass energy for survey spectra was 93.9 eV, for detail spectra we used 29.35 eV. Survey spectra were recorded with 17 scans, detail spectra were recorded with roughly 200 scans.

Raman measurements were conducted on a confocal microscope WITec Alpha 300R with a UHTS-300 spectrometer. The spectra were recorded with 10 acquisitions, 5 s integration time and at a laser power of 1.0 mW (532 nm).

XPS-analysis: The binding energies (BEs) of all spectra were calibrated with respect to the C (1s) peak. The data evaluation and peak convolution was performed using the commercial software CasaXPS 2.3.23PR1.0 (www.casaxps.com). A Tougaard-type background was subtracted before the peak-fitting process. C1s-spectra were deconvolved to following peaks: C-sp² (284.3 eV), C-sp³ (285.1-285.2 eV), C-OH (286.7 286.3 eV), C=O (287.9 eV) and O-C=O (288.9-289.4 eV).

Table S1. Ratio of deconvolved peak-areas in Figure 2c.

Sample	Ratio of peaks in deconvolved C1s spectra [%]					
	C-sp²	C-sp³	C-OH	C=O	O-C=O	other
Stabilized PAN	31.8	31.0	26.3	5.4	2.7	2.8
Plasma carbonized (center)	58.1	13.2	12.1	9.1	4.7	2.8
Plasma carbonized (edge)	66.3	16.9	6.5	5.1	4.4	0.8
Carbonized by convective heat	72.7	13.2	3.3	3.2	4.7	2.9

Table S2. Atomic ratios of plasma jet carbonized samples, extracted from XPS-measurements.

Sample	Atomic ratio [%]				
	C	O	N	Na	Si
Stabilized-PAN	71	16	11	0	2
Front carbonization - center	74	13	12	1	0
Front carb. edge	81	11	6	1	1
Back carb. center	84	5	11	0	0
Back carb. edge	84	8	6	1	1
Carb. by heat conviction	91	4	5	0	0

Table S3. Fitting parameters of the equivalent circuit fit in the of the Nyquist plots in Figure 4a.for various plasma-jet exposure times t.

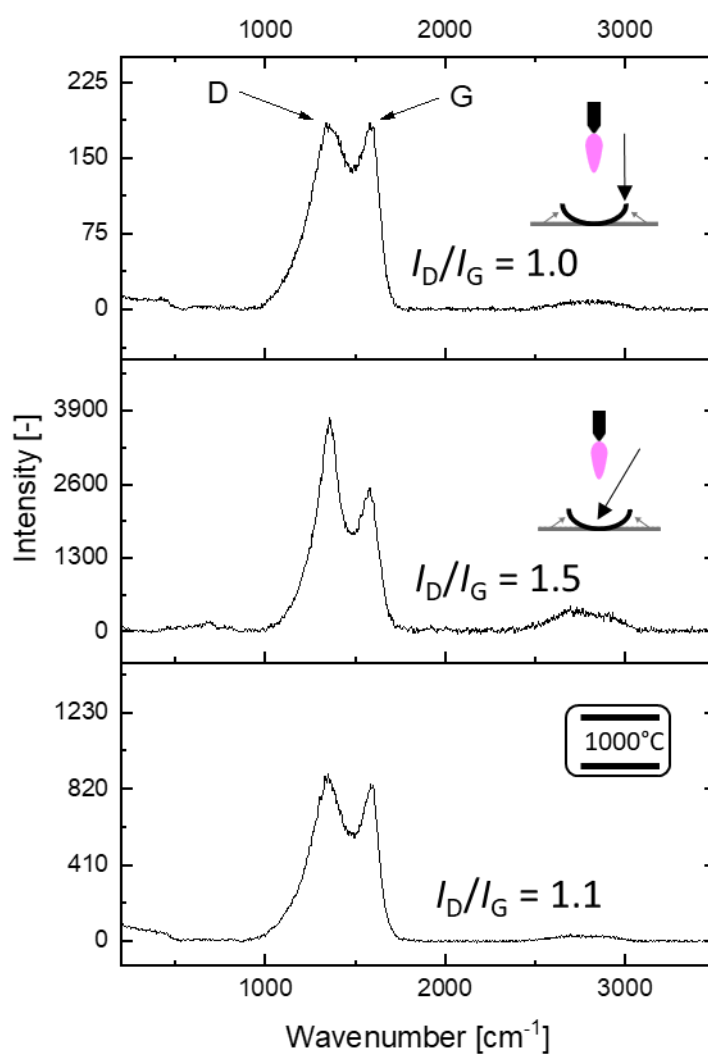| parameters	$t = 5$ s	$t = 30$ s	$t = 60$ s	$t = 120$ s	$t = 180$ s
L1	0.0476 H	6.53E-4 H	6.22E-4 H	5.48E-5 H	2.68E-5 H
R1	3.38 Ω	1.17 Ω	1.59 Ω	1.50 Ω	1.31 Ω
Rs	12.42 Ω	5.39 Ω	5.65 Ω	7.90 Ω	8.15 Ω
RP1	36.2 Ω	50.9 Ω	35.1 Ω	67.3 Ω	12.5 Ω
CPE1(Q)	1.90E-5 F	8.63E-4 F	4.26E-4 F	3.87E-4 F	3.09E-4 F
CPE1(n)	0.75	0.85	0.62	0.58	0.75
RP2	122.3 Ω	18.6 Ω	9.06 Ω	7.96 Ω	10.03 Ω
CPE2 (Q)	8.92E-4 F	1.94E-3 F	6.84E-3 F	1.26E-4 F	2.41E-5 F
CPE2 (n)	0.78	0.35	0.40	0.67	0.71
C3	8.97E-4 F	2.46E-3 F	4.84E-3 F	6.04E-4 F	8.97E-4 F
fval	7.28	3.49	1.72	9.36	4.01

Figure S2: Raman spectra of a (bottom) CNF, which have been carbonized by convective heat, (middle) the central area of a CNF which have been carbonized by a plasma-jet and (top) the edge area of a CNF which have been carbonized by a plasma-jet. D (1357 cm-1) and G (1583 cm-1) bands have been indicated by arrows and the ratio of those bands I_D/I_G are given for all three samples.
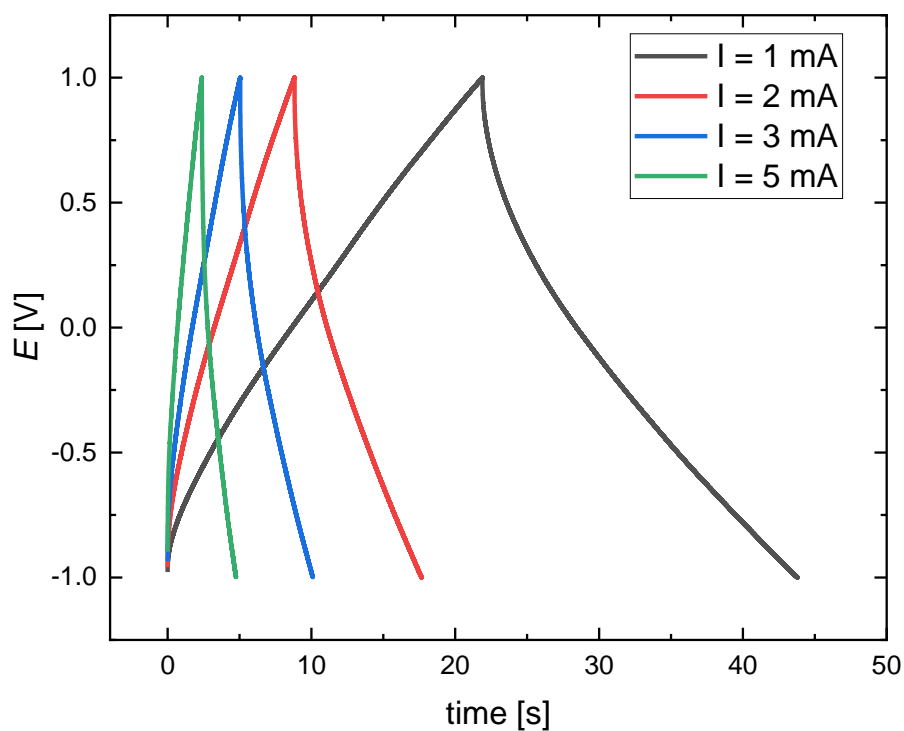
Figure S3: Galvanostatic charge/discharge curves of a plasma-jet carbonized (t = 60 s) carbon fiber nonwoven electrode.
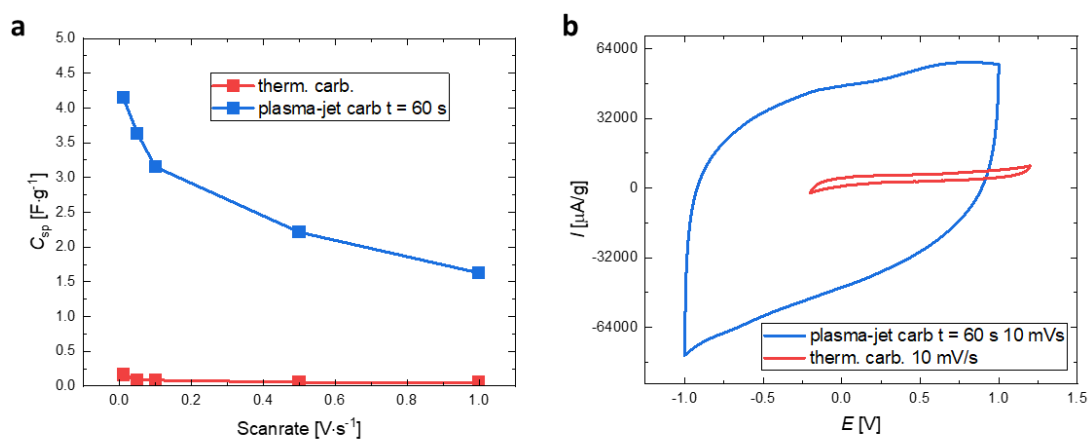

Figure S4. a) Scanrate dependent specific capacitance C_{sp} for thermally carbonized and a plasma-jet carbonized carbon fiber nonwoven electrode. b) Cyclic voltammograms of a thermally carbonized and a plasma-jet carbonized carbon fiber nonwoven electrode. The potential window was found to be smaller for thermally carbonized carbon fiber nonwoven electrodes.