

Short communication

Nomex-derived activated carbon fibers as electrode materials in carbon based supercapacitors

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Abstract

Electrochemical characterization has been carried out for electrodes prepared of several activated carbon fiber samples derived from poly (*m*-phenylene isophthalamide) (Nomex) in an aqueous solution. Depending on the burn-off due to activation the BET surface area of the carbons was in the order of 1300–2800 m² g⁻¹, providing an extensive network of micropores. Their capability as active material for supercapacitors was evaluated by using cyclic voltammetry and impedance spectroscopy. Values for the capacitance of 175 F g⁻¹ in sulfuric acid were obtained. Further on, it was observed that the specific capacitance and the performance of the electrode increase significantly with increasing burn-off degree. We believe that this fact can be attributed to the increase of surface area and porosity with increasing burn-off.

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1. Introduction

In recent years, activated carbons have found big attraction as electrode material for the storage of energy in supercapacitors due to their very high surface area, simple processability and low costs [1–3]. Chemical and physical methods of carbon activation are well known and allow producing materials, which are defined in terms of surface area and pore size distribution [4–8]. When fibrous precursors are used activated carbon fibers are obtained, which exhibit high adsorption/desorption rates and narrow pore size distribution. Using fibrous materials gives an additional profit from the construction point of view and thus offer a number of advantages over conventional powdered activated carbons [9–16].

Our previous work has shown that physically activated carbon fibers derived from poly (*m*-phenylene isophthalamide) (Nomex, Fig. 1) have a very homogeneous (micro)-pore

size distribution and can be prepared with very high pore volumes and/or ultrahigh surface areas up to 2600 m² g⁻¹ [17,18]. This seems to be an excellent prerequisite for the use of such fibers in electrochemical supercapacitors [19]. In this work we will compare the electrochemical performance of different Nomex-based activated carbon fiber materials and evaluate whether an application for supercapacitors is promising.

2. Experimental

2.1. Material

The starting material was commercially available Nomex aramid fiber in a variety known as Crystalline Nomex (T450 2.2 dtex.). Various series of activated carbon fibers were prepared from either fresh Nomex (N), or Nomex pre-impregnated with different amounts of H₃PO₄ (NP). The impregnation ratio (calculated as the weight gain after

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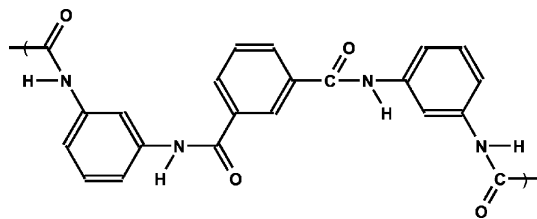


Fig. 1. Chemical structure of the precursor Nomex.

impregnation relative to the mass of Nomex) amounted to 1 and 7 wt.%, and the samples are named NP1 and NP7, respectively. The burn-off degrees of samples were calculated from the final mass (after pyrolysis and activation) relative to the initial mass of pyrolysed Nomex. Thus, N-76 is an ACF obtained from fresh Nomex pyrolysed and then activated in CO_2 to 76% burn-off, whereas NP7-72 is an ACF obtained from Nomex impregnated with 7 wt.% H_3PO_4 and activated in CO_2 to 72% burn-off. As concerns the activating agent, samples NP7-72, N-76 and NP1-90 were activated with carbon dioxide, whereas sample N-42 was activated with water vapour. The impregnation process as well as the pyrolysis/activation step is described in detail in previous reports [17,18]. Fig. 2a is an SEM micrograph of sample NP1-90, which shows that the diameter of the fibers is in the order of $10\ \mu\text{m}$. The fibers have a bilobular section, which is more easily appreciated in the higher-resolution image of a single fiber, shown in Fig. 2b. The bilobular morphology is already present in the parent Nomex polymer, and is maintained along with pyrolysis and activation treatments.

2.2. Electrochemical techniques and instrumental details

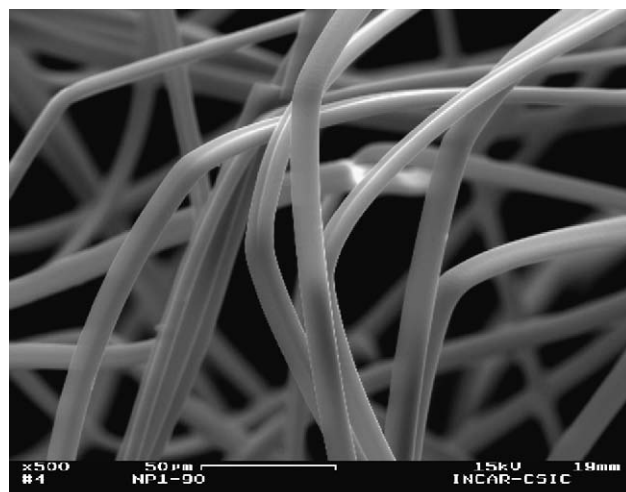
Cyclic voltammograms (CVs) were recorded with a Zahner IM6 measurement system in a potential range of -600 to $+300\ \text{mV}$ versus $\text{Hg}/\text{Hg}_2\text{SO}_4$. Cyclic voltammetry experiments started at open circuit potential (OCP) and were carried out at room temperature ($25 \pm 2\ ^\circ\text{C}$). CVs were recorded at three different scan rates (5 , 10 and $20\ \text{mV s}^{-1}$) to obtain information about the rate behavior of electrical double layer formation.

To obtain more information about the frequency behavior of the electrodes electrochemical impedance spectroscopy (EIS) was performed. For EIS the same measurement system was used. Therefore, at $-100\ \text{mV}$ versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ an ac amplitude of $5\ \text{mV}$ was applied and data were collected in a frequency range of $10\ \text{kHz}$ to $5\ \text{mHz}$.

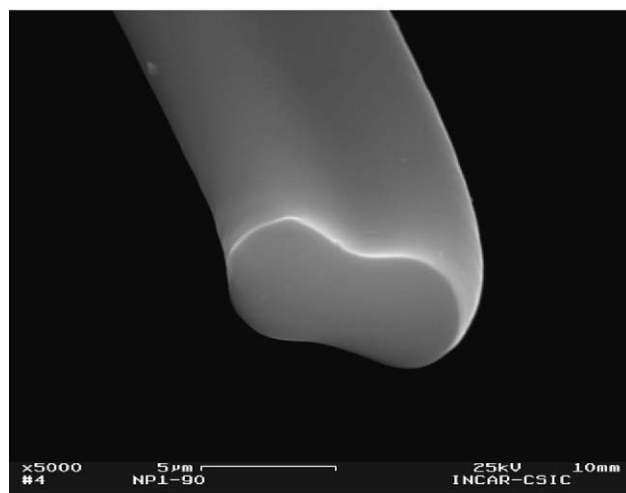
All electrochemical experiments have been performed in a three-electrode glass cell with a carbon counter electrode and an $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode using $5.25\ \text{M}$ sulfuric acid as the electrolyte.

2.3. Preparation of electrodes

The fibers were milled using an agate mortar and pestle to a fine powder and mixed with up to 10% PVdF (Aldrich) as



(a)



(b)

Fig. 2. SEM micrographs of NP1-90 sample: general overview (a); detailed view of a single fiber, showing the bilobular section (b).

binder for 1 h using a magnetic stirrer. Even after extensive milling, a fibrous morphology of the powder remains and is well observable under the light microscope. *N*-methyl pyrrolidinone (NMP) was slowly added to the resulting powder until a paste-like consistency was obtained. The paste was further homogenised using a spatula. The resulting active material was applied on the current collector with a doctor blade. A $10\ \text{mm} \times 10\ \text{mm}$ titanium grid was used as current collector. Each electrode was pressed five times for $60\ \text{s}$ (ca. $10^6\ \text{N m}^{-2}$) between filter paper to remove excess NMP. Finally, the electrodes were dried under vacuum for $24\ \text{h}$ at $120\ ^\circ\text{C}$ and afterwards weighted to estimate the mass of active material. All calculations of specific capacitance are referring to the total mass of active material (carbon and binder). Before the electrochemical measurements, all electrodes were vacuum-wetted with electrolyte in a desiccator for $30\ \text{min}$ in order to allow the electrolyte to penetrate into pores.

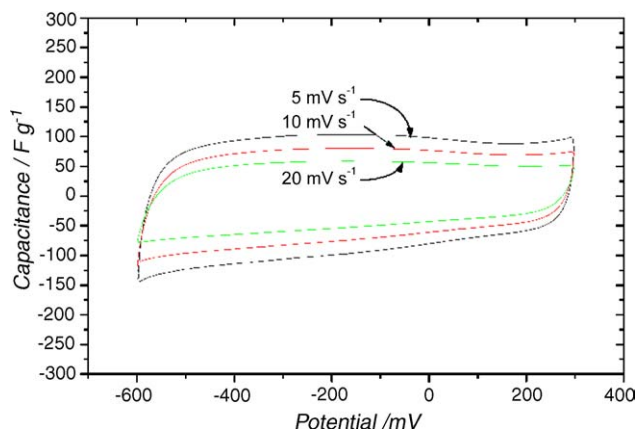


Fig. 3. CVs of sample N-42 expressed as capacitance vs. potential. Electrolyte: 5.25 M H₂SO₄, scan rates 5, 10 and 20 mV s⁻¹, Ref.: Hg/Hg₂SO₄.

3. Results and discussion

The stability window of the electrolyte was found to be in the range of -600 to 300 mV versus Hg/Hg₂SO₄. Depending on the type of fibers we obtained values of the capacitance of about 90 up to 175 F g⁻¹, as determined by means of CV. As demonstrated in Fig. 3, N-42 fibers show the strongest scan rate dependency of capacitance indicating that the accessibility of the electrolyte to this carbon is not as good as in the phosphoric acid activated fibers. In contrast to N-42 the CVs of all other investigated samples are almost congruent at different scan rates (Figs. 4–6). It is also noticed that at the fiber surfaces of NP7-72, N-76 and NP1-90 a significant pseudocapacitance seems to be manifested indicated by a broad hump in the potential area of -100 mV (Figs. 4–6).

Based on the results of CV, the origin of the increase in capacitance can be attributed to the larger specific surface area and porosity brought about by a greater burn-off degree. Sample NP1-90 seems to be completely activated, whereas the other samples with lower burn-off degree are only partial activated. Therefore, at samples with low burn-off residual

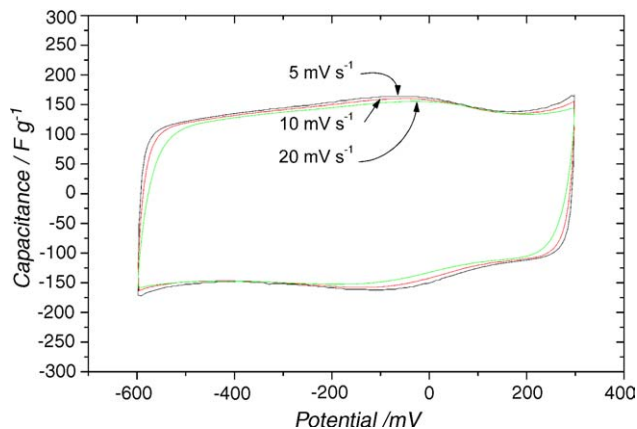


Fig. 4. CVs of NP7-72 expressed as capacitance vs. potential. Electrolyte: 5.25 M H₂SO₄, scan rates 5, 10 and 20 mV s⁻¹, Ref.: Hg/Hg₂SO₄.

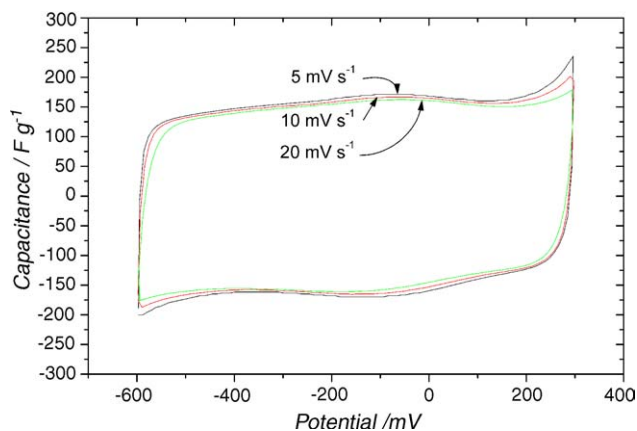


Fig. 5. CVs of N-76 expressed as capacitance vs. potential. Electrolyte: 5.25 M H₂SO₄, scan rates 5, 10 and 20 mV s⁻¹, Ref.: Hg/Hg₂SO₄.

inactive carbon is still contributing to the total mass and thus reducing the gravimetric capacitance.

Fig. 7 presents impedance spectra of electrodes made of the different activated carbon fiber samples. For better comparison, in all spectra the corresponding equivalent series resistance (ESR) has been subtracted from the real part of the impedance. Thus, all spectra are starting from the origin. The electrodes prepared from samples NP7-72, N-76 and NP1-90 follow the expected behavior of an ideal capacitor with low internal resistance, whereas sample N-42 shows indications of diffusional barriers and significant higher resistance in the interior of the electrodes or the fibers themselves. Furthermore it can be observed that electrodes with higher burn-off behave more capacitively, as demonstrated by a nearly vertical line in the mid to low frequency range. This indicates that the electrolyte penetration into the electrode is improved with higher surface area development [20]. Moreover, samples NP7-72, N-76 and NP1-90 exhibited a pore size distribution in the 2 – 3 nm range [17], whereas sample N-42 had a narrower pore size (below 1 nm) [18].

Finally, Fig. 8 illustrates the frequency behavior of capacitance of the investigated activated carbon fiber samples. It

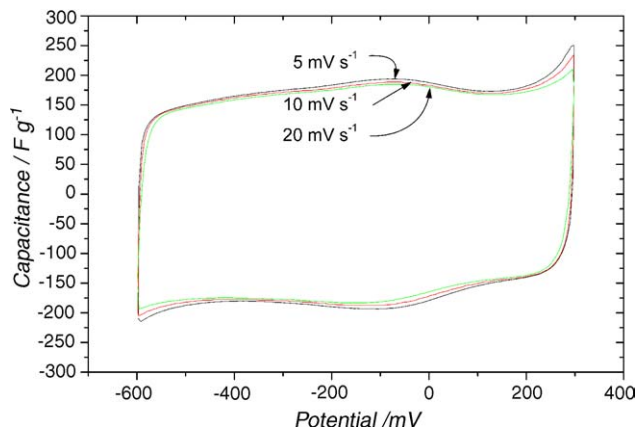


Fig. 6. CVs of NP1-90 expressed as capacitance vs. potential. Electrolyte: 5.25 M H₂SO₄, scan rates 5, 10 and 20 mV s⁻¹, Ref.: Hg/Hg₂SO₄.

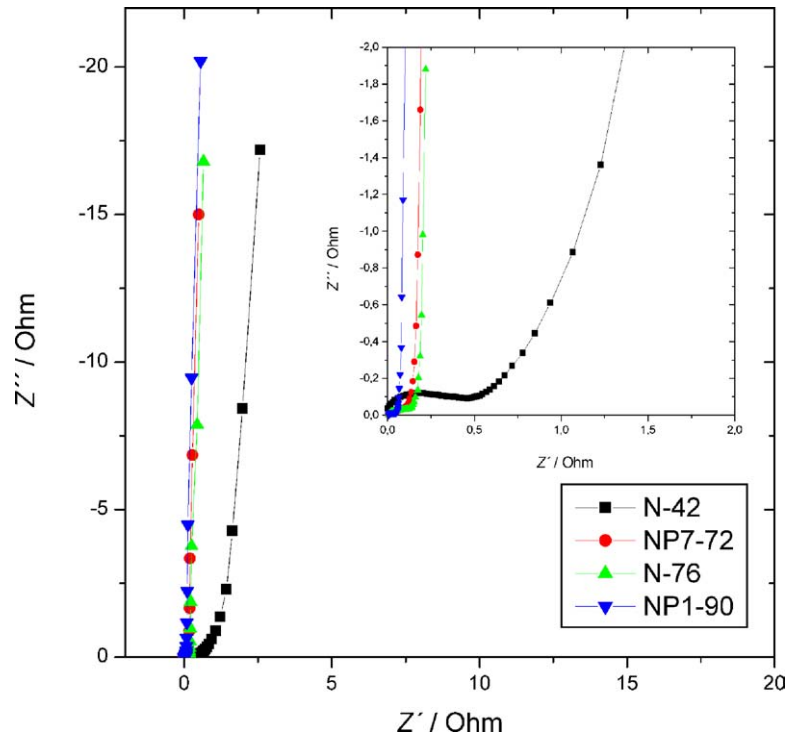


Fig. 7. Impedance spectra between 50 kHz and 5 mHz of all investigated carbon samples (ESR has been subtracted from real part of impedance). Electrolyte: 5.25 M H_2SO_4 , potential: -100 mV, Ref.: $\text{Hg}/\text{Hg}_2\text{SO}_4$.

should be pointed out that the values of capacitance obtained by EIS confirm the values obtained by CV. Depending on the samples we obtained values of the capacitance in the range of 90 up to 175 F g^{-1} . In contrary to all other samples, N-42 fibers show less increase of capacitance at lower frequencies than the other samples indicating again that the accessibility of the electrolyte to this carbon is minor. As

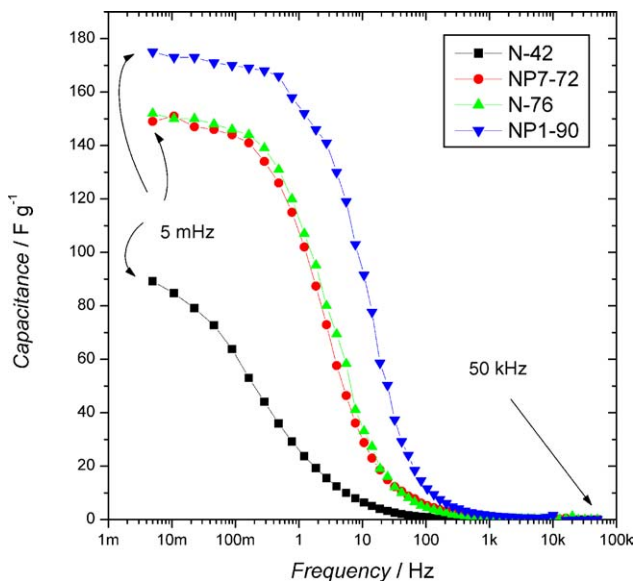


Fig. 8. Frequency behavior between 5 mHz and 50 kHz of all investigated carbon samples. Electrolyte: 5.25 M H_2SO_4 , potential: -100 mV, Ref.: $\text{Hg}/\text{Hg}_2\text{SO}_4$.

the burn-off arises, an increase of capacitance is detectable, additionally the increase of capacitance shifts to a higher frequency domain, which confirms that the electrolyte penetration into the pores of the electrode is improved at higher burn-off degrees. The plots of samples NP7-72 and N-76 are almost congruent due to their similar BET surface areas (see Fig. 8 and Table 1, respectively). NP1-90 shows the best frequency dependence and exhibits a capacitance of approximately 175 F g^{-1} .

Table 1 shows the specific BET surface areas as well as the external surface area of activated carbon fiber samples determined from adsorption/desorption isotherms of N_2 at 77 K [18]. It should be noted that apart from the impregnation step the surface area is directly proportional to the burn-off degree. As found by density functional theory (DFT), all studied activated carbon fiber samples except N-42 exhibit a sharp maximum of pore volume in the range of 2–3 nm [17,18]. In agreement with their low external (or non-microporous) surface areas, neither of the studied samples has pores larger than 4 nm. Therefore the porosity of samples N-42, NP7-72

Table 1

Surface area (BET), external surface area (S_{ext}) and specific capacitance (C) of investigated activated carbon fiber samples obtained from N_2 isotherms and EIS at 5 mHz, respectively

Sample	Burn-off (%)	BET ($\text{m}^2 \text{ g}^{-1}$)	S_{ext} ($\text{m}^2 \text{ g}^{-1}$)	C (F g^{-1})
N-42	42	1329	90	90
NP7-72	72	2408	150	150
N-76	76	2592	150	150
NP1-90	90	2832	175	175

and N-76 might be termed microporous close to the border to mesoporous. In contrast to this, most pores in sample N-42 are narrower than 1 nm (ultramicropores), which explains the accessibility limitations of the electrolyte to this carbon.

4. Conclusion

The aim of this study was to evaluate whether nanoporous activated carbon fibers derived from poly (*m*-phenylene isophthalamide) are suitable for the use as active material in supercapacitors. Their capability as active material was evaluated by using cyclic voltammetry and impedance spectroscopy. It was found that the fibers are easily processable to mechanically very stable electrodes. NP1-90 (prepared by pre-impregnation of Nomex with H₃PO₄ followed by activation in CO₂ to 90% burn-off) was the most suitable sample for the application in supercapacitors and exhibits excellent capacitive behavior. Values for the capacitance of 175 F g⁻¹ in sulfuric acid were obtained. Further on it was observed that the specific capacitance and the performance of the electrode increasing significantly with increase burn-off degree. The investigated activated carbon fiber samples exhibit increasing performance in following manner: N-42 < NP7-72 = N-76 < NP1-90, i.e. relative to their BET surface area and pore size distribution.

Acknowledgement

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