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Freestanding Flexible Carbon Nanofiber Mats for Energy Storage Applications †

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Abstract: Carbon nanofiber mats can be applied for diverse energy applications. Usually, they should be freestanding and show sufficient structural stability. Poly(acrylonitrile) (PAN) is often used as the base material for electrospinning due to its high carbon yield during carbonization. Carbonized PAN nanofiber mats, however, may be brittle and break under mechanical load. Here, we report a study of the impact of ZnO and tetraethyl orthosilicate (TEOS) as nanoparticle additives on the stabilization, carbonization and resulting morphology of the respective nanofiber mats. By comparing morphological, mechanical, and chemical properties of these mats, it is shown that carefully tailoring nanoparticular additives and spinning parameters enables the production of flexible freestanding carbon nanofiber mats for possible applications as electrodes in energy storage devices.

Keywords: carbon nanofibers; poly(acrylonitrile) (PAN); freestanding electrode; nanoparticles; ZnO; TEOS

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1. Introduction

Carbon nanofibers are a class of nanomaterials that have recently been widely investigated for their utility in energy storage devices [1]. They can be applied as electrodes in lithium ion, sodium ion or metal–air batteries without the necessity of binders, as electrodes in supercapacitors, or as separators in supercapacitors, etc., [2,3]. In most applications, freestanding and ideally even flexible nanofiber mats with sufficient structural stability in addition to high porosity are preferred as electrodes. In many cases, PAN is used as the base material for electrospinning due to its outstanding carbon yield during carbonization [4]. After prior stabilization and subsequent carbonization, however, carbon nanofiber mats from pure PAN tend to be brittle and to break even under small mechanical loads. Because of this, several research groups investigate different possibilities to increase the flexibility of carbon nanofiber mats by optimizing spinning, stabilization, and carbonization parameters, as well as by adding diverse nanomaterials, such as graphene to increase the spinning solution's conductivity, ZnO, TEOS, or others [5–7].

In this work, we demonstrate the benefits of such nanoparticles (NPs) on PAN/NP electrospun nanofiber mats on the flexibility after stabilization and carbonization, comparing the physical and chemical properties of these nanofibrous mats. We show that

nanoparticular additives, especially ZnO, can significantly improve the flexibility of the carbon nanofiber mats, which is already noticeable after the stabilization process.

2. Materials and Methods

Electrospinning was performed using a wire-based machine, "Nanospider Lab" (Elmarco, Czech Republic). Spinning was performed for 50–60 min with a nozzle diameter of 0.9 mm, a carriage speed of 100 mm/s, a wire–substrate distance of 240 mm, and a substrate–ground electrode distance of 50 mm. Table 1 gives an overview of the spinning solutions prepared from PAN (X-PAN copolymer, Dralon, Dormagen, Germany) in dimethyl sulfoxide (DMSO, min. 99.9%, obtained from S3 chemicals, Bad Oeynhausen, Germany) and spinning parameters optimized for the respective samples.

Table 1. Spinning and solution parameters. TEOS: tetraethyl orthosilicate; nickel ferrite: Fe_2NiO_4.

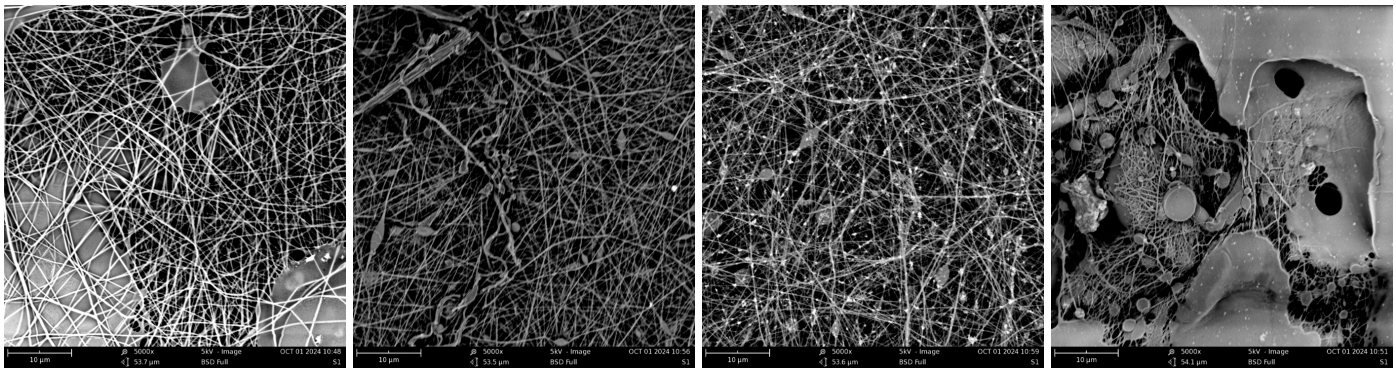
Sample	PAN Content	Blend Content	Voltage	Temperature	Rel. Humidity
PAN	16.0%	-	65 kV	22.4 °C	33%
PAN/TEOS	13.6%	4.9%	45 kV	20.3 °C	34%
PAN/ZnO	13.2%	4.6%	50 kV	21.1 °C	35%
PAN/nickel ferrite	12.7%	3.9%	55 kV	20.2 °C	35%

Parts of the samples were stabilized in a muffle oven B150 (Nabertherm, Lilienthal, Germany) at a temperature of 280 °C for 1 d, approached with a heating rate of 1 K/min. Carbonization was performed in a tube furnace CTF 12/TZF 12 (Carbolite Gero Ltd., Sheffield, UK) at 500 °C for 1 h under constant nitrogen flow of 160 mL/min, approached with a heating rate of 1 K/min.

Characterization of the samples was performed by scanning electron microscopy (SEM, Phenom ProX G3 Desktop SEM, Thermo Fisher Scientific, Waltham, MA, USA), X-ray diffractometry (XRD, X'Pert Pro MPD PW3040-60 diffractometer, Malvern Panalytical GmbH, Kassel, Germany), thermogravimetric analysis (TGA, Hi-Res TGA 2950 Thermogravimetric Analyzer from TA Instruments, New Castle, DE, USA), and Fourier transform infrared (FTIR) spectrometry (Excalibur 3100, Varian Inc., Palo Alto, CA, USA) in attenuated total reflection mode (ATR-FTIR).

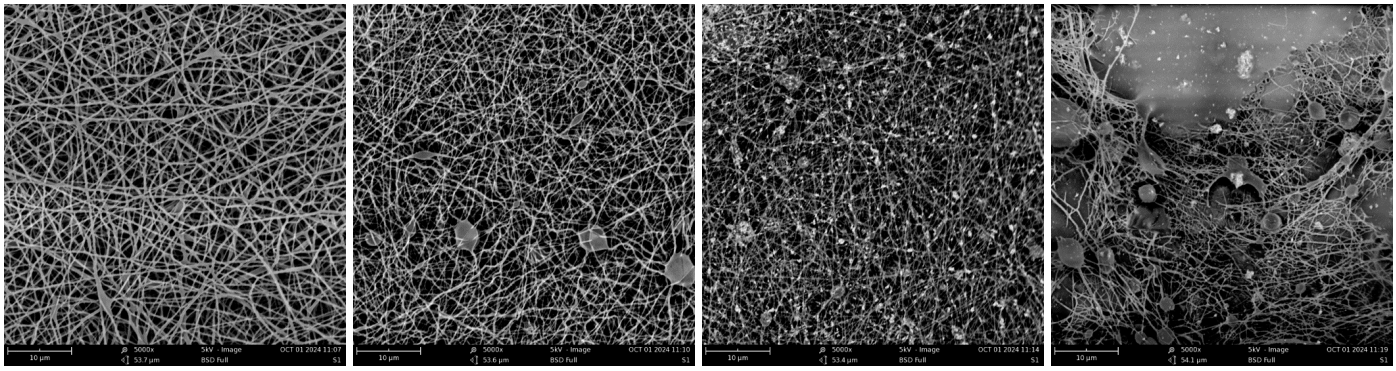
3. Results and Discussion

The surface of the as-spun samples is shown in Figure 1, followed by the stabilized (Figure 2) and carbonized samples (Figure 3). PAN, PAN/TEOS, and PAN/ZnO show common nanofiber mats, with small particles visible on the PAN/ZnO nanofiber mat which apparently stem from ZnO agglomerations. PAN/nickel ferrite is mostly non-fibrous, which may be attributed to the high relative humidity of 35% during spinning. No significant deviations from the original morphology were observed for the stabilized and carbonized samples.



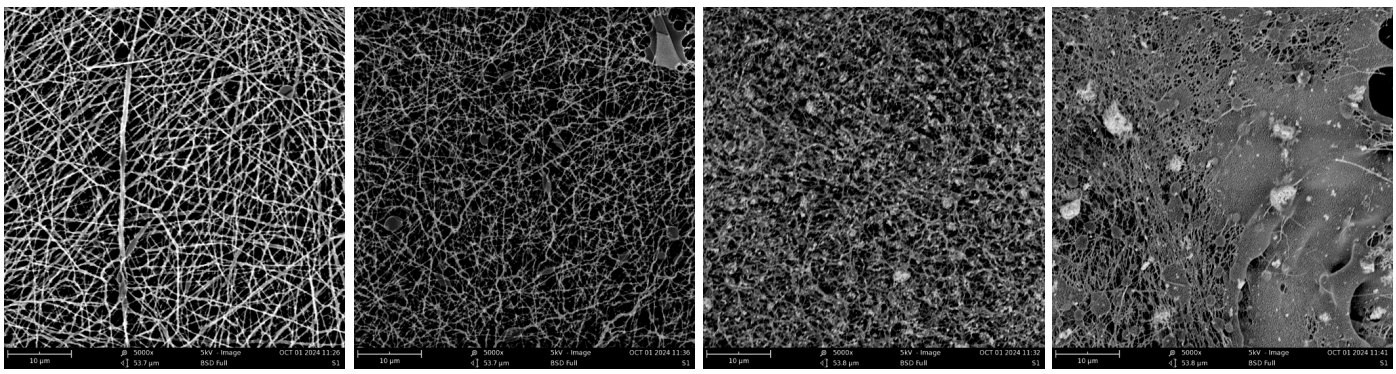
(**a**) (**b**) (**c**) (**d**)

Figure 1. Scanning electron microscopy (SEM) images of as-spun samples: (**a**) PAN; (**b**) PAN/TEOS; (**c**) PAN/ZnO; (**d**) PAN/nickel ferrite.



(**a**) (**b**) (**c**) (**d**)

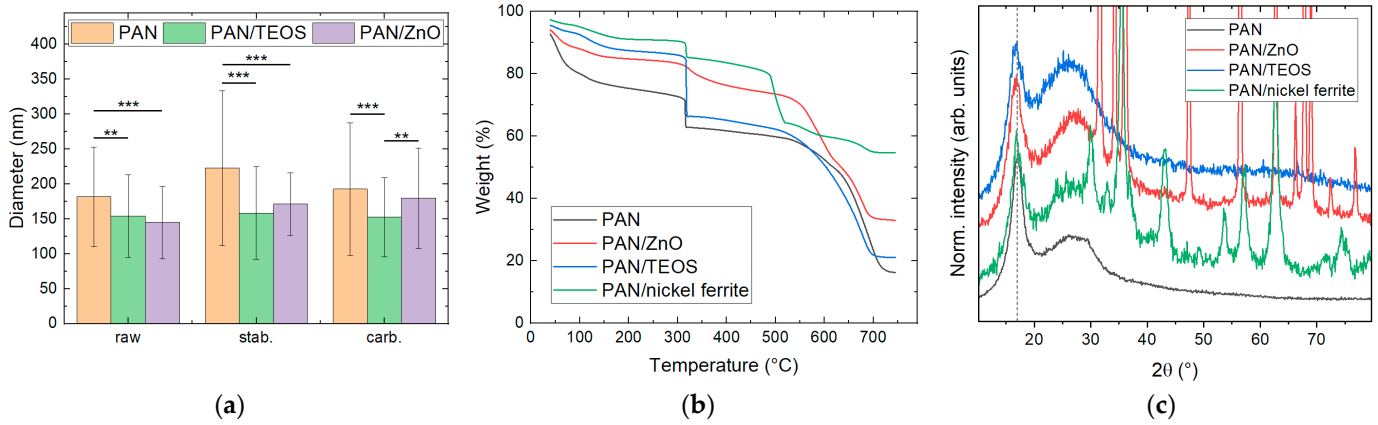
Figure 2. SEM images of stabilized samples: (**a**) PAN; (**b**) PAN/TEOS; (**c**) PAN/ZnO; (**d**) PAN/nickel ferrite.



(**a**) (**b**) (**c**) (**d**)

Figure 3. SEM images of carbonized samples: (**a**) PAN; (**b**) PAN/TEOS; (**c**) PAN/ZnO; (**d**) PAN/nickel ferrite.

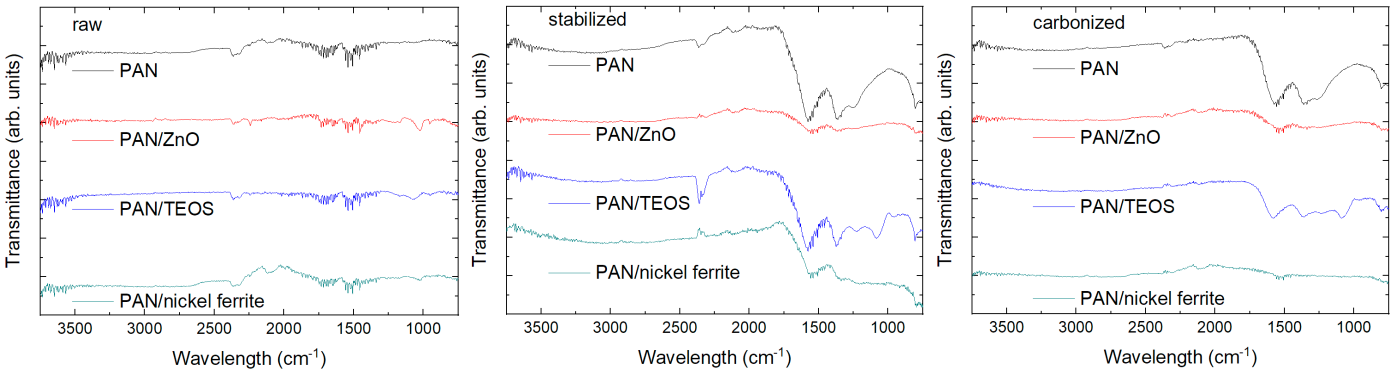
The nanofiber diameter distribution for the three fibrous samples is depicted in Figure 4a. PAN/TEOS keeps the diameter mostly constant, which seems to make it advantageous for stabilization and carbonization. TGA measurements (Figure 4b) show a steep decrease in sample mass due to the cyclization of nitrile groups at around 300 °C, which is increased by TEOS and reduced by ZnO. XRD measurements of the as-spun nanofiber mats (Figure 4c) reveal, besides the PAN diffraction peak at 17°, no contribution from the amorphous TEOS and the typical sharp peaks of ZnO nickel ferrite, respectively.



(**a**) (**b**) (**c**)

Figure 4. (**a**) Nanofiber diameters; (**b**) TGA measurements; (**c**) XRD measurements of the samples under investigation. Significant differences are indicated by ** ($p < 0.01$), or *** ($p < 0.001$), respectively.

FTIR measurements of all samples are depicted in Figure 5. While raw PAN shows typical C-H_2 bending and stretching (1451 cm^{-1}, 1363 cm^{-1}), the Si-O-Si peak of TEOS at 1083 cm^{-1} only becomes visible after stabilization, along with common peaks of stabilized PAN [6]. Large peaks after carbonization indicate a lower degree of carbonization [6].



(**a**) (**b**) (**c**)

Figure 5. FTIR measurements of (**a**) as-spun, (**b**) stabilized, and (**c**) carbonized samples.

Bending tests on stabilized samples revealed the expected brittle behavior of carbon nanofiber mat from pure PAN, while the other samples, especially PAN/ZnO, were much more flexible. This underlines that adding nanoparticles to PAN nanofiber mats is a promising approach to improve the flexibility of the resulting carbonized nanofiber mats.

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