Title	Preparation of sub-micron carbon fibre web
Author(s)	Heikkilä, Pirjo; Pasanen, Antti.T.; Virtanen, Sanna; Vähä-Nissi, Mika
Citation	Annual World Conference on Carbon "Innovation with Carbon Materials", CARBON 2015, 12 - 17 July 2015, Dresden, Germany German Carbon Group (AKK)
Date	2015
Rights	This presentation may be downloaded for personal use only.

Preparation of sub-micron carbon fibre web

Pirjo HEIKKILÄ, Antti T. PASANEN, Sanna VIRTANEN, Mika VÄHÄ-NISSI

VTT Technical Research Centre of Finland, P.O.Box 1300, FI-33101 Tampere, Finland
pirjo.heikkila@vtt.fi

INTRODUCTION

Electrospinning is a method capable for production of submicron and nanosized fibres in industrial scale. In electrospinning, the electrostatic field stretches the polymer solution into fibres at the same time when the solvent is evaporating. The diameters of formed fibres are typically in sub-micron range and they can be collected as interconnected fibrous web onto surface of a substrate. Submicron fibres composing of suitable polymeric material can be converted into carbon fibres having submicron and even nanosized fibre diameters by stabilization and carbonization processes. In this presentation we will review preparation and properties of carbon fibre sheet material composing of sub-micron sized fibres intended to catalysts supports to be used in fuel cell applications in automotive MEA's.

MATERIALS AND METHODS

Precursor fibre sheet were prepared from polyacrylonitrile (PAN) and mixture of PAN and carbon nanotubes (CNT's) by electrospinning method. PAN solutions were prepared by direct dissolution into heated N,N-dimethylformamide (DMF). Mixture solutions was prepared by adding CNT's into dilute PAN solution in DMF, using ultrasonic device to disperse CNT's while PAN acted as surfactant, and then adding rest of the PAN in order to obtain preferred concentration. Electrospinning setup used composed of horizontally moving needle and rotating collector drum enabling formation of fibre sheet. These sheets were stabilized/oxidized (270°C, air) and carbonized (T_{max} 1500°C, N_2) using quasi continuous thermal process in tubular furnace, see figure 1.

Figure 1. Tubular furnace for carbonization of electrospun sheets.

RESULTS AND DISCUSSION

Electrospun fibre diameters depended on PAN and CNT concentrations. Average fibre diameters of precursors, stabilized and carbon fibres obtained from five solution types are presented in table 1. Stabilization and carbonization reduced fibre diameters and weight of fibrous sheets, as can be seen from figure 2. Carbonized sheets had thicknesses ranging from 10 to 30 µm.

Table 1. Average fibre diameters, sheet thicknesses and conductivities of samples. Pre=precursor, Ox=stabilized/oxidized, Carb=carbonized.

Solution	Diameter [nm]			Sheet thickness [µm]	Conductivity [S/cm]
	Pre	Ox	Carb	Carb	Carb
6.7% PAN	180	170	140	11,6	20,0
7 % PAN	270	260	180	19,6	14,2
6.6% PAN, 0.25% CNT	240		160	28,3	12,7
6.6% PAN, 0.5% CNT	240	190	160	20,4	8,4
6.6% PAN, 1.0% CNT	220	200	170	24,5	6,6

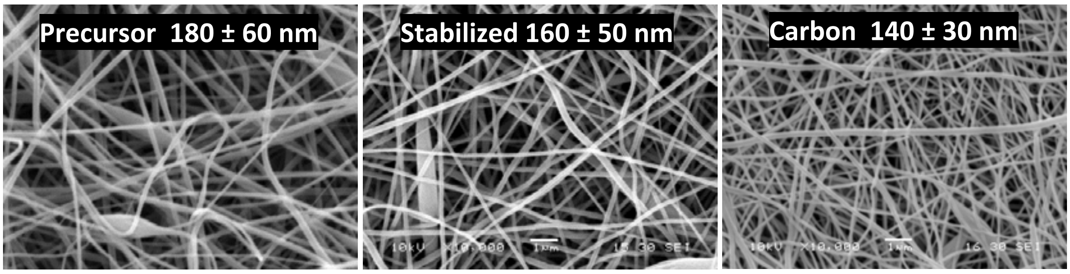
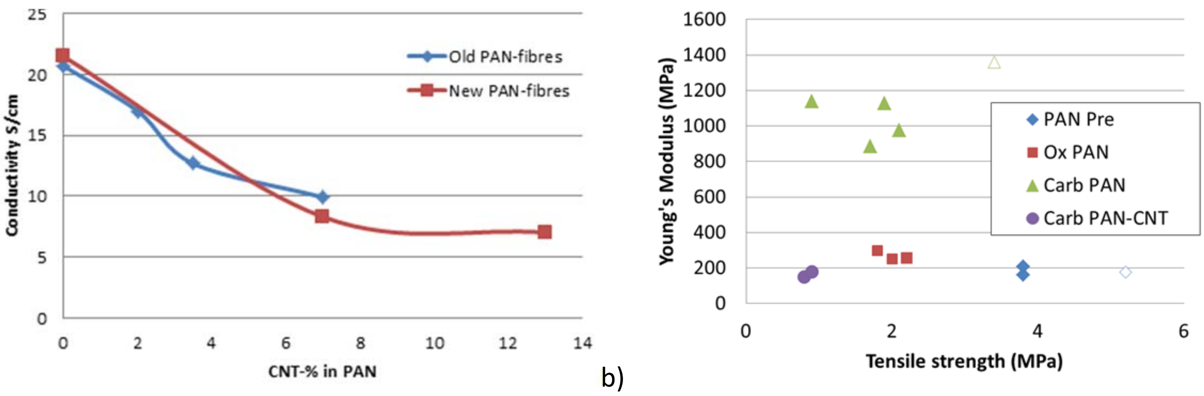


Figure 2. Appearance of precursor, stabilized and carbonized fibres (PAN 6.7% solution).

Average conductivities of carbonized fibre sheet were in the range 5-20 S/cm (table 1). Even though highly organized CNT's are conductive, we did not observe increase of conductivity. On the contrary we observed reduced conductivity with increasing CNT's, see figure 2a. The also studied mechanical behaviour of sheets, see figure 2b. We observed that stabilization mainly reduced tensile strength of material without affecting Young's modulus compared to precursor, and while Young's modulus increased during carbonization. Both tensile strength and Young's modulus values of our carbonized samples are lower than those of carbonized commercial electrospun PAN samples with larger fibre diameters. Young's modulus of CNT containing samples was lower than those without CNT's.



a) b)

Figure 2. a) Dependence of conductivity of carbonized samples on CNT amount; and b) mechanical properties of different types of precursor (Pre), stabilized (Ox) and carbonized (Carb) sheets. Hollow markings refer to commercial samples with larger fibre diameter compared to ours.

SUMMARY AND CONCLUSIONS

Electrospinning is feasible method for production of precursor materials for sub-micron carbon fibre web. The small fibre diameter, small pore size, and high surface area of the electrospun web are properties that are advantageous for various applications including catalysis. Carbonization process carried out in temperatures of 1500°C produce material having conductivities in range suitable for catalyst supports. Fibre web quality can be adjusted by changing solution concentration and composition. Even though CNT additive have been suggested to be promising additive, we did not see any positive impact on carbon fibre web quality. Both conductivity and mechanical properties of PAN based carbons were better than those of PAN-CNT based carbon.

ACKNOWLEDGEMENTS

Authors like to acknowledge technical staff of VTT, especially Kati Heikkinen and Timo Flyktman, for carry out the work. We would also like acknowledge Catapult project; novel CATAlyst structures employing Pt at Ultra Low and zero loadings for auTomotive MEAs; supported by EU FCH-JU; Grant agreement no 325268.