

Title	Fibrous and tubular support materials using in catalyst support materials for low-Pt PEM fuel cells for automotive MEAs
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Citation	Electrolysis & Fuel Cell Discussions Conference "Challenges towards zero platinum for oxygen reduction", EFCD 2015, 13 - 16 September 2015, La Grande Motte, France
Date	2015
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novel CATALyst structures employing Pt at Ultra Low and zero loadings for auTomotive MEAs



FP7, FCH-JU, grant agreement 325268

# Fibrous and tubular support materials for low-Pt PEM fuel cells for automotive MEAs

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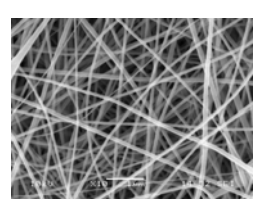
## Introduction

The general requirements for PEM fuel cell catalyst support materials are high electronic conductivity, high specific surface area and high electrochemical and chemical stability. Current structures typically consist of Pt particles on carbon black support material, but the mass activity of these high surface area nanoparticulate catalysts is restrainer for a large-scale commercialization of PEM fuel cell for vehicles. Reduction of platinum content per vehicle and increase of mass activity are solutions paving the way for a larger utilization of the PEM fuel cells. New approach for automotive PEM fuel cell catalysts are being developed in project Catapult. In this new approach platinum is deposited as an extremely thin layer on corrosion resistant supports of various morphologies including fibrous and tubular structures.

## Experimental and Results

VTT's approach is to produce two type of structures: 1) fibrous sub- $\mu\text{m}$  core-shell carbon-ceramic, and 2) ceramic sub- $\mu\text{m}$  tubular catalyst supports utilizing atomic layer deposition (ALD) method on electrospun sub- $\mu\text{m}$  fibres, with processes shown below. Electrospun PAN was precursor for carbon fibres which were stabilized and carbonized, and electrospun PVA as sacrificial template fibres for tube structure. Carbonized PAN and polymeric PVA fibres were ALD coated with titanium-niobium mixed oxide which was annealed in forming gas at 700°C. PVA was removed during annealing leading to tubular structures. Fibrous support sheets and tubular support flakes were obtained. Carbonized sheets had thicknesses ranging from 10 to 30  $\mu\text{m}$ . Average conductivities of carbonized fibre sheet were in the range 5-20 S/cm. Nb:Ti precursor pulsing ratios of 1:10 produced Nb:Ti ratio of 0.03 on deposited films. As-deposited films were amorphous and insulating but crystallised during annealing with (101) preferred oriented anatase type  $\text{TiO}_2$ . Annealing at 700 °C increased conductivity above target value of  $10^{-2}$  S/cm. In future work the Pt/Nb-Ti-O/nanofibre materials with different Pt contents will be electrochemically characterized in a RDE cell and the ORR activity and stability after extended cycling will be investigated.

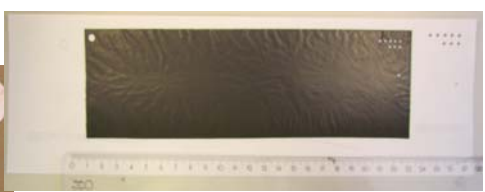
### 1) Fibrous supports



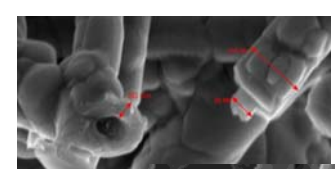
Polyacrylonitrile (PAN) with a fibre target dia. < 200nm



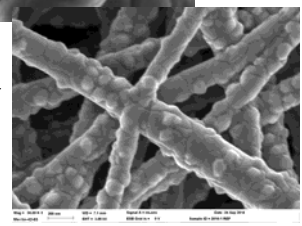
Electrospun PAN and carbonized sheet



Carbonized sheet, paper below sheet shows size of PAN sheet



Nb-Ti-oxide/carbon core-shell nanofibre sheets

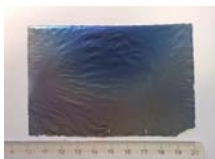


Electrospinning setup with rotating collector drum

Carbonization

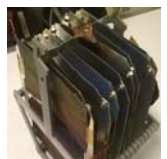


Stabilization (<300°C) and carbonization (<1500°C) at R2R oven.



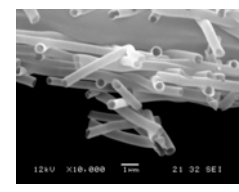
Thin oxide layer changed the color of carbon sheet

ALD of Ti-Nb-Ox



Sample holder and ALD reactor

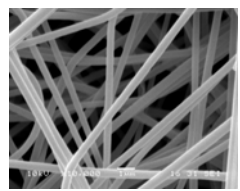
Forming gas annealing 700°C and polymer removal



Nb-Ti-oxide tubes formed by PVA decomposition during annealing process, sheets were broken down to flakes

Pt catalyst deposition

### 2. Tubular support



Electrospun polyvinylalcohol (PVA) with a fibre target dia. < 0.5  $\mu\text{m}$



Details of support production and ALD layer production is presented elsewhere e.g.

- Heikkilä P., Pasanen A.T., Virtanen S., Vähä-Nissi M., Preparation of sub-micron carbon fibre web, Carbon 2015, 12-17 July 2015, Dresden, Germany
- Heikkilä P., Putkonen M., Pasanen A.T., Rautkoski H., Tapper U., Ihonen J., Bosund M., Geppert T., El-Sayed H., Gasteiger H.A., Simell P., Vähä-Nissi M., ALD deposition of core-shell structures onto electrospun carbon webs for PEM fuel cell MEAs, ALD 2015, 28 June - 01 July 2015, Portland, USA