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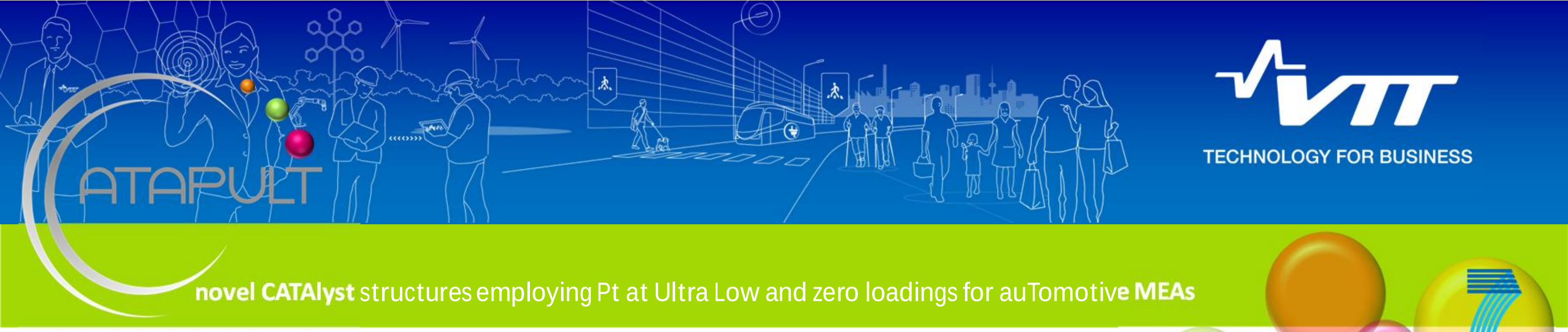

ALD deposition of core-shell structures onto electrospun carbon webs for PEM fuel cell MEAs

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Introduction

Electrocatalyst support materials for PEM fuel cells require high electronic conductivity, high specific surface area and high stability. Conventional support structure typically consists of Pt particles on carbon black. High cell potentials can cause oxidative corrosion of carbon thus requiring either non-carbon catalyst support materials or modifying existing carbon supports. We have been studying the use of ALD deposited Nb-Ti-O films as a conductive protective layers for electrocatalyst support structures and Pt deposition for catalyst layer.

Experimental

Sub-µm scale carbon substrates have been prepared by electrospinning of polyacrylonitrile (PAN) using N,N-dimethylformamide (DMF) as a solvent. Electrospun sheets were stabilized/oxidized (270°C, air) and carbonized (T_{max} 1500°C, N_2). Nb-Ti-O films were deposited by using $Nb(OEt)_5$ and $TiCl_4$ and H_2O as precursors. Platinum catalyst was deposited from $MeCpPtMe_3$ and O_2 using 10-200 deposition cycles.

Deposited Nb-Ti-O structures were annealed at 700 °C in forming gas to increase conductivity. Deposited structures were further analysed by XRD and SEM. The Pt/Nb-Ti-O/nanofibre materials with different Pt contents were electrochemically characterized in a RDE cell and the ORR activity and stability after extended cycling was investigated.

Materials were horn-sonicated in isopropanol, deposited on a glassy carbon disk and covered with Nafion solution. Stability test was conducted in Ar-saturated 0.1 M $HClO_4$ (0.5 - 1.0 V vs. RHE) for 10000 cycles. Every 200 cycles, five cyclovoltammograms (CVs) between 0.05 - 1.1 V and three CVs (0.05 - 0.5 V), for the determination of electrochemical active surface area (ECSA), were recorded. Activity of oxygen reduction reaction was evaluated in O_2 sat. 0.1 M $HClO_4$, sweeping from 0.06 to 1.1 V at 1600 rpm at 10 mV/s.

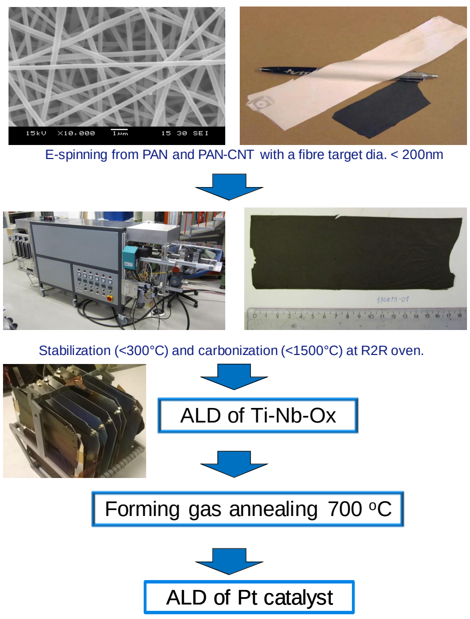

Figure 1. Support of core-shell structure materials by using electrospinning and ALD.

Results

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 TiO_2. Annealing at 700 °C increased conductivity above target value of 10^{-2} S/cm.

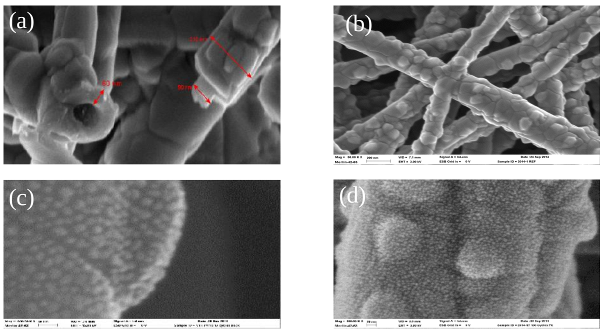

Figure 2. Nb-Ti-O/carbon nanofibre core-shell structures films on carbon fiber after forming gas anneal (a,b) and Pt-coatings on Nb-Ti-O support after 17 and 75 cycles (c,d).

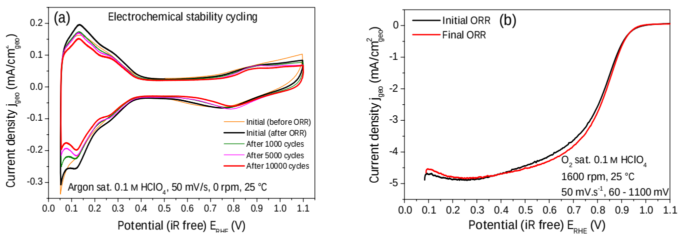

Figure 3. Electrochemical characterization of 17 cycles Pt on Nb-Ti-O/carbon nanofiber core-shell structures. a) CVs collected between stability cycling b) ORR polarization curves.

The ECSA determined by H-absorption/desorption (Fig. 3a) increases slightly after the ORR testing, which may be related to the gradual removal of organic residues from the ALD process. Compared to its maximum value, the ECSA decreases by 15 and 25% after 5000 and 10000 cycles, respectively.

For the catalyst with platinum deposited by 17 ALD cycles on Nb-Ti-O support, the RDE-based oxygen reduction currents change insignificantly over 10000 voltage cycles (Fig. 3b), even though the platinum surface area does decrease by 25%. Thus, the specific activity for the ORR actually increases from ≈210 µA/cm$^2_{Pt}$ to ≈270 µA/cm$^2_{Pt}$.

Conclusions

ALD deposition of Nb-Ti-O and Pt has been demonstrated onto carbon nanofibers. Good electrochemical stability has been observed with constant ORR performance before and after stability cycling.

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