Pt nanoparticles on N-doped carbon nanofibers with remarkable size stability during heat treatment

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Erneuerbare Energien

Introduction

State of the art fuel cell catalysts suffer under severe support corrosion problems. To overcome these Problems there is a lot of research on alternative support materials such as conductive oxides.
An other strategy to prepare support materials with enhanced long term stability is to dope the carbon material with Nitrogen [1]. Up to date all known preparation techniques require expensive laboratory equipment, harsh experimental conditions, like HF etching or expensive starting materials.
Here we chose PANI, a cheep, N-containing polymer as starting material which was decorated with Pt before carbonization.

Experimental

- fresh prepared PANI fibers were loaded with 10% Platinum by a formic acid reduction method.
- Carbonization was conducted under nitrogen flow at T = 750 °C (heating rate: 1 °C/min, 90 min).
- The same heat treatment was conducted on a commercial available carbon supported catalyst and a not Pt loaded PANI
- Accelerated aging tests were performed using CV (for aging: 0-1.1 V vs. SCE, 150 mV/s , for measuring: -0.32 – 1.1 V vs. SCE, 50 mV/s)

Structural Characterization

XRD measurements

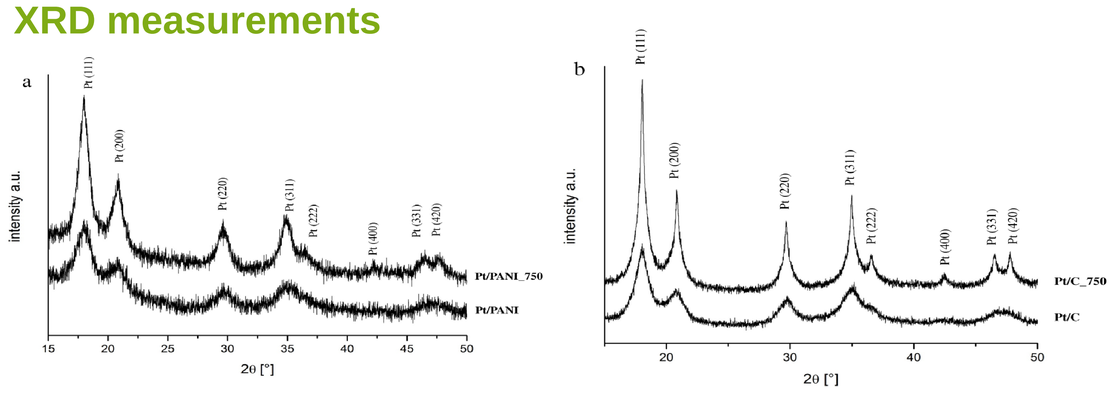

Fig. 1: XRD patterns of the different catalysts; crystallite sizes obtained by Rietfeld refinement a: Pt/PANI before and after heat-treatment, the crystallite size increases only from 1.6 to 2.6 nm. b: Pt on carbon black, fresh with 1.9 nm; after the heat-treatment two Pt phases are necessary for a refinement; one with a crystallite size of 2.3, the other with 16.8 nm.

TEM analysis

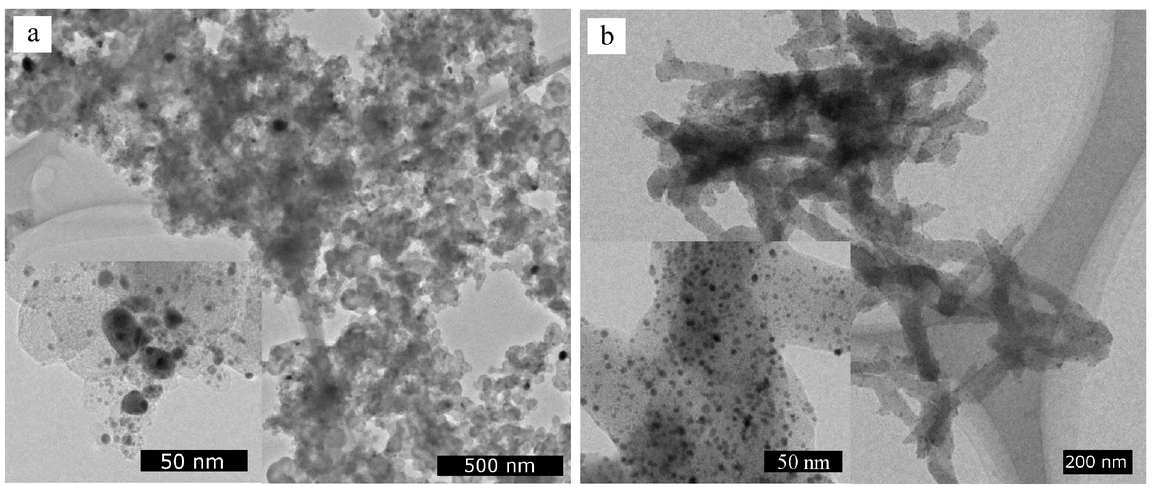

Fig. 2:TEM images of heat treated catalysts. a: commercial available Pt/C; the Pt grew a lot and agglomerated. b: Pt/PANI the particles did not grew significantly; a narrow size distribution is obtained.

	XRD [nm]	TEM [nm]
Pt/PANI	1.5 ± 0.3	1.6 ± 0.5
Pt/PANI_750	2.6 ± 0.2	2.0 ± 0.8
Pt/C	1.9 ± 0.3	1.9 ± 0.4
Pt/C_750	2.3 ± 0.2 / 16.8 ± 0.5	2.6 ± 1.7

Tab. 1: Pt particle size before and after heat treatment. While the sizes for the PANI supported material did not change much, the Pt-nanoparticle of the commercial carbon supported catalyst grew a lot, which is in good agreement with literature [2].

CV- Aging

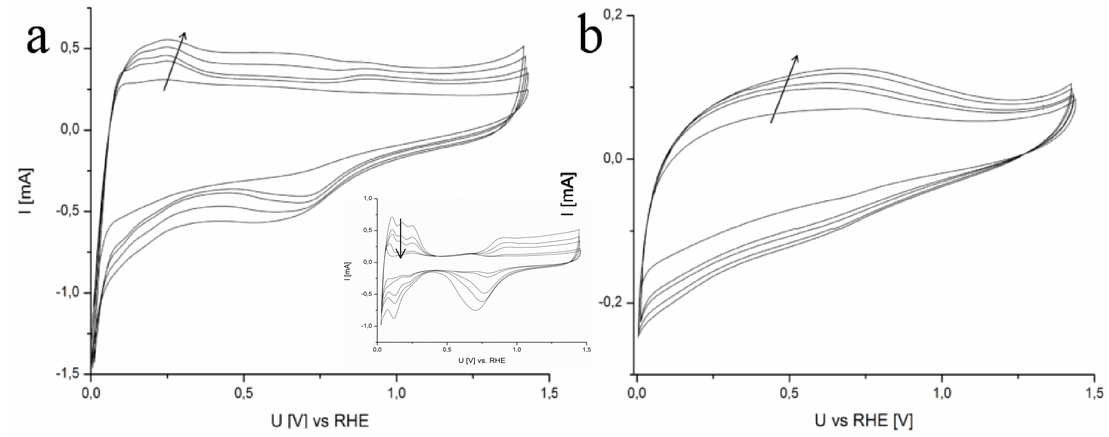

Fig. 3: CV-Aging of a: Pt on carbonized PANI, b: carbonized PANI, inset: aging of a commercial catalyst. Arrows indicate the rising cycle number, shown cycles: fresh, 500, 1000, 3000 and 5000.

- With higher cycle number an enhanced current and increasing double layer is observed.
- it is not possible to determine the ECSA reliably, but there is no clear change in the shape like for the commercial catalyst.
- Electro-active surface oxides and redox couples form on the support.

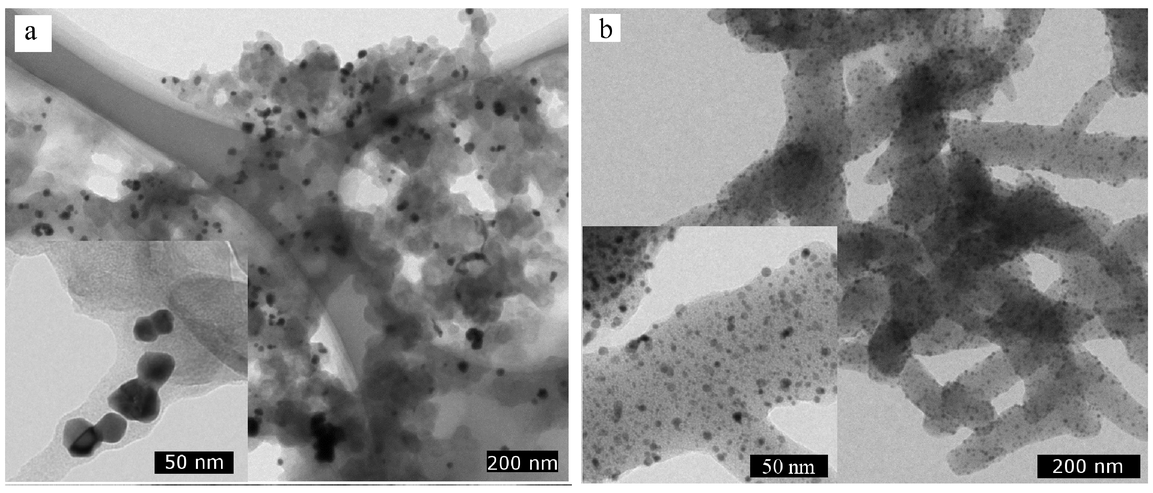

Fig. 4: TEM images after the aging experiment. a: Pt/C and b: Pt/PANI_750. In the higher magnification (insets) a huge particle growth for Pt/C is visible, while the size and the dispersion for Pt/PANI_750 does not change significantly.

- The shape of the carbonized PANI support is preserved during the aging, while there is a change visible for the carbon support.

	[nm]
Pt/PANI_750	3.2 ± 2.4
Pt/C_750	15.6 ± 7.1

Tab. 2: Pt particle size after the CV-aging. The particles supported on carbonized PANI still show a narrow particle size distribution with a mean value still being in the optimal range for catalysis in PEMFC

Conclusion:

- A simple, cheap and easy scalable synthesis for long term stable Pt on N-doped carbon is presented.
- During heat treatment at 750 °C the PANI supported catalyst shows significant less particle growth compared to a commercial catalyst.
- After accelerated aging tests the Pt particle showed no agglomeration and little particle growth

References:

[1] Zhou, Y., et al. (2010). *Energy & Environmental Science*, *3*(10), 1437. doi:10.1039/c003710a
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Acknowledgment:

We acknowledge financial support from the German Research Association DFG (contract No. RO 2454/10-1).

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