N-doped Carbon Nanofibers: Pt support interaction studied by C-K-edge NEXAFS and XPS

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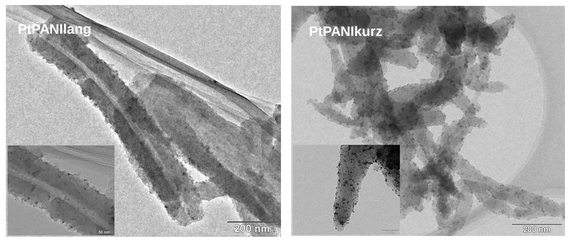
Introduction

Motivation

Polymer electrolyte membrane fuel cells are efficient energy converters which suffer from large overpotentials for the oxygen reduction reactions and a limited life time. The later being linked to carbon corrosion leading the Pt agglomeration and loss in activity. In order to enhance catalytic activity and stability, N-doped carbons are used as catalyst support [1]. However, the effects of N-groups are various and still under debate.

PANI Synthesis



PANI was synthesized by oxidative polymerization [2] from Aniline using 1M H_2SO_4 and 0.4M acetic acid as reduction medium, to produce long and short nanofibers, respectively.

The deposition of Pt on the PANI were prepared by a modified synthesis route proposed by Guo et al. [3].

Experiment

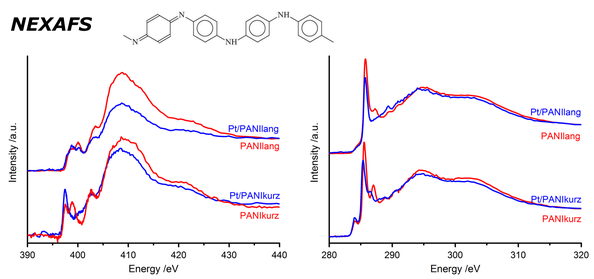
Precursor	Carbonization	N-doped Carbon Nanofiber	Investigations
PtPANIlang PANIlang	@T750, N_2 1Kmin^{-1}, τ=90min	PtPANIlang750 PANIlang750	NEXAFS* XPS LSV
	@T1000, N_2 1Kmin^{-1}, τ=90min	PtPANIlang1000 PANIlang1000	
PtPANIkurz PANIkurz	@T1000, N_2 5Kmin^{-1}, τ=1min	PtPANIkurz1000 PANIkurz1000	NEXAFS*

*C- and N-K-edge NEXAFS measurements were performed in PEY at the He-SGM beamline

Experiments & Results

PANI Nanofibers

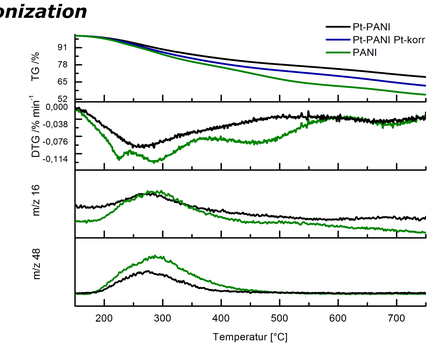
NEXAFS



- Decrease of π* transition at 285e V, due to Pt
- Ratio between imine and amine changes

→ N-groups work as nucleation centers for Pt nanoparticles

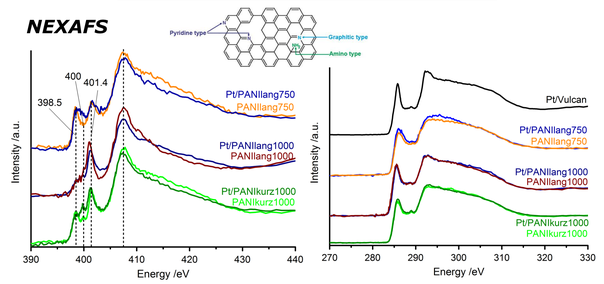
Carbonization



- Polymer mass loss: PtPANIlang 37.84%, PANIlang 44.60%
- 200 to 400°C → CO_2, CH_4 and sulfur groups
- 400 to 650°C → ?, Peak vanishes with Pt
- 650 to 700°C → HCN

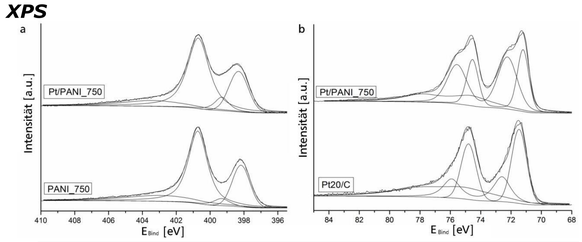
N-doped Carbon Nanofibers

NEXAFS



- 3 N-groups, pyridinic, amino, graphitic
- Increased amount of amino type groups for PtPANI
- Type of N-group can be influenced by the carbonization step

XPS

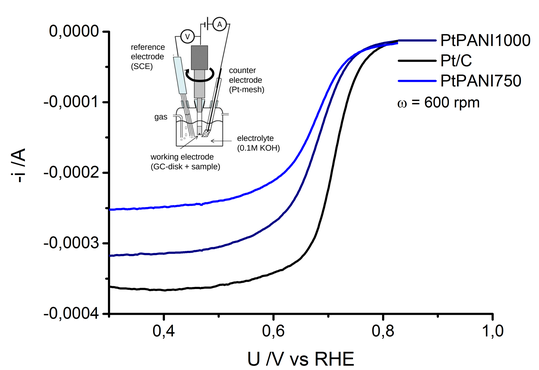


	Maxima [eV]	PANI_750	Pt/PANI_750	Pt20/C
N1s	398.3[1]	44.2	39.0	X
	399.2[2]	4.2	7.8	X
	400.7[3]	56.0	56.1	X
	403.8[4]	17.1	16.6	X
Pt4f	71.2[5]	X	32.4	43.8
	72.3[6]	X	43.4	33.0
	74.4[7]	X	24.2	23.2

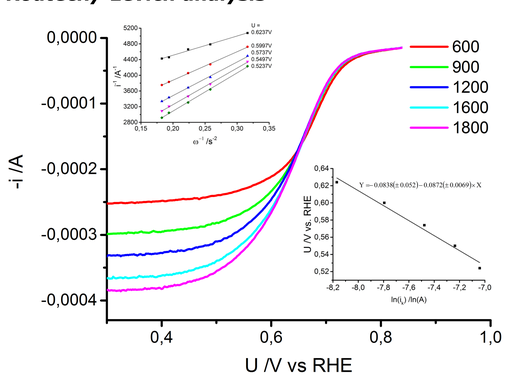
N-species: 1 pyridinic, 2 pyrrolic, 3 quaternary, 4 higher oxidized, Pt-species: 5 Pt^0, 6 Pt^{2+}, 7 higher oxidized Pt

Activity of N-doped Carbons

Linear Sweep Voltammetry



Koutecky-Levich analysis



Pt/C	1,0x10^{-6} Acm^{-2} (36,1 cm^2 mg^{-1})
PtPANI750	2,8x10^{-6} Acm^{-2} (16,0 cm^2 mg^{-1})
PtPANI1000	2,1x10^{-6} Acm^{-2} (6,3 cm^2 mg^{-1})

Conclusions & Outlook

Conclusion

- Pt interacts with the N-groups in PANI, as observed by NEXAFS spectroscopy
- The carbonization step of PANI is influenced by Pt as found by TGA-MS experiments
- The N-doping is influenced by synthesis conditions of the PANI, the carbonization temperature and the Pt
- Pt interacts with the N-groups in the carbon nanofibers as visible in N-K-edge NEXAFS and XPS
- This interaction influences the electrochemical activity
- Largest exchange current density is found for PtPANI750

Outlook

- LSV on short carbon nanofibers, PtPANIkurz
- Determination of diffusion coefficients to determine mass transport effects
- Modification of synthesis/carbonization
- Other precursor materials

Acknowledgements

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References

[1] Y. Zhou, K. Neyerlin, T. S. Olson, S. Pylypenko, J. Bult, H. N. Dinh, T. Gennett, Z. Shao, R. O'Hayre, *Energy & Environmental Science* **2012**(3) 1437.

[2] J. Stejskal, I. Sapurina, M. Trchová *Progress in Polymer Science* **2010**(35) 1420–1481.

[3] S. Guo, S. Dong, and E. Wang, *Small (Weinheim an der Bergstrasse, Germany* **2009** (5) 1869–76.

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