

Stable platinum nanostructures on nitrogen-doped carbon obtained by high-temperature synthesis for use in PEMFC

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Abstract We propose a novel, facile synthesis route to produce stable platinum-based polymer electrolyte membrane fuel cell catalysts supported on nitrogen-doped carbon. Platinum nanoparticles were decorated on polyaniline (PANI), a nitrogen-containing polymer, before its subsequent carbonization at 750 °C under nitrogen atmosphere. Thus, nitrogen-doped carbon-supported platinum catalysts were produced with homogeneously distributed small metal particles, which are otherwise difficult to obtain. Most remarkably the platinum nanoparticles did not grow significantly during the carbonization step. In contrast, commercially available standard catalysts on carbon materials subjected to the same heat treatment showed severe particle growth. In accordance with the high thermal stability, the PANI-derived catalyst shows good long-term stability in accelerated stress test and a promising performance as cathode material in $5 \times 5 \text{ cm}^2$ single cells. The synthesis is carried out without the need for special laboratory equipment, so it will be easy to scale up for industrial catalyst production.

Keywords PEMFC · Nitrogen-doped carbon · Carbonization · PANI · Particle size · Catalyst stability

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1 Introduction

Fuel cell technology is a promising candidate for future energy economies, because it is considered to be both efficient and nonpolluting. Due to its manifold varieties in system design it can be used in different applications such as portable power, uninterrupted power supply, stationary heating systems, and many more. Depending on the application, there are different requirements for the lifetime ranging from 5,000 h for cars, 20,000 h for buses, and up to 40,000 h for stationary applications [1].

Polymer electrolyte membrane fuel cells (PEMFCs) are the most promising candidates for low-temperature applications (60–80 °C). At these temperatures, a catalyst is needed to provide fast reaction kinetics, and platinum is the most commonly used material for this purpose. As platinum is expensive and quite rare, high specific surface area is needed to lower the total amount of noble metal in order to become commercially competitive. The most common method to increase the surface area is the use of supported nanoparticles [2]. There are numerous impregnation and colloidal-based methods to prepare platinum nanoparticles supported on carbon materials [3]. A common step in these preparation techniques is a heat treatment under flowing N_2 or Ar at up to 900 °C for several hours. These heat treatments are supposed to lead to nanoparticles with higher crystallinity, which are more active in the oxygen reduction reaction (ORR) and also more stable in the long-term operation [4]. Another common observation during heat treatment of nanoparticles is undesired particle growth [3–10], which leads to a decrease of the active surface area.

Furthermore, carbon-supported catalysts applied in PEMFCs suffer from different aging mechanisms which preferentially occur at the cathode, resulting in a performance decrease with operation time [1, 11, 12]. The main

mechanisms of the observed losses are carbon corrosion, Ostwald ripening, and the loss of complete nanoparticles [13], all leading to a reduction of electrochemically active platinum surface during use.

One effective possibility to enhance catalytic activity and stability of the carbon support materials is nitrogen doping [14]. The most common strategies are chemical vapor deposition and pyrolysis of nitrogen-containing organic compounds. A variety of these methods is reviewed by Zhou et al. [14]. The authors pointed out that nitrogen doping of carbon materials leads to a true intrinsic catalytic enhancement, which is not only due to improved catalyst dispersion, but also leads to higher current produced per catalyst area. This can be attributed to the ORR activity of the nitrogen-doped carbon material itself [15]. In addition, several electrochemical studies demonstrated an enhanced long-term stability of the nitrogen-doped support, which was being attributed to a stronger bonding between the active catalyst particles and the support. Unfortunately, all the reported preparation techniques require either expensive laboratory equipment, or harsh experimental conditions like HF etching, [14] or expensive materials such as ionic liquids [16].

In this study, we present a new facile synthesis of platinum-decorated nitrogen-doped carbon nanofibers by simple heat treatment of fibrous Pt/PANI (platinum on polyaniline). The important difference in our approach is that the platinum nanoparticles are decorated on the support material *prior* to the carbonization step at elevated temperatures. Unlike other studies of heat-treated platinum nanoparticles in various atmospheres [4, 6, 7, 9] no particle growth and no coarsening were detected after heat treatment using X-ray diffraction (XRD) and transmission electron microscopy (TEM) for structural characterization. Besides the size stability during heat treatment, heat-treated Pt/PANI shows good performance and long-term stability during accelerated aging tests with only minor particle growth. First, results as cathode material in PEMFC tests show sufficient performance. Although there are some reports in the literature showing higher performance using nitrogen-doped carbon materials as support, these synthesis approaches are either not facile to scale up [17] or they use high catalyst loadings [18].

2 Experimental

2.1 Support preparation

2.1.1 Wet-chemical PANI preparation

PANI nanofibers were prepared in a modified oxidative polymerization reaction proposed by Stejskal et al. [19].

Aniline (450 μ l) and ammonium peroxodisulfate (APS, 1.428 g) were dissolved in 50 ml 1 M H₂SO₄ separately. The APS solution was quickly poured into the aniline solution under vigorous stirring at room temperature and then left overnight. The green precipitate was filtered and washed with distilled water until a clear filtrate with neutral pH was obtained. Thus, we insure that no residual sulfuric acid is contained in the polymer. To maintain a good dispersion, the filter cake is stored in wet conditions until further use.

2.1.2 Synthesis of Pt/PANI

To obtain 250 mg supported catalyst after the carbonization step (20 wt% Pt on carbonized PANI), 450 mg Pt/PANI (10 wt% Pt) was produced following a modified synthesis route proposed by Guo et al. [20]. The nanofibers were dispersed in 20 ml ultrapure water (MilliQ 18.2 M Ω at 25 °C) followed by the addition of 125 mg H₂PtCl₆ and 2 h stirring, to allow a good contact between the support and the platinum precursor. Afterward, 2 ml HCOOH was added. The mixture was stored at room temperature for 24 h to reduce the platinum precursor completely. Then, the solution was filtered, washed several times with MilliQ water, and dried under vacuum.

2.1.3 Carbonization of Pt/PANI

The Pt/PANI fibers (already decorated with platinum nanoparticles) were transformed into nitrogen-doped carbon nanofibers by subjecting them to a well-known carbonization procedure [21–23]. The samples were heated up to 750 °C in a tube furnace under nitrogen gas flow with a heating rate of 1 °C/min and held for 90 min. At this temperature, the PANI is expected to lose 50 % of its weight [22]. So the PANI with 10 wt% Pt loading is converted into nitrogen-doped carbon nanofibers with 20 wt% Pt loading. For comparison the same heat treatment procedure was carried out on two industrial catalysts, one with 20 % Pt loading (platinum, nominally 20 wt%, on carbon black, Alfa Aesar), the other one with 10 % Pt loading (platinum/charcoal activated 10 % Pt, Merck). All the samples are summarized in Table 1 together with the performed investigations.

2.2 Structural characterization

X-ray powder diffraction (XRD) measurements were carried out with a STOE STADI-P diffractometer using germanium monochromized Mo K α 1 radiation ($\lambda = 0.71069$ Å). To determine the average crystallite size of the platinum particles Rietveld refinement using the FULLPROF software package [24] was performed.

Table 1 Sample nomenclature, description, and investigations

Sample name	Pt20/C	Pt10/C Pt10/C_750	Pt20/C_750	Pt/PANI	Pt/PANI_750
Description	Pt on carbon	Pt on carbon	Heat-treated Pt/C	Pt on PANI	Heat-treated Pt/PANI
Pt loading (wt%)	20	10	20	10	20
Measurements	TEM, XRD, CV aging, and PEMFC	XRD	TEM and XRD	TEM and XRD	TEM, XRD, CV aging, and PEMFC

TEM investigations were performed with an FEI CM20 operating at 200 kV acceleration voltage. For sample preparation a small amount of the powder was dispersed in ethanol using ultrasonic dispersion and one drop was transferred to a standard holey carbon film-covered copper grid. The average particle size distribution was determined by analyzing at least 200 particles of each sample using the software package LINCE [25].

2.3 Electrochemical studies: cyclic voltammetry (CV)

An accelerated aging test was performed in a three-electrode cell at room temperature in nitrogen-purged 0.1 M HClO₄ as electrolyte using a multichannel VMP2 from Princeton Applied Research with EC-Lab 10.02 for control and analysis. The ink was prepared by dispersion of 15 mg catalyst in 1.4 ml MilliQ water and 100 µl Nafion[®] solution (5 % in aliphatic alcohols, DuPont) by ultrasonic treatment for 5 min. The measurement was done with 10 µl ink applied to a glassy carbon disk electrode (7 mm diameter) and dried at 60 °C in air for 15 min. After 5,000 aging cycles from 0 to 1.1 V versus SCE with a scan rate of 150 mV/s the glassy carbon tip was transferred into ethanol and ultrasonically treated. By this procedure, a suspension for TEM analysis was prepared.

2.4 Membrane preparation and testing

For MEA preparation a slightly modified airbrushing method was used. Both inks contained 200 mg catalyst dispersed in 3 ml MilliQ Water, 1 ml Nafion[®] solution, and 5 ml isopropanol. First, the anode ink containing commercial platinum on carbon (Alfa Aesar, platinum nominally 20 % on carbon black); second, the cathode ink containing the newly prepared catalysts (Pt/PANI_750) were sprayed on an upright standing Nafion[®] 117 membrane heated at 100 °C covered with a 5 × 5 cm² spraying mask. The MEAs were tested in a homemade testbench using a Quickconnect[®] fixture (5 bar contact pressure). The MEA was sandwiched between two Freudenberg I3 gas diffusion layers (Freudenberg, Weinheim) and two graphitic flow fields with lamellar four-channel structure. The cell temperature was set to 70 °C, hydrogen with a flow rate of 150 ml/min and oxygen with 80 ml/min were both humidified using a humidifier at 80 °C. For

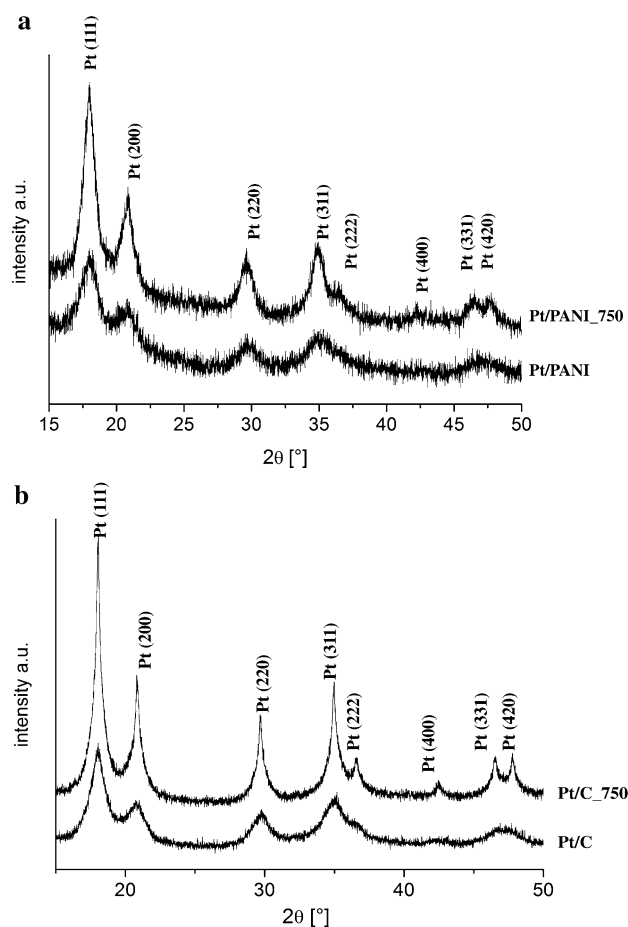


Fig. 1 XRD patterns of the different catalysts; crystallite sizes obtained by Rietveld refinement. **a** Pt/PANI before and after heat treatment, the crystallite size increases only from 1.6 to 2.6 nm. **b** Pt on carbon black, fresh with 1.9 nm; after the heat treatment two Pt phases are necessary for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

comparison, reference MEA using platinum on carbon on anode and cathode side was tested with the same conditions.

3 Results and discussion

The freshly filtered PANI was a greenish slurry containing 5–7 % solid matter. SEM and TEM analysis showed that fibers with lengths between 300 and 500 nm and

Table 2 Pt particle sizes of the different samples

	Pt/PANI	Pt/PANI_750	Pt10/C	Pt10/C_750	Pt20/C	Pt20/C_750
XRD (nm)	1.5 ± 0.3	2.6 ± 0.2	1.5 ± 0.3	3.6 ± 0.7	1.9 ± 0.3	$2.3 \pm 0.2/16.8 \pm 0.5$
TEM (nm)	1.6 ± 0.5	2.0 ± 0.8	–	–	1.9 ± 0.4	2.6 ± 1.7
TEM–CV aged (nm)	–	3.2 ± 2.4	–	–	15.6 ± 7.1	–

thicknesses in the range of 20 nm were obtained, which is in good agreement with the literature [19]. After decoration with platinum a homogeneous distribution of small nanoparticles was observed (not shown here, as it looks similar to Fig. 2b). XRD measurements (Fig. 1) showed only the face-centered cubic (fcc) platinum phase, with large full width at half maximum in good agreement with nanoparticulate crystallites. The Rietveld refinement for the as-synthesized Pt/PANI gave an average particle size smaller than 2 nm. For comparison, the particle size of Pt10/C and Pt20/C was also determined using XRD (Fig. 1b) and yields particle sizes smaller than 2 nm in both cases. TEM analysis confirmed the XRD results (see Table 2). The as-received Pt/PANI and the reference sample (Pt20/C) show a very symmetric and similar size distribution. The mean values for the particle size are 1.6 ± 0.5 and 1.9 ± 0.4 nm for Pt/PANI and Pt20/C, respectively.

The heat-treated samples (Pt/PANI_750 and Pt20/C_750) were also investigated using XRD and TEM analysis. Representative TEM images of the samples are shown in Fig. 2. The TEM analysis of Pt/PANI_750 shows a homogeneous particle distribution over the complete sample with almost no agglomeration. The largest particle being observed was slightly larger than 5 nm. The mean value for the particle size is 2.0 ± 0.8 nm. This is in good agreement with the XRD analysis, which gave a value of 2.6 ± 0.2 nm.

In contrast, the heat-treated reference sample (Pt20/C_750) shows an inhomogeneous particle distribution (Fig. 2a), large particles up to 100 nm were imaged with low magnification. To determine the particle size distribution, high-magnification images were used so that the small particles could be resolved, but excluding the large particles. The mean particle size determined this way is 2.7 ± 1.7 nm, which is in good agreement with the literature [5, 6]. The larger standard deviation (1.7 nm for Pt20/C_750 vs. 0.8 nm for Pt/PANI_750) and the fact that the largest particles could not be considered due to the need of high resolution underline the high inhomogeneity for Pt20/C_750.

This inhomogeneous particle size distribution for Pt20/C_750 is also visible by XRD. Rietveld refinement of this sample (XRD pattern, Fig. 1b) did not yield satisfying results using one fcc platinum phase only. As the reflections have an unusual shape with sharp top and broad base,

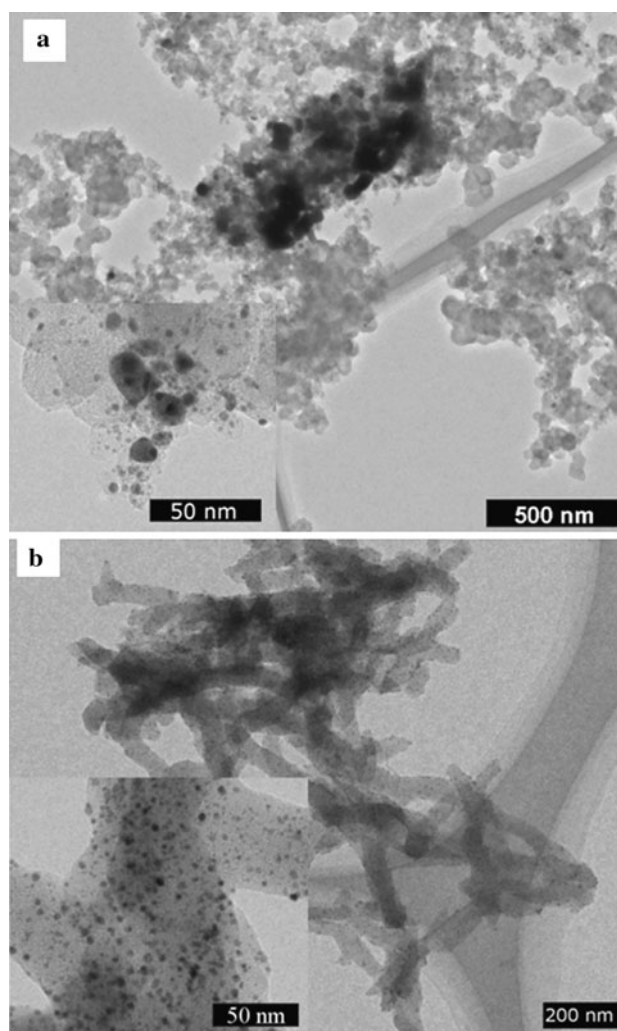


Fig. 2 TEM images of **a** Pt/C_750 and **b** Pt/PANI_750. In higher magnification (*inset*) for Pt/PANI_750 only small particles in high dispersion were observed, while some particles grew significantly for Pt/C_750

two fcc platinum phases were used to obtain a good agreement between the calculated fit and the measured data. Fits for the magnified (111) and (200) reflections are shown in Fig. 3. It is clearly visible that with only one platinum phase the top of the peak is not fitted accurately. All the other samples have been fitted with one platinum phase.

For better comparison of the particle growth of the starting material with 10 % loading, a conventional

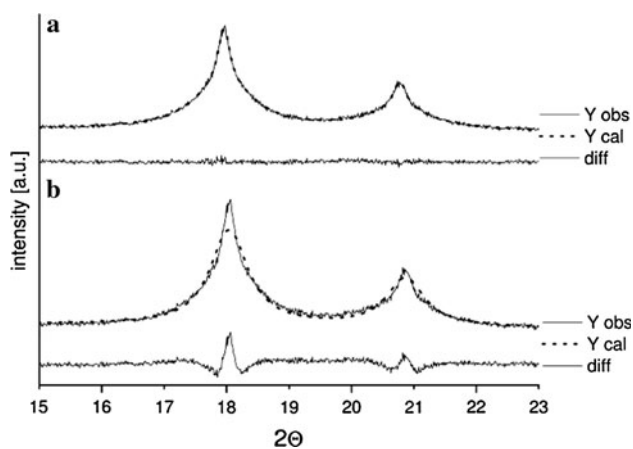


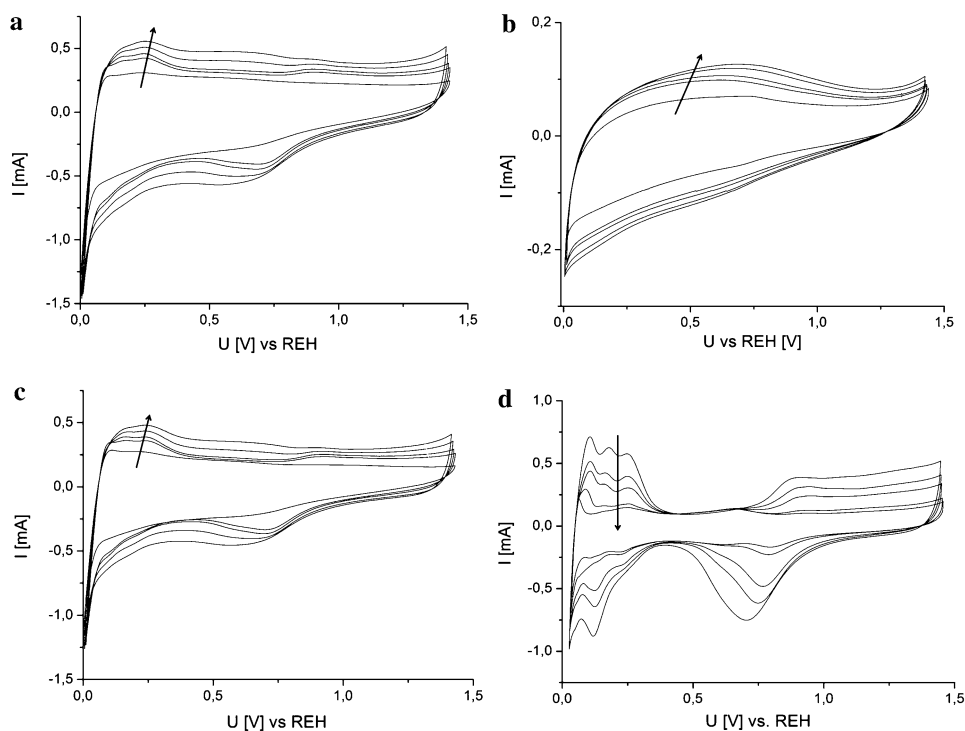
Fig. 3 Magnified (111) and (200) reflections from Pt/C₇₅₀. (a) Fit with two platinum phases and (b) fit with one platinum phase. Measured data, calculated fit, and difference between measurement and fit are shown, two fcc platinum phases are necessary to obtain good agreement

catalyst with 10 % loading (Pt10/C) was heat treated and the particle size was determined using XRD. For this material the starting particle size was the same as for Pt/PANI (1.5 ± 0.3 nm), but it shows a significantly enhanced particle growth during the heat treatment (3.6 ± 0.7 vs. 2.6 ± 0.2 nm for Pt/PANI₇₅₀).

In summary, particle growth is visible for all the samples (Table 2), but significantly less particle growth is observed for Pt/PANI₇₅₀ compared to both Pt/C₇₅₀ samples. The synthesis of platinum supported on carbonized PANI by precipitation of the platinum before the carbonization step leads to an active catalyst with a very homogeneous particle size distribution showing almost no agglomeration, which is an indication of a strong platinum support interaction.

The electrochemical aging by an accelerated stress test of Pt/PANI₇₅₀ is depicted in Fig. 4a. Voltammograms showed an enhanced current and increased double layer with higher cycle numbers; consequently it was not possible to determine the electrochemically active surface area reliably. When the aging procedure was carried out with carbonized PANI without platinum, a similar increase of the double layer was observed but not as pronounced as for the platinum-decorated sample (Fig. 4b). This increase can be attributed to formation of electroactive surface oxides and redox couples on the support material, such as the quinone and hydroquinone redox couple at 0.6 V [26]. Platinum seems to accelerate this reaction, as the increase is more pronounced in the aging for the platinum-supported sample. In order to mathematically remove the influence of electroactive

Fig. 4 Cyclic voltammetry aging for **a** Pt/PANI₇₅₀, **b** PANI₇₅₀ (Pt-free support material), and **d** Pt/C; **c** difference between **a** and **b**. Shown cycles: fresh, 500, 1000, 3000, and 5000; *arrows* indicate rising cycle number. The adsorption current decreases for Pt/C with rising cycle number, while it stays constant for Pt/PANI₇₅₀



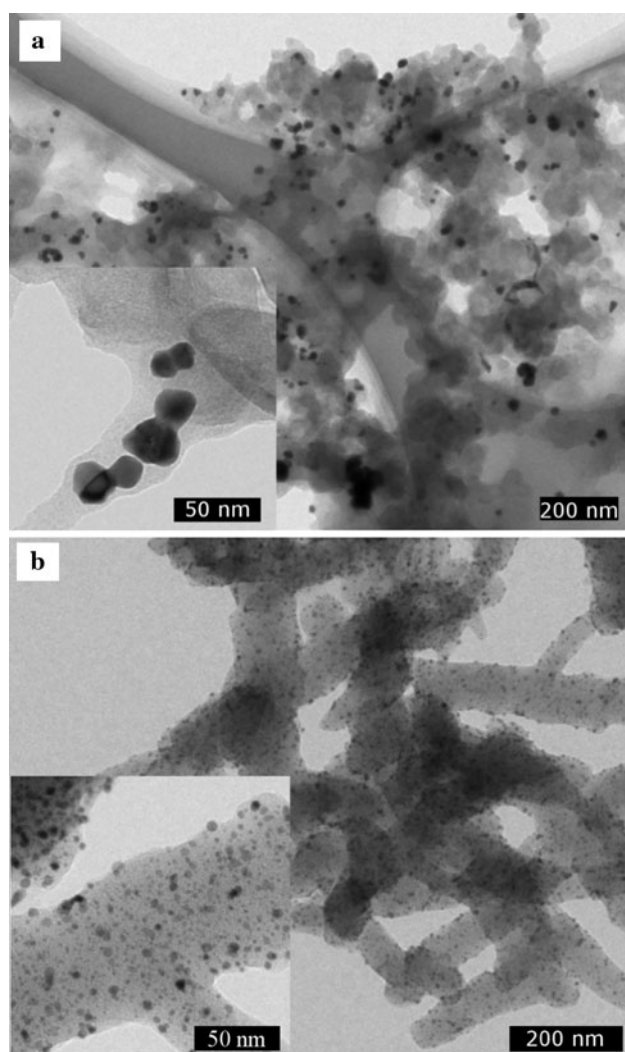
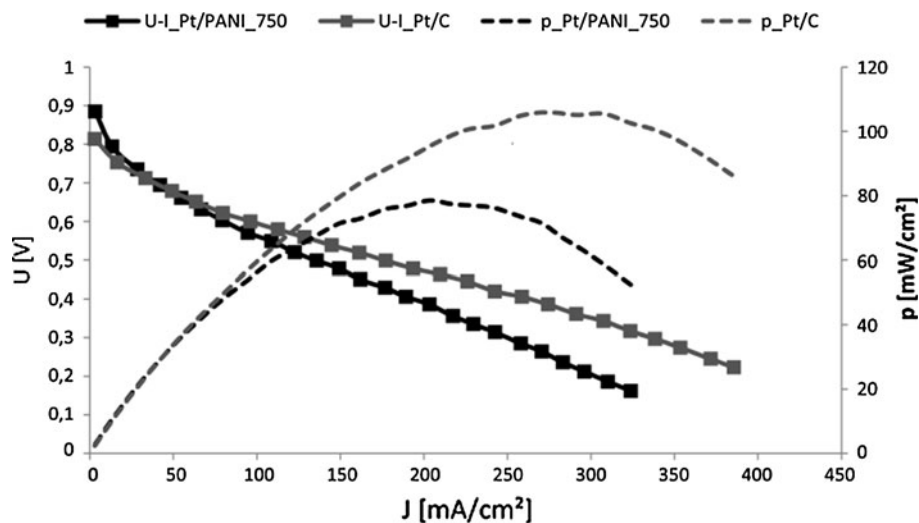


Fig. 5 TEM images after the aging experiments of **a** Pt/C and **b** Pt/PANI_750. In the higher magnification (*insets*) a huge particle growth for Pt/C is visible, while the size and the dispersion for Pt/PANI_750 do not change significantly

Fig. 6 U - I curve using the new synthesized catalyst as cathode material compared to a commercial catalyst (loading in all cases approx. 0.1 mg Pt/cm^2)



oxidized species on the support material, the CV from PANI_750 was subtracted from Pt/PANI_750 (Fig. 4c). When compared to the aging of Pt/C (Fig. 4d) two major facts become obvious: First, the maximum current in the hydrogen desorption region of Pt/PANI_750 is rising with increasing cycle number; while it is reduced for Pt/C. Second, the area under the hydrogen desorption peak almost remains constant for Pt/PANI_750; while this peak nearly vanishes for Pt/C. From these observations we conclude a much lower aging rate for the carbonized PANI, which is consistent with literature for nitrogen-doped carbon materials [14, 16, 21].

TEM investigations after the aging test demonstrate that the shape of the nitrogen-doped carbon support (Pt/PANI_750) is maintained during the aging treatment (Fig. 4b). This implies that support corrosion hardly takes place. In addition, large areas show only small platinum particles. The majority of the particles are in the preferable size range for catalysts of 3–5 nm. In contrast, the TEM images of aged Pt/C (Fig. 5a) show a significant particle growth. The detected particle size of Pt20/C after aging is five times higher than that of Pt/PANI_750 after the same cyclic aging procedure (see Table 2).

First, fuel cell tests of Pt/PANI_750 show a reasonable performance with 78.5 mW/cm^2 maximum power density (Fig. 6). This is still lower than the maximum performance of the reference catalyst (106.0 mW/cm^2), but it must be pointed out that the system used here is not yet optimized. Regarding this issue, several synthesis parameters like heating rate, maximum temperature, and holding time can be tuned to improve the electrochemical performance. First, HRTEM results show that the carbonized PANI did not start to form graphitic layers. This might lead to a lower electric conductivity of this material compared to the well-optimized commercial platinum on carbon catalyst. Detailed investigations using higher temperatures for

carbonization, which might lead to a higher fraction of graphite in the support material, are planned. However, further increase in temperature is expected to lead to more particle growth in the platinum nanoparticles, while the amount of stabilizing nitrogen will decrease.

4 Conclusions

In this work, a novel, low cost and easily scalable synthesis route for platinum catalysts on nitrogen-doped carbon nanofibers is presented and compared to a commercially available catalyst supported on carbon black. In contrast to the other reported synthesis routes for platinum on nitrogen-doped carbon materials, no expensive materials and no harsh experimental conditions like HF etching are needed. Specifically, small platinum nanoparticles were deposited by a simple wet-chemical means on PANI fibers prior to the carbonization to form nitrogen-doped carbon nanomaterials. Though heated up to temperatures as high as 750 °C, the platinum nanoparticles showed remarkable size stability. This allows us to fabricate very homogeneously distributed platinum nanoparticles on nitrogen-doped carbon materials, which cannot easily be obtained otherwise [21]. Accelerated electrochemical aging tests of the freshly prepared Pt/PANI_750 also showed five times reduced particle growth in comparison to a commercial Pt/C catalyst. This enhanced long-term stability is discussed to be due to a stronger anchoring of the platinum on nitrogen atoms at the support surface [14]. First, fuel cell tests show promising results; but it is still a long way to prepare commercial catalysts with better performance than the optimized platinum on carbon black. Further optimization of the heating parameters with respect to the maximum temperature, heating rate, holding time, etc., will be required. The results presented in this work show a first step for preparing stable platinum nanoparticles on nitrogen-doped carbon materials in commercially scalable amounts.

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References

- Knights SD, Colbow KM, St-Pierre J, Wilkinson DP (2004) Aging mechanisms and lifetime of PEMFC and DMFC. *J Power Sources* 127:127–134. doi:10.1016/j.jpowsour.2003.09.033
- Sharma S, Pollet BG (2012) Support materials for PEMFC and DMFC electrocatalysts—a review. *J Power Sources* 208:96–119. doi:10.1016/j.jpowsour.2012.02.011
- Antolini E (2003) Formation, microstructural characteristics and stability of carbon supported platinum catalysts for low temperature fuel cells. *J Mater Sci* 38:2995–3005
- Bezerra CWB, Zhang L, Liu H et al (2007) A review of heat-treatment effects on activity and stability of PEM fuel cell catalysts for oxygen reduction reaction. *J Power Sources* 173:891–908. doi:10.1016/j.jpowsour.2007.08.028
- Wang W, Chen X, Cai Q et al (2008) In situ SAXS study on size changes of platinum nanoparticles with temperature. *Eur Phys J B* 65:57–64. doi:10.1140/epjb/e2008-00322-7
- Han K, Moon Y, Han O et al (2007) Heat treatment and potential cycling effects on surface morphology, particle size, and catalytic activity of Pt/C catalysts studied by ¹³C NMR, TEM, XRD and CV. *Electrochem Commun* 9:317–324. doi:10.1016/j.elecom.2006.09.027
- Zhang L, Lee K, Zhang J (2007) The effect of heat treatment on nanoparticle size and ORR activity for carbon-supported Pd–Co alloy electrocatalysts. *Electrochim Acta* 52:3088–3094. doi:10.1016/j.electacta.2006.09.051
- Bett J, Kinoshita K, Stonehart P (1974) Crystallite growth of platinum dispersed on graphitized carbon black. *J Catal* 133:124–133
- Bett J, Kinoshita K, Stonehart P (1974) Crystallite growth of platinum dispersed on graphitized carbon black. *J Catal* 35:307–316
- Lisiecki I, Sack-Kongehl H, Weiss K et al (2000) Annealing process of anisotropic copper nanocrystals. 1. Cylinders. *Langmuir* 16:8802–8806. doi:10.1021/la0003443
- Blurton KF, Kunz HR, Rutt DR (1978) Surface area loss of platinum supported on graphite. *Electrochim Acta* 23:183–190
- Shao Y, Yin G, Gao Y (2007) Understanding and approaches for the durability issues of Pt-based catalysts for PEM fuel cell. *J Power Sources* 171:558–566. doi:10.1016/j.jpowsour.2007.07.004
- Mayrhofer KJJ, Meier JC, Ashton SJ et al (2008) Fuel cell catalyst degradation on the nanoscale. *Electrochem Commun* 10:1144–1147. doi:10.1016/j.elecom.2008.05.032
- Zhou Y, Neyerlin K, Olson TS et al (2010) Enhancement of Pt and Pt-alloy fuel cell catalyst activity and durability via nitrogen-modified carbon supports. *Energy Environ Sci* 3:1437–1446. doi:10.1039/c003710a
- Kundu S, Nagaiah TC, Xia W et al (2009) Electrocatalytic activity and stability of nitrogen-containing carbon nanotubes in the oxygen reduction reaction. *J Phys Chem C* 113:14302–14310. doi:10.1021/jp811320d
- Tuavev X, Paraknowitsch JP, Illgen R et al (2012) Nitrogen-doped coatings on carbon nanotubes and their stabilizing effect on Pt nanoparticles. *Phys Chem Chem Phys* 14:6444–6447. doi:10.1039/c2cp40760d
- Saha MS, Li R, Sun X, Ye S (2009) 3-D composite electrodes for high performance PEM fuel cells composed of Pt supported on nitrogen-doped carbon nanotubes grown on carbon paper. *Electrochem Commun* 11:438–441. doi:10.1016/j.elecom.2008.12.013
- Subramanian NP, Li X, Nallathambi V et al (2009) Nitrogen-modified carbon-based catalysts for oxygen reduction reaction in polymer electrolyte membrane fuel cells. *J Power Sources* 188:38–44. doi:10.1016/j.jpowsour.2008.11.087
- Stejskal J, Sapurina I, Trchová M (2010) Polyaniline nanostructures and the role of aniline oligomers in their formation. *Prog Polym Sci* 35:1420–1481. doi:10.1016/j.progpolymsci.2010.07.006
- Guo S, Dong S, Wang E (2009) Polyaniline/Pt hybrid nanofibers: high-efficiency nanoelectrocatalysts for electrochemical devices. *Small* 5:1869–1876. doi:10.1002/sml.200900190
- Mabena LF, Sinha Ray S, Mhlanga SD, Coville NJ (2011) Nitrogen-doped carbon nanotubes as a metal catalyst support. *Appl Nanosci* 1:67–77. doi:10.1007/s13204-011-0013-4

22. Trchová M, Konyushenko EN, Stejskal J et al (2009) The conversion of polyaniline nanotubes to nitrogen-containing carbon nanotubes and their comparison with multi-walled carbon nanotubes. *Polym Degrad Stab* 94:929–938. doi:[10.1016/j.polydegradstab.2009.03.001](https://doi.org/10.1016/j.polydegradstab.2009.03.001)
23. Stejskal J, Trchová M, Hromádková J et al (2010) The carbonization of colloidal polyaniline nanoparticles to nitrogen-containing carbon analogues. *Polym Int* 59:875–878. doi:[10.1002/pi.2858](https://doi.org/10.1002/pi.2858)
24. Roisnel T, Rodríguez-Carvajal J (2000) WinPLOTR: a windows tool for powder diffraction pattern analysis. In: Delhez R, Mittenmeijer EJ (eds) *Material Science Forum. Proceedings of the seventh European powder diffraction conference (EPDIC 7)*, pp 118–123
25. Lucato dos Santos e. S (1999) Lince. Version 2.4.2. Softw. aus dem Fachbereich Mater. und Geowissenschaften, Fachbereich Nichtmetallische Anorg. Werkstoffe, TU Darmstadt, Darmstadt
26. Ball SC, Hudson SL, Thompsett D, Theobald B (2007) An investigation into factors affecting the stability of carbons and carbon supported platinum and platinum/cobalt alloy catalysts during 1.2 V potentiostatic hold regimes at a range of temperatures. *J Power Sources* 171:18–25. doi:[10.1016/j.jpowsour.2006.11.004](https://doi.org/10.1016/j.jpowsour.2006.11.004)