



# Effective debundling of carbon nanotubes and simultaneous synthesis of Pt nanoparticles by Nafion<sup>®</sup> induced emulsions

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## ABSTRACT

Carbon nanostructures and, in particular, Single Wall Carbon Nanotubes (SWNT) or Multi Wall Carbon Nanotubes (MWNT) provide unique properties, notably outstanding chemical stability and electronic conductivity. Therefore they can be seen as a potential replacement for carbon black, which is frequently used as support material for polymer electrolyte membrane fuel cell (PEMFC) catalysts. This paper describes a new synthesis method to deposit platinum nanoparticles on carbon by using MWNT/Nafion<sup>®</sup> emulsions in the reduction reaction of hexachloroplatinate with ethylene glycol and butyl acetate. In contrast to other syntheses described in the literature, the formation of an emulsion allows effective debundling and a good dispersion of MWNTs in the solvent. This strategy helps to maintain a narrow Pt particle size distribution of  $3 \text{ nm} \pm 0.5 \text{ nm}$  and a homogeneous dispersion of the nanoparticles on the support even at loadings of up to 50 wt%. It furthermore reduces agglomeration of the MWNTs during electrode manufacturing, so that an airbrush technique can be used, and enhances the ionic conductivity of the electrode layer. Catalyst morphology and distribution are investigated by transmission electron microscopy, X-ray diffraction and scanning electron microscopy. Electrodes are produced by a conventional airbrush technique on Nafion<sup>®</sup> membranes (Nafion<sup>®</sup> 117 and Nafion<sup>®</sup> NRE 212) and tested in a fuel cell test bench.

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## 1. Introduction

Climate change and limited fossil fuel resources strongly push the development of more efficient energy conversion technologies e.g. the fuel cell technology, in which chemical energy is directly converted to electricity. Besides the high temperature fuel cells like SOFC and MCFC, which are used for small and mid range stationary combined heat and power plants, the low-temperature Polymer Electrolyte Membrane Fuel Cell (PEMFC) shows promising features for mobile and portable application. However, high cost and poor durability so far hinder their commercial market introduction, and therefore spark the interest in novel materials and innovative electrode preparation processes.

Carbon nanotubes, discovered by Iijima in 1991 [1], show unique properties regarding chemical stability, electronic conductivity [2] and tensile strength [3,4]. They also provide a high surface area of up to  $2200 \text{ m}^2 \text{ g}^{-1}$  [5], which is essential for good catalytic efficiency. Without oxidative treatment hydrophobic surface properties can be observed. Depending on their morphology, carbon nanotubes (CNT) are separated into single wall (SWNT) and multi wall nan-

otubes (MWNT). Both types have a high aspect ratio with diameters of 1–20 nm and lengths of a few micrometers. Usually they form parallel bundles consisting of 2–50 tubes and can be prepared in ordered (aligned) [6] and disordered state (powders, networks) [7]. Many groups focus on carbon nanotubes as a replacement for the commercial carbon black as electrode substrate [8–11]. Carbon nanotubes have the disadvantage that they apparently offer less anchor sites for the deposition of metallic nanoparticles. Therefore, they require specific pre-treatments, as for example the addition of hydrophilic groups by acid treatment [12] or organic groups like diazonium salts [13]. However, probably due to their higher crystallinity they undergo less support corrosion in the extreme environment of PEM fuel cells.

A common way to deposit nanometer-sized catalyst particles with a narrow size distribution homogeneously on a high-surface area carbon support, e.g. Vulcan XC-72 or Ketjen black, is the reduction via ethylene glycol as described by Bock et al. [14]. This method is rather facile, reproducible and also cheap, as compared to e.g. chemical vapour deposition and the like. It is also suitable to deposit Pt on CNTs [15] [16], but unfortunately the 1-dimensional nature of the CNTs is prone to form aggregates and “nests” in ethylene glycol or other polar liquids [17]. These cannot easily be penetrated by the reactants. And thus, it proves difficult to obtain homogeneous nanoparticle dispersions on CNTs, especially at the high metal load-

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ings required for direct methanol fuel cells (DMFC) [9]. Usually, surfactants like sodium dodecyl sulfate [18] [19] or block copolymers [20] are used to mediate between polar liquids and CNTs. For fuel cell operation and also other catalytic reactions, these have to be removed prior to their application, as they might affect further reactions negatively. Moreover, surfactants seem to increase the contact resistances within a CNT buckypaper [21].

This paper presents a method to debundle and finely disperse CNTs in aqueous solution by using Nafion<sup>®</sup> ionomer and butyl acetate to form a stable emulsion. This helps to make a larger fraction of the CNTs accessible to the reducing agent, so that 3 nm Pt particles with a very narrow size distribution are homogeneously deposited on the support. In the same step, the CNTs are coated with Nafion<sup>®</sup> to improve their ionic conductivity. This appears to be also advantageous for the final electrode manufacturing step, since it allows applying the conventional airbrush technique also in those cases, in which CNTs are used as support material.

## 2. Experimental

### 2.1. Sample synthesis

60 mg multi wall carbon nanotubes (Elicarb<sup>®</sup> from Thomas Swan, U.K.) are mixed and stirred with 60 mL nitric acid (68%) and treated with ultrasound (Hielscher UPV 100) for 10 min to remove metallic impurities. After diluting with water, the suspension is vacuum-filtrated over a 47 mm polycarbonate membrane with 0.4  $\mu\text{m}$  pore size. Remaining acid is removed by rinsing with water several times. The wet CNT residue is removed from the polycarbonate membrane and mixed with 60 mL butyl acetate while stirring and ultrasonic treatment for 10 min, leading to a homogeneous dispersion. For the platinum precursor solution, 145 mg potassium hexachloroplatinate (Sigma–Aldrich) is dissolved in 10 mL ultra pure water at 50 °C. 60 mL ethylene-glycol and the platinum precursor solution are mixed with the MWNT-butylacetate dispersion in a 250 mL round bottom flask. After adding 0.5 mL of 5% Nafion<sup>®</sup> solution (Dupont D521) and another 15 min of ultrasonic treatment and stirring, the two phase boundary between the liquids disappears and a homogeneous milky-grey emulsion is created.

The emulsion is heated in an oil bath from room temperature to 170 °C and the mixture is held for 120 min under reflux conditions while stirring. Samples are taken during the synthesis for a detailed investigation by XRD. After cooling down, the catalyst-solvent mixture is filtered over a polycarbonate filter. Rinsing with 1:1 isopropanol–water removes the remaining ethylene glycol and butyl acetate. After removal of the filter, the wet residue is mixed with 30 mL isopropanol and 30 mL water by ultrasonic treatment to create a sprayable ink. Nafion<sup>®</sup> and/or PTFE solution can be added here.

### 2.2. Sample characterization by XRD, TEM, SEM and TGA-MS

For X-ray diffraction (XRD) measurements, samples (<1 mL) are taken from the liquid phase during the synthesis repeatedly. The fluid is dropped slowly onto a polycarbonate filter and a mild vacuum is applied. After drying, the polycarbonate membrane is mounted in an XRD sample holder and measured in a STOE STADI P in transmission geometry with Ge-monochromized Cu-K $\alpha$  radiation and a position-sensitive detector with a 40° aperture. Average particle sizes are estimated by Rietveld refinement using the FULL-PROF suite [22]. Transmission electron microscopy (TEM) samples are prepared by dispersing a few micro litres of catalyst ink in methanol and letting 1 drop of this mixture dry on a copper TEM grid. Subsequently, a JEOL JEM 3010 with LaB<sub>6</sub> cathode and an acceleration voltage of 300 kV is used for examination. Scanning electron

microscopy (SEM) images are recorded by cutting the sample with a razor blade and mounting the pieces on a SEM sample holder to determine the electrode thickness. Secondary electron (SE) images are recorded with a FEI Quanta 200 FEG. For the thermogravimetric analysis (TGA-MS) a fragment of the as prepared MWNT-Pt filter substrate (61.4 mg MWNTs, 147.5 mg K<sub>2</sub>PtCl<sub>6</sub>, 0.5 mL Nafion<sup>®</sup> solution) is dried in air at 120 °C for 24 h and heated under a flow of 25 mL min<sup>-1</sup> O<sub>2</sub> and 10 mL min<sup>-1</sup> Ar to 1000 °C using a Netzsch STA 429. Residual gases are analysed by mass spectrometry.

### 2.3. MEA preparation and electrochemical investigation by IV curves

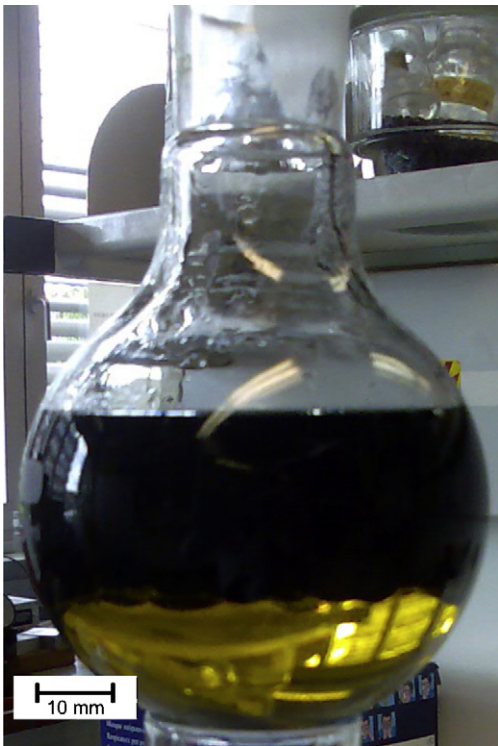
For membrane preconditioning, 5 × 5 cm pieces of Nafion<sup>®</sup> 117 are heated up to 80 °C in 500 mL of 1 M sulphuric acid with 20 mL of 30% hydrogen peroxide solution for 2 h. After rinsing with DE-water, the membrane is fixed to a heated table (110 °C) by means of a mild vacuum. Airbrush is used to apply the aqueous catalyst ink onto the membrane, which is covered by a mask to form a round centred area ( $\varnothing = 37$  mm). 2 mL ink is sprayed on each side, which corresponds to a maximum Pt loading of 0.2 mg cm<sup>-2</sup>. The given loadings correspond to the upper limit, because it is difficult to determine the amount of overspray (estimated: 10–20%). Each layer is allowed to dry before it is covered by the next one. The MEA is covered with two pieces of carbon cloth (Elat<sup>®</sup> LT1400, with micro porous layer, by Etek Inc.) and fixed between gold-plated stainless steel plates with a meander flow field. The cell is fed with pure H<sub>2</sub> and O<sub>2</sub> at atmospheric pressure. Both gases are humidified by bubblers at 90 °C. The cell temperature is set to 75 °C. After a couple of hours in cell conditioning, IV curves are recorded in potentiostatic mode with an electronic load, compensating contact resistances. Gas flows are adjusted in such a way that reaction products are removed even at highest currents (stoichiometry >1).

## 3. Results and discussion

### 3.1. Deposition of noble metals

It is commonly observed that CNTs form aggregates and “nests”, when added into polar solvents for the deposition of nanoparticles. A mixture of CNTs and butyl acetate, however, leads to a homogeneous black dispersion, which is stable for days after ultrasonic treatment. Adding ethylene glycol and yellow-coloured aqueous K<sub>2</sub>PtCl<sub>6</sub> solution, a sharp phase boundary is observed in Fig. 1. Even with strong ultrasonic treatment it is not possible to mix the phases. If some Nafion<sup>®</sup> solution is added, a stable grey emulsion can be created by ultrasonic treatment. It seems that Nafion<sup>®</sup> acts as a surfactant. Microscopic analysis shows spheres (diameter of ~50  $\mu\text{m}$ ) with a black shell in clear liquid (Fig. 2).

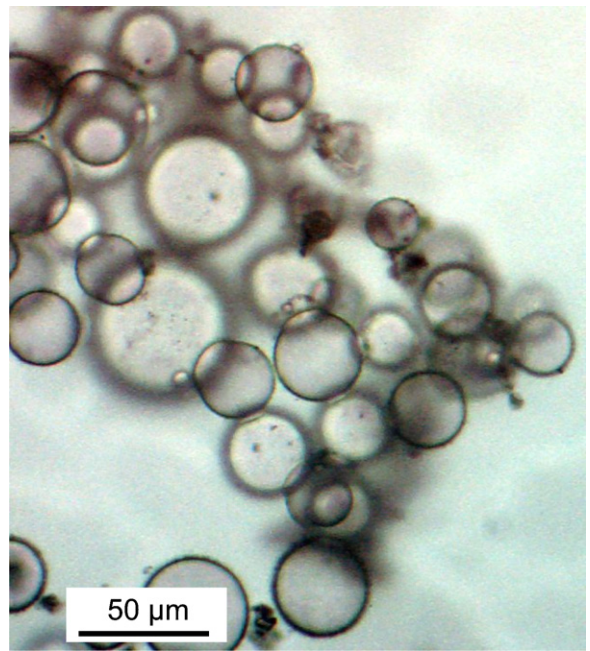
To distinguish ethylene glycol and butyl acetate, fluorescein (CAS: 2321-07-5) is used as colouring agent. Without the black MWNTs, it can be clearly seen in Fig. 3 that the colourless butyl acetate is located inside the spheres, whereas the ethylene glycol phase remains outside. This effect can be explained by the amphiphilic nature of Nafion<sup>®</sup> with its hydrophobic tetrafluoroethylene backbone and hydrophilic SO<sub>3</sub><sup>-</sup> groups. A Critical Micelle Concentration (CMC) could not be detected with diluting experiments with the Nafion<sup>®</sup> solution. Therefore, the influence of other surfactants could be excluded. For the observed effects we assume a model as depicted in Fig. 4: Nafion<sup>®</sup> forms the boundary between ethylene glycol and butyl acetate. The CNTs tend to move towards the hydrophobic backbone of the Nafion<sup>®</sup> molecules, whereas the hygroscopic SO<sub>3</sub><sup>-</sup> groups become oriented towards the ethylene glycol phase. This leads to a high interface area of approx. 12 m<sup>2</sup> for this 120 mL batch, and provides an excellent debundling of



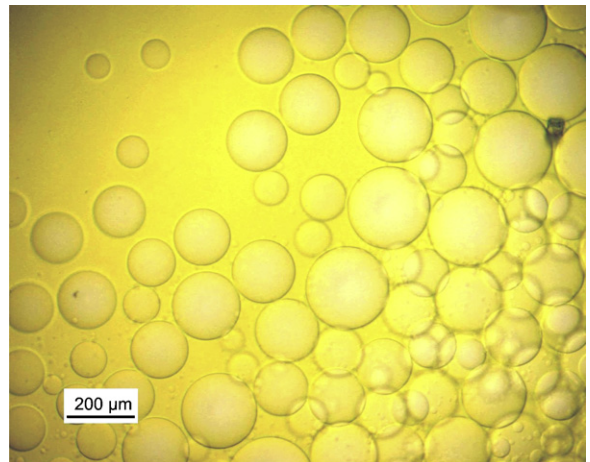
**Fig. 1.** CNT-butylacetate phase (black) and ethylene glycol with platinum precursor (yellow) before ultrasonic treatment. A clear phase separation is observed.

the CNTs. The more homogeneous dispersion of the CNTs in the solvent allows for a more facile access of the Pt precursors and thereby increases the homogeneity of the deposition of nanoscaled platinum particles. Concurrently, Nafion<sup>®</sup> and CNTs are perfectly mixed, which is essential for a good three-phase contact of the catalyst particles. Butyl acetate has been chosen, as it was reported by Uchida [23] that a Nafion<sup>®</sup> solution tends to form colloids with solvents having a dielectric constant between 3 and 10.

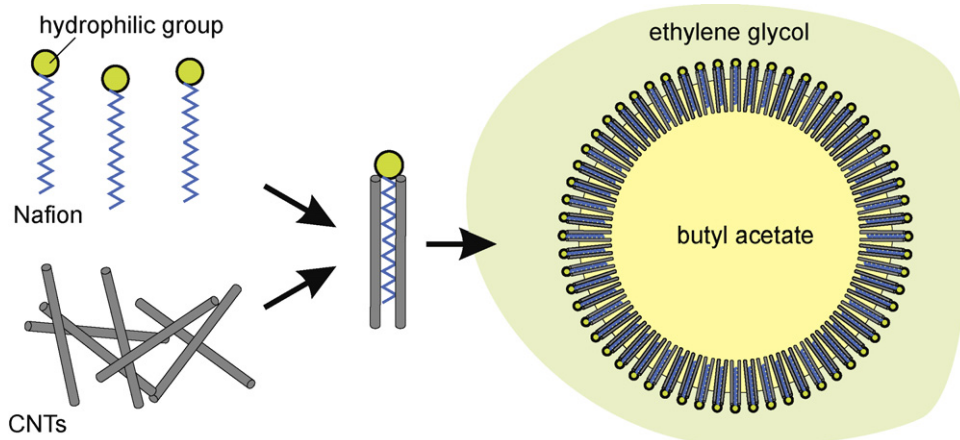
Fig. 5 shows the time dependent changes during catalyst synthesis. Shortly before the reactor temperature reaches the boiling point of the solution (~120 °C), the decomposition of the emulsion was visible with the naked eye as a phase boundary between the polar and the non-polar phase. The orange dots indicate the sampling points, numbered from 1 to 10. First particles are detectable by XRD after 45 min (sample 7). Fig. 6 shows the diffraction patterns of samples 3 to 10 after subtraction of the background intensity. Because



**Fig. 2.** Optical microscopy image of CNT-butyl acetate emulsion: Micro spheres of butyl acetate with walls of CNT- Nafion<sup>®</sup> composite in ethylene glycol.



**Fig. 3.** Ethylene glycol (colored yellow with fluorescin) and butyl acetate (inside the spheres) without CNTs.



**Fig. 4.** Model for the CNT-Nafion<sup>®</sup> emulsion and formation of the micro spheres.

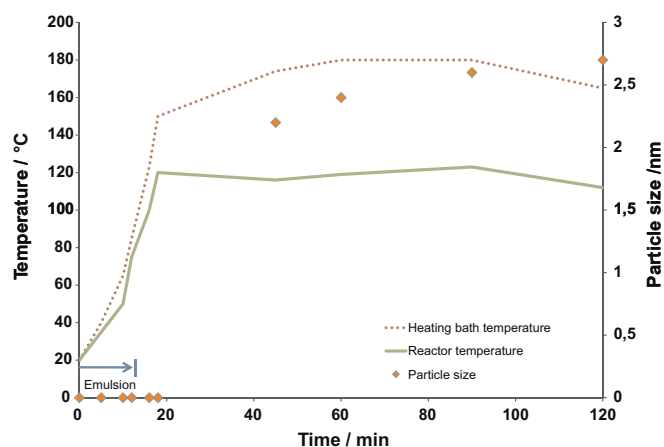


Fig. 5. Temperatures and platinum particle sizes during synthesis.

only a very small amount was sampled at each step, we could not see the MWNT reflections at  $26^\circ$ . The particle size increases from 2.2 nm (sample 7) to 2.7 nm (sample 10) at the end of this experiment. After cooling down, the two liquid phases could be observed. According to the black colour of the ethylene glycol phase the MWNTs moved to this phase, whereas the butyl acetate contains only a few black particles. This indicates a decreased hydrophobicity of the Pt/MWNT/Nafion<sup>®</sup> composite material, which increases its dispersibility especially in aqueous solutions.

### 3.2. Structural analysis

Fig. 7 shows the uniform distribution of platinum on the multi walled carbon nanotubes. The derived particle statistics (Fig. 8) show a narrow size distribution of  $3 \pm 0.5$  nm, providing a high active area for catalytic reactions. This has been verified by XRD measurements during the catalyst synthesis. The yield of the platinum deposition is nearly 100%, as no traces of Pt could be found in the filtrate using XRF analysis (not shown here).

Fig. 9 shows the mass spectrometry data and the mass of the Pt/MWNT/Nafion<sup>®</sup> composite as a function of temperature. Here, the characteristic curve  $m/z = 19$  has been divided by 100 to fit to the same scale. Two striking features can be separated: A mass loss of 10% at  $300^\circ\text{C}$  and a mass loss of 46% at  $\sim 400^\circ\text{C}$ . According to the mass spectrometry data we can assume that the first peak is caused by water ( $m/z = 18, 19$ ) and hydrogen ( $m/z = 1, 2$ ). The second

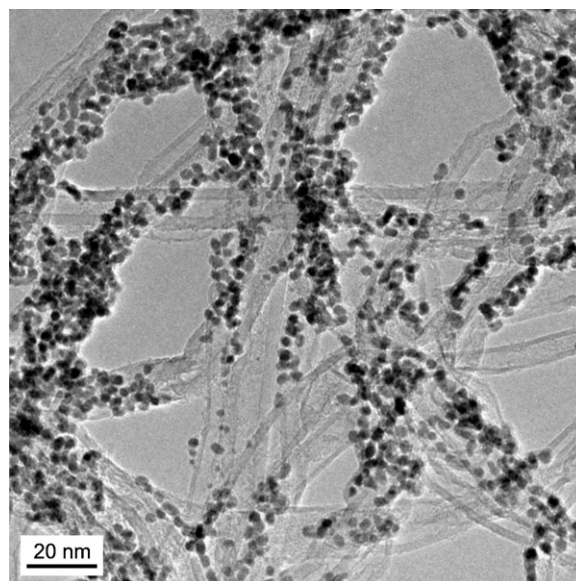


Fig. 7. TEM image of Pt/MWNTs after synthesis.

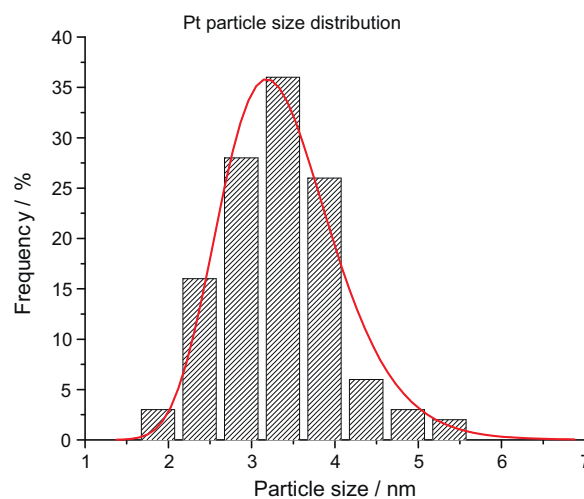


Fig. 8. Pt particle size distribution after synthesis (derived from TEM image figure 7).

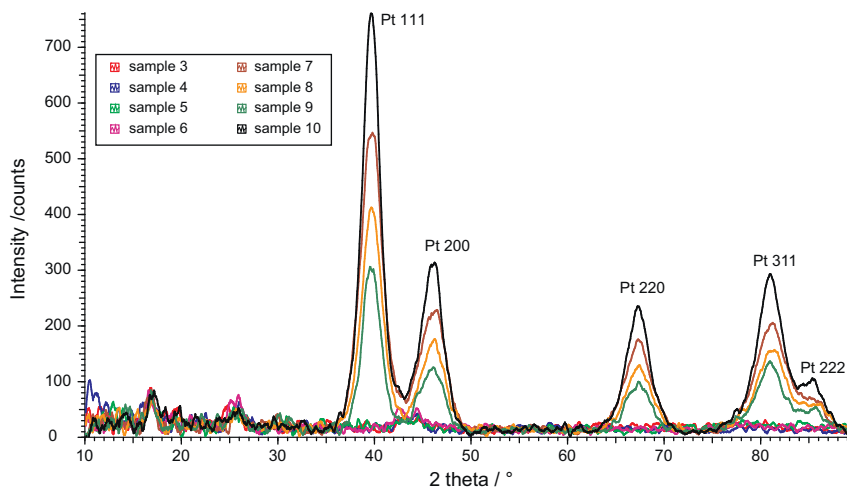


Fig. 6. Background-subtracted X-ray diffraction patterns of samples during synthesis.

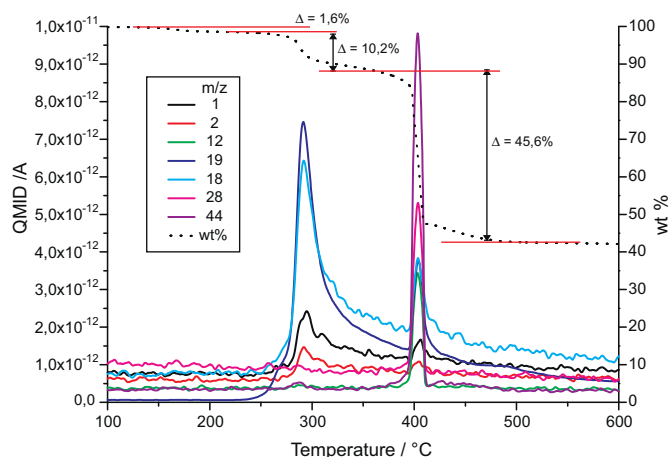


Fig. 9. TGA/MS plot of CNT-Pt-Nafion® composite (25 mL min<sup>-1</sup> O<sub>2</sub> and 10 mL min<sup>-1</sup> Ar).

peak also contains some water, but shows mainly reaction products of carbon with oxygen ( $m/z=28, 44$  for CO<sub>2</sub> and CO). The residual mass after heating to 600 °C remains stable until 1000 °C (not shown here), and shows a good correlation with the desired amount of Pt.

### 3.3. Electrode preparation and fuel cell tests

Dispersions of carbon nanotubes and water form paper-like structures while drying. If this dispersion is dried directly on a sheet of Nafion® 117, the catalytic layer formed by the residue is very inhomogeneous. The resulting CNT paper tends to shrink during drying, while the highly hygroscopic Nafion® substrate swells. Both effects can be prevented using a heated vacuum table for the substrate (see [24]) and airbrush technique for applying the aqueous Pt/MWNT/Nafion® dispersion. Here, the good blending between Nafion® and MWNTs leads to a good dispersibility of solid matter in water/isopropanol. By the new synthesis procedure agglomerations also in the electrode ink are prevented, which could otherwise block the nozzle of the airbrush device. The liquid is separated into small droplets during spraying, which dry immediately on the heated Nafion® membrane surface. Thus, shrinking is limited to a very small region and a homogeneous dull black surface can be obtained. Each layer is allowed to dry by moving the airbrush pistol in serpentine movements. The mechanical stability of the electrode was suitable for different layer thicknesses. The electrode material sticks tightly on the membrane even without additional temperature or pressure treatment. The SEM image in Fig. 10 shows the surface of an as-prepared electrode surface using the SE mode. A porous felt-like nanotubes-structure can be observed, which provides a good electrical contact to the GDL as well as an excellent permeability for gases. Typical electrode thicknesses range between 10 and 20 μm. The suitability of the device for fuel cell applications was demonstrated in single cell tests as depicted in Fig. 11, which yield a maximum power density of ~450 mW cm<sup>-2</sup>. Here, the maximum amount of Nafion®, which could be added in the synthesis step without decomposition of the emulsion, was utilized. For higher fuel cell performances, however, additional optimization of the electrode preparation was necessary.

By varying the thickness of the electrode layer, we observed that only a part of the electrode is active during the reaction. Therefore, the Nafion® content of the electrode was increased to ~0.3 mg cm<sup>-2</sup> by adding Nafion® solution to the catalyst ink before spraying. In addition, the membrane thickness was reduced by using Nafion® NRE212. After these optimization steps, a maximum peak power

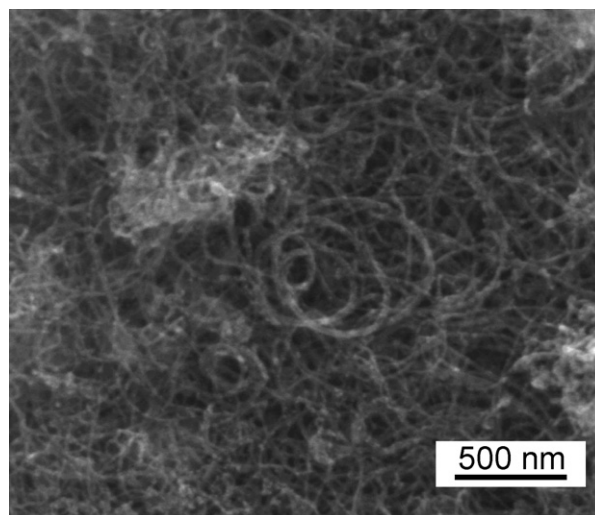


Fig. 10. Electrode surface before operation (CNT-Pt-Nafion® composite sprayed on Nafion 117, SEM, SE-Mode).

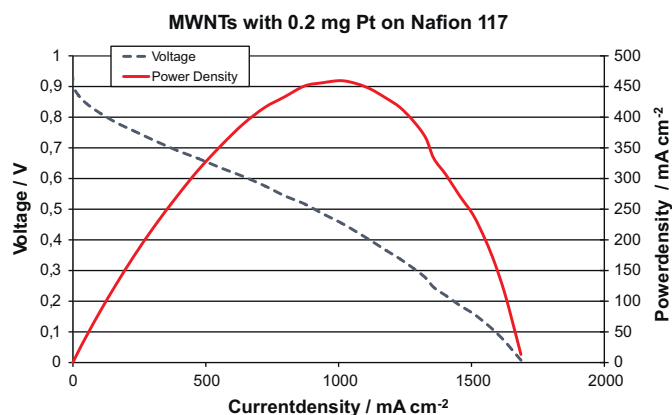


Fig. 11. Characteristic IV curve and power density of Pt/MWNT electrode on Nafion® 117.

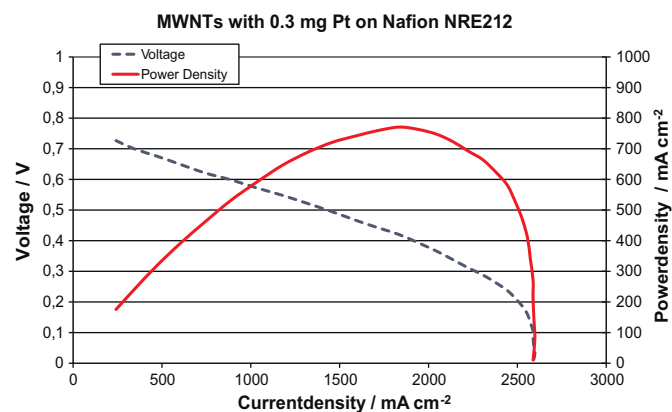


Fig. 12. Characteristic IV curve and power density of Pt/MWNT electrode with enhanced ionomer content on Nafion® NRE212.

density of 770 mW cm<sup>-2</sup> was achieved (Fig. 12) at a platinum loading of 0.3 mg cm<sup>-2</sup>.

## 4. Conclusions

The presented work describes a new emulsion-based method to finely disperse CNTs in a polar liquid. It significantly reduces aggre-

gation of the support material by providing an excellent debundling of the CNTs during synthesis. Consequently, the support is easily accessible to the hydrophilic Pt precursors so that even at high metal loadings a high dispersion of the catalytically active nanoparticles was obtained. By using Nafion® as a surfactant, a homogeneous distribution of the proton conductive ionomer in the electrode was achieved. The resulting Pt/MWNT/Nafion® composite material is more hydrophilic than the untreated MWNTs, which is needed to create a homogeneous ink suitable for airbrush spraying onto a hot substrate. Nafion® contents were optimized for both synthesis and fuel cell operation. Consequently, highly efficient CNT electrodes could be manufactured as proven by characteristic IV curves with peak power densities of 770 mW cm<sup>-2</sup>.

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### References

- [1] S. Iijima, *Nature* 354 (1991) 56–58.
- [2] H. Ago, T. Kugler, F. Cacialli, K. Petritsch, R. Friend, W. Salaneck, et al., *Synthetic Metals* 103 (1999) 2494–2495.
- [3] R. G.D. Saito, M.S. Dresselhaus, *Physical properties of carbon nanotubes*, Imperial College Press, London, 2003.
- [4] P.M. Ajayan, *Chemical Reviews* 99 (1999) 1787–1800.
- [5] T. Hiraoka, A. Izadi-Najafabadi, T. Yamada, D.N. Futaba, S. Yasuda, O. Tanaiki, et al., *Advanced Functional Materials* 20 (2010) 422–428.
- [6] B.J. Hinds, N. Chopra, T. Rantell, R. Andrews, V. Gavalas, L.G. Bachas, *Science* 303 (2004) 62–65.
- [7] C. Journet, W.K. Maser, P. Bernier, A. Loiseau, M.L. de la Chapelle, S. Lefrant, et al., *Nature* 388 (1997) 756–758.
- [8] M. Carmo, V. Paganin, J. Rosolen, E. Gonzalez, *Journal of Power Sources* 142 (2005) 169–176.
- [9] C. Chien, K. Jeng, *Materials Chemistry and Physics* 99 (2006) 80–87.
- [10] G. Girishkumar, K. Vinodgopal, P.V. Kamat, *Journal of Physical Chemistry B* 108 (2004) 19960–19966.
- [11] Y. Liang, H. Zhang, B. Yi, Z. Zhang, Z. Tan, *Carbon* 43 (2005) 3144–3152.
- [12] Yangchuan Xing, *Journal of Physical Chemistry B* 108 (2004) 19255–19259.
- [13] M.M. Waje, X. Wang, W. Li, Y. Yan, *Nanotechnology* 16 (2005) S395–S400.
- [14] C. Bock, C. Paquet, M. Couillard, G.A. Botton, B.R. MacDougall, *Journal of the American Chemical Society* 126 (2004) 8028–8037.
- [15] V. Lordi, N. Yao, J. Wei, *Chemistry of Materials* 13 (2001) 733–737.
- [16] W. Li, C. Liang, W. Zhou, J. Qiu, H. Li, G. Sun, et al., *Carbon* 42 (2004) 436–439.
- [17] F. Scheiba, *Electrode structures of polymer-electrolyte fuel cells (PEFC)*, TU Darmstadt, 2008.
- [18] L. Jiang, L. Gao, J. Sun, *Journal of Colloid and Interface Science* 260 (2003) 89–94.
- [19] L. Zhao, L. Gao, *Journal of Materials and Chemistry* 14 (2004) 1001.
- [20] V.A. Sinani, M.K. Gheith, A.A. Yaroslavov, A.A. Rakhnyanskaya, K. Sun, A.A. Mamedov, et al., *Journal of the American Chemical Society* 127 (2005) 3463–3472.
- [21] M. Lebert, *Characterization of carbon nanotube gas diffusion electrodes for low temperature H<sub>2</sub>/O<sub>2</sub> fuel cells*, Autonomous University of Madrid, 2009.
- [22] T. Roisnel, J. Rodríguez-Carvajal, *Material Science Forum* 374 (2001) 118–123.
- [23] M. Uchida, Y. Aoyama, N. Eda, A. Ohta, J. Electrochem. Soc. 142 (1995) 4143–4149.
- [24] M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 139 (1992) L28–L30.