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Direct support mixture painting, using Pd(0) organo-metallic compounds – an easy and environmentally sound approach to combine decoration and electrode preparation for fuel cells

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An inventive, fast and straight-forward approach for the direct preparation of fuel cell electrodes has been developed and tested. Our approach avoids long catalyst preparation and post-synthesis treatment. It reduces the use of chemicals and thereby concomitantly lowers the environmental impact and improves cost efficiency. It combines decoration of the support by palladium nanoparticles with electrode preparation through a simple one-step ink-painting and annealing

process. The composites have been investigated by high resolution transmission electron microscopy, scanning electron microscopy, and x-ray diffraction. Crystalline particles are well attached and well distributed on the support. Particles are few nanometers and spherical for decorated Vulcan whereas they are larger and irregularly shaped for decorated helical carbon nanofibers (HCNFs). Electrodes with a metal loading of 0.8 mg/cm^2 have been tested in a direct formic acid fuel cell. Both the Vulcan and the HCNF electrodes show similar and high power output of up to 120 mW/mg . They also show similar performances in deactivation experiments conducted at 200 mA/cm^2 even when using only high purity grade formic acid. After deactivation the electrodes show no structural damage, making them superior to most commercial catalysts. The electrodes can be completely regenerated to initial activity by simple treatment in water. The easy regeneration process indicates that CO-adsorption on the fuel cell anode catalyst is not the main poisoning mechanisms responsible for electrode degeneration.

Keywords: Direct formic acid fuel cells, Electrocatalysts, Nanoparticles, Palladium, Helical carbon nanofibers, Decoration.

1. Introduction

Fuel cells are undoubtedly the number one candidate for future clean energy due to the ability to convert a variety of fuels into electricity. One of the strengths of the fuel cell technology is its versatility making it adaptive for fuels ranging from the most commonly used hydrogen [1-3], methanol [4, 5], glucose [6], phosphoric acid [7] and formic acid [8-11]. For all these designs the principle of spatial separation of oxidation and reduction remains the same but yet the scientific and engineering challenges are very different. Such challenges include the hazards and

1 limitation of hydrogen storage [12], proper design of flow fields [13, 14], the water management
2 in the fuel cell membrane [15, 16] or a too fast deactivation of the catalyst material [9, 10, 17].

3 A specific class of fuel cells is based on proton exchange membranes (PEM) [8, 18, 19] which
4 solely conduct protons but not electrons or fuel and thereby achieve the spatial separation. Nafion
5 is the most prominent building block for PEMs. A PEM fuel cell performance depends mainly on
6 the membrane electrode assembly (MEA) encapsulated in between flow fields. Currently, noble
7 metals such as platinum (Pt) [20], palladium (Pd) [8] or Ruthenium (Ru) [21] are most frequently
8 used as catalysts[8, 22, 23] but also novel catalyst materials for oxygen reduction such as metal
9 free nitrogen doped carbons[24, 25] have attracted recent interest. To enhance the active surface
10 area and thereby lowering the loading of the precious noble metals, a common approach is to
11 decorate supports like Vulcan [26], carbon black [27], carbon nanotubes (CNTs) [4] or helical
12 carbon nanofibers (HCNFs) [8, 9] with nanoparticles which also improves the conduction
13 towards/from the electrodes. Key factors for a good performance of a MEA are high active
14 surface area of the catalyst, good conduction of the catalyst layer for both electrons and protons
15 and high diffusion rates of the fuel or the oxygen. Long term stability is an additional parameter
16 which needs to be addressed to make fuel cells practically useful. Fulfilling all these key factors
17 and simultaneously obtaining high catalytic activity and an easy preparation of the complete
18 MEA, including the catalyst, is challenging and therefore new approaches are of large interest. A
19 certain issue concerns the decoration of the catalyst support and the subsequent preparation of a
20 catalyst ink which can be either deposited on the electrode [8] or directly on the membrane [28].
21 Commonly the catalyst ink is prepared by mixing Nafion and the decorated catalyst support in
22 appropriate ratios and to apply the resulting ink by spraying or painting [23, 29, 30]. However
23 this method relies on an already prepared catalyst material which are obtained in a separate and

usually time consuming and complex process by for example the reduction of metal salts [8, 23]. Besides being time consuming, the processes also often lead to toxic waste products which need special handling. So far the only reported methods on the direct preparation of a catalyst support on the electrode are by electro-deposition [4] or by a combination of spray deposition followed by reduction [31].

With this report we present a low-cost, fast and very simple approach of directly combining the decoration of the catalyst support with the electrode preparation. The resulting procedure significantly facilitates the preparation process of the fuel cell MEA. To achieve this we use tris(dibenzylideneacetone)-dipalladium(0) ($\text{Pd}_2(\text{dba})_3$), a Pd zero charge organo-metallic complex. It has been shown earlier that the decoration of carbon support like C_{60} [32] or CNTs [33] is possible by boiling in toluene. We show that our approach results in well decorated supports, Vulcan and HCNFs, and that the electrode preparation requires a maximum of 30 min plus additional 2 h of annealing time, which effectively removes the dba ligands [32]. The choice of a zero charge organo-metallic complex ($\text{Pd}_2(\text{dba})_3$) is both a cheaper alternative compared to for example palladium acetate and concurrently makes the reduction step in classical impregnation methods obsolete. Altogether the practically solvent free process reduces the use of chemicals to a minimum and increases thereby cost efficiency and environmental compatibility. The electrodes show very high activities in a direct formic acid fuel cell (DFAFC). Formic acid is a very attractive fuel that can be produced solely from biomass, in some processes even as an “unwanted” waste product [34] and yet formic acid generates higher power density than methanol [35]. After deactivation of the catalyst no structural damage is detected by transmission electron microscopy (TEM) or X-ray diffraction (XRD), manifested also by that the initial activity easily can be restored by keeping the electrodes in water. Although our study focuses on the anodic

electrode of a DFAFC we foresee that the method is generally applicable for other type of fuel cell electrodes. Our method also opens up for direct electrode preparation using other organo-metallic complexes.

2. Method

2.1. Hydrophilization of the support

Two different supports were tested. Commercially available carbon black Vulcan (Cabot Corporation) and high quality HCNFs synthesized according to our recent report [36]. Prior to use the support was hydrophilized by sonication and boiling in hydrogen peroxide (H_2O_2) and nitric acid (HNO_3). 250 mg of support was mixed with 62.5 ml deionized water ($\text{H}_2\text{O}_{(\text{deio})}$) in a 500 ml glass beaker. Subsequently 62.5 ml HNO_3 (65 % Scharlau reagent grade) and 125 ml H_2O_2 (30 % Normapur VWR) was added and briefly hand-stirred. The mixture was ultrasonicated (60 W, USC300P V) for 7 min under occasional hand-stirring. The achieved dispersion was heated on a hotplate (VWR) until boiling. The functionalized support was separated and washed with $\text{H}_2\text{O}_{(\text{deio})}$ in a vacuum-filter setup on a PTFE (Omnipore, pore size 1 μm , Millipore). To remove residual H_2O from the product it was dried in vacuum at 100 °C for at least 30 min.

2.2. Combined decoration and electrode preparation

The schematic procedure is illustrated in Scheme 1. Functionalized support and $\text{Pd}_2(\text{dba})_3$ (Sigma-Aldrich) were mixed in a glass bottle to achieve a 20 wt% metal loading. To achieve a paintable ink 25 $\mu\text{l}/\text{mg}$ (support) of toluene was added. The mixture was sonicated for 15 min at 30 °C bath temperature. The ink was carefully applied layer by layer with a brush to a 5 cm^2 torray paper (Sigratec GDL 10 AA, Ion Power) on a hotplate at 60 °C until 20 mg of corresponding dry catalyst 20 wt.% metal loading was applied. The resulting electrode was

annealed for 2 h in air at 200 °C. The electrode was covered with Nafion dispersion 175 µl Nafion 5 wt.%, DE520, Ion Power Inc., 350 µl ethanol 99.5 % Kemetyl and H₂O_(deio) in a 1:1 volume ratio, corresponding to 30 wt.% by careful painting on a hotplate at 50 °C and dried for at least 30 min.

Standard commercial catalyst 60 wt.% Pt on Vulcan XC-72 (Premetek) was used as counter electrode. 42 mg 60 wt.%, Pt/Vulcan, 280 µl Nafion 5 wt.% and 700 µl ethanol were mixed by 30 min sonication. The ink was painted on torray paper (Sigratec GDL 10 AA, Ion Power) on a hotplate at 50 °C. TEM images were obtained on a JEOL 2100F high resolution TEM at 200 keV and Tecnai at 200 keV. Scanning electron microscopy (SEM) analysis was conducted on a Hitachi S-5500 In-lens high resolution FE-SEM. The metal loading of the anodic electrodes were checked by thermogravimetric analysis (TGA) of the ash after burning complete electrodes using a Mettler Toledo TGA/DSC 1 LF/948.

2.3. Cyclic voltammetry

The electrocatalytic activity tests of the prepared materials was performed on Autolab PGSTAT30 with a three-electrode cell at the room temperature. A Pt wire and a saturated calomel electrode were used as counter and reference electrodes, respectively. The catalyst layer was scratched of from the torray paper prior to coverage with Nafion. A glassy carbon electrode coated with the catalyst was used as working electrode. The preparation of the working electrode lists as follow: 1) the glassy carbon electrode was carefully polished with 0.05 m aluminum oxide paste on a polishing pad and then washed in acetone, ethanol and water under ultrasonication for 5 min, successively; 2) 4 µl Pd/Vulcan (or Pd-HCNFs) suspension mixed with dimethylformamid (DMF) (2 mg/mL) was dropped onto the upward surface of the glassy carbon electrode and dried

in room temperature; 3) 2 μ l of Nafion solution (0.5 wt%) was covered on the surface of the catalyst-modified glassy carbon electrode and dried in air without any heating process. 0.5 M phosphate buffer solution (pH 6.8) was used as the electrolyte solution during the electrochemical measurement. Prior to each measurement, the test solution was bubbled with argon for at least 30 min to remove the dissolved oxygen of the electrolyte solution.

2.4. Fuel cell tests

DFAFC test were conducted in a 5 cm² quickCONNECT cell fixture from Quintech with carbon serpentine flowfields at 30 °C cell and fuel temperature. The cathodic side with the Pt based electrode was fed 1 l/min dry O₂. Two different, Vulcan and HCNFs, anodic Pd based electrodes were tested at a flow of 0.7 ml/min + 0.7 ml/minA 3 M aqueous formic acid (Formic acid $\geq$ 98 %, puris analysis (p.a.), Sigma Aldrich) solution distributed by a peristaltic pump. Output voltage as function of applied current was measured. Based on these results deactivation test were conducted at constant current of 1000 mA corresponding to 200 mA/cm² or 250 mA/mg(Pd) and a flow of 0.7 ml/min + 0.7 ml/minA 3 M aqueous formic acid and 1 l/min dry O₂.

3. Results

3.1. Transmission electron microscopy

Transmission electron microscopy (TEM) images of the resulting structures are shown in Fig. 1 for Vulcan and HCNFs. As shown in Fig 1c and f the particles are highly crystalline, but contain some twinning for the NPs on HCNFs. On neither support the NPs show any signs of thick oxide layers or amorphous carbon coverage. The particles are highly crystalline revealed by a clear selected area electron diffraction pattern (an example SAED is shown in supporting information Fig. 1 †). The absence of amorphous carbon or other covering layers manifest that the annealing

step after the painting process effectively removes the dba ligands, leaving only fresh metallic Pd particles. The effective removal of dba ligands at 200 °C has been shown in [32] and proven by XRD, Raman and TGA. Despite the fast and direct decoration process which does not involve any sonication or boiling, the distribution of the NPs are surprisingly good. The homogeneity is better for Vulcan in the sense that the overall particles are smaller and the diameter range is narrower. For Vulcan most particles are spherical, while they are irregularly ellipsoid-like shaped for HCNFs. The size (averaged of 100 individual particles for each support) for HCNFs measured over the long axis is 13.6 ± 4.1 nm. The spherical diameter for Vulcan 5.4 ± 1.0 nm. By the analysis of TEM images we cannot find any significant difference in particle size between used and fresh samples. It is not entirely clear if the elliptic particles for HCNFs result from an agglomeration of individual NPs or if they are crystallized like this, but the cauliflower-like appearance particularly clear in the SEM image (Fig. 2c) point in the direction of agglomerated particles. The smaller size of the NPs on the Vulcan support is most likely explained by a larger number of negatively charged functional groups compared to the HCNF support. This is supported by that the pH value of Vulcan in aqueous dispersions is between 4-5, whereas it is around 5-6 for the HCNF support. The larger number of functional groups provide more attachment sites for Pd crystal seeds and correspondingly smaller and more numerous NPs. Another reason might originate from the better dispersability of Vulcan compared to HCNFs which leads to a better integration of the NP-solution with the Vulcan support.

3.2. Scanning electron microscopy

The scanning electron microscopy images shown in Fig. 2 reveal that our approach results in well-defined and uniform catalyst films of about 30 μm on the torray paper for both the Vulcan and the HCNF. The HCNFs based electrode films are generally rougher than for Vulcan. We

1 explain this with the structural difference in the two support types, HCNFs being long wire-like
2 and Vulcan being round ball like. Investigating the electrode catalyst films before and after use
3 reveals no difference. Neither does the appearance of the catalyst support assembly change after
4 deactivation indicating that catalyst migration or catalyst leakage is negligible (see supporting
5 information Fig. 2 and 3 †).

6 3.3. X-ray diffraction

7 The x-ray diffraction spectra in Fig. 3 confirm the high crystallinity of the nanoparticles. The
8 main features result from the (111) and (002) reflection of a pure Pd fcc crystal, which give
9 reflections at $2\theta = 39.9^\circ$, and 46.4° respectively. A small contribution of a PdC phase is
10 represented by a weak downshifted shoulder on the (111) Pd peak, resulting from an expansion of
11 the lattice in the case of PdC. We note however that a peak at similar position also appears for
12 pure torray paper. Possible contributions of a PdO are below the detection limit. All other
13 features result from the torray paper. The lower limit of the grain sizes of Pd nanoparticles for
14 HCNF and Vulcan is 16 and 13 nm respectively for the fresh electrodes and 18.5 and 16.5 nm for
15 the used electrodes, which agrees well with the TEM analysis of the Pd- NPs on the HCNFs but
16 is slightly larger than the values derived for the Vulcan support. It should be noted that since
17 larger particles give a strong contribution to the intensity, the XRD provides a volume-averaged
18 value and tend to overestimate the particle diameter [37, 38]. The discrepancy for the particle size
19 deduced from HRTEM and XRD might originate from some few larger NPs embedded in the
20 torray paper. We believe that these larger particles are not well attached on the carbon support
21 and therefore not detectable by TEM/HRTEM due to the TEM grid preparation. However, when
22 dispersing whole pieces of electrode including carbon paper, it is possible to find large particles
23 of about 10-20 nm also by TEM (see supporting information Fig 4). They are also not likely to

contribute much to the catalytic performance of the fuel cell catalyst. The XRD pattern of the Pd-NPs on the Vulcan support shows a weak but still slight decrease in the FWHM of the (111) peak after fuel cell tests compared to the freshly prepared sample, assigned to some agglomeration of smaller particles.

3.4. Cyclic Voltammetry and fuel cell tests

In order to investigate the electrocatalytic performance of the as-produced Pd-HCNFs towards formic acid oxidation, a series of cyclic voltammetry (CV) measurements have been carried out in N₂-saturated phosphate buffer solution (PBS). Fig. 4a shows the blank CV for the N₂ saturated PBS. Three distinct features can be identified. The peak around -0.3 V and the broad feature above 0.5 V can be attributed to adsorption/desorption of hydrogen and oxygen, respectively. The reduction peak of Pd oxide can be found at 0.12 V and 0.14 V for Vulcan and HCNFs, respectively. From the reduction peak area of Pd oxide and the loading measured by TGA, the electrochemical active surface area of Pd-HCNFs can be calculated to 3.76 m²·g⁻¹(Pd), which is just about 55.4% of the electrochemical active area for the conventional catalyst Pd-Vulcan (6.79 m²·g⁻¹(Pd)). This is rationalized by the larger size of the Pd-NPs on HCNFs compared to the Vulcan based catalyst, in agreement with the TEM results. The catalytic performance of Pd-HCNFs and Pd-Vulcan catalyst towards formic acid oxidation is shown in Fig.4b. The predominant oxidation peak of formic acid on Pd between -0.3 to 0.2 V covers all weaker peaks originating from hydrogen adsorption/desorption or Pd oxide reduction. The oxidation potential is upshifted for the HCNF support. The current density resulting from formic acid oxidation on Pd-HCNFs is about 504 mA·cm²·mg⁻¹(Pd) which is about 78 % of the current density of the Vulcan catalyst (647 mA·cm²·mg⁻¹Pd). However, taking the significantly lower electroactive area for the Pd-HCNFs into account indicates that the catalytic process proceeds more efficiently on

the HCNF support, ascribed to the 3D helical structure of HCNFs, which might result in faster and more efficient electron transfer processes relative to the Vulcan carbon material, in line with earlier reports [39].

The metal loading of 0.8 mg/cm^2 on both electrodes was confirmed by TGA. The activities are comparable to tests of commercial 20 wt.% on Vulcan under similar conditions [10]. Also, although the catalytically active area derived from the blank CV measurements is twice as large for Pd-Vulcan than for the Pd-HCNFs, originating from the smaller Pd-NP size, the catalytic activity is higher for HCNF as shown in Fig. 4. It has been shown in several reports [40, 41] that irregularly shaped particles can have higher catalytic activity than spherical ones. However, compared to the here presented method the synthesis in these approaches are highly complex and time consuming. We believe that i) the irregularly shaped particles with many edges which improve the catalytic activity, ii) the good conductivity originating from the wire-like character of HCNFs, and iii) the more porous film morphology for HCNFs (Fig 2 a-b) leading to better diffusion channels altogether overcompensates the effect of a lower electroactive area. Deactivation tests shown in Fig. 6 furthermore reveal that the Vulcan and HCNF based assemblies deactivate at similar rates. At a constant current of 1000 mA or 250 mA/mg(Pd) giving maximum power output, the cells deactivated over approximately 1 h for both HCNFs and Vulcan. In a similar study [10] with a Pd loading of 0.5 mg/cm^2 the cell deactivated with p.a. grade formic acid within less than 300 sec at 84 mA/mg(Pd). It should however be noted that this study was conducted at room temperature. The results in our study are well comparable to studies using commercial catalysts or with by far more complicated catalyst preparations. A summary of the comparison is found in table 1. Also, we note that, the initial activity of the catalysts can be completely restored by simply washing the electrodes for 1 h with water without any applied

potential similar to the observations made by Zhou et al. [11]. This strongly indicates that the deactivation occurs by adsorbed substances only loosely bond to the Pd surface and not by adsorption of CO [11]. The easy regeneration by water purging supports that the deactivation occurs only by the agglomeration of CO₂ bubbles in the anode catalyst layer as suggested by Mikołajczuk et al. [10]. Fig. 5 and 6 shows the power outputs, and the deactivation curves for catalyst samples before a deactivation run (continuous line) and in a second deactivation run (dotted line) after a one hour washing procedure. The performance is very similar, indicating that the deactivation is purely induced by impurities in the fuel, and do not result from catalyst leakage or catalyst agglomeration. This is supported by that we do not observe any structural change for neither support by TEM or SEM. Although commercial catalysts can show slightly better performance than the catalyst prepared by our approach tests show that commercial catalyst exhibit strong structural damage after use [9]. Altogether, this makes our synthesis highly advantageous over earlier reported methods.

4. Conclusion

We have presented a low-cost, easy and very fast approach for the preparation of poison resistant fuel cell electrodes based on a one-step ink-painting process. The prepared catalysts have excellent electrocatalytic properties for DFAFCs explained by well dispersed, ligand free decorated Pd nanoparticles. The structural stability of both Vulcan and HCNF based catalysts is outstanding, and the HCNF based catalysts shows a slightly higher activity compared to Vulcan. Complete deactivation of the electrodes does not result in any structural damage and can be completely reversed by simple water treatment indicating a deactivation mechanism which is not caused by CO adsorption but rather by CO₂ bubbles or weakly adsorbed poisons. Our presented method is environmentally friendly, cost efficient, and highly suitable for industrial upscaling.

Studies to improve the performance and to understand the underlying deactivation mechanisms are necessary to evaluate the full potential of the method, but we note that the method is not only applicable for DFAFC but for all MEA based fuel cells also with different organo-metallics.

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1 **Figure captions:**

2 **Scheme 1** *Illustration of the decoration and electrode preparation method.*

3 **Fig. 1** *Transmission electron microscopy images of Pd nano particle decorated HCNFs (a-c) and*
4 *Vulcan (d-f).*

5 **Fig. 2** *Cross-section scanning electron microscopy images of the prepared electrodes a) HCNFs,*
6 *b) Vulcan. c) SEM image of irregular shape particles with edges and twinning on HCNFs.*

7 **Fig. 3** *X-ray diffraction pattern of a) Vulcan and b) helical fiber based electrodes. The lower*
8 *black are recorded on unused, the upper red on electrodes after deactivation. # identifies some*
9 *strong peaks originating from the background including the torray paper.*

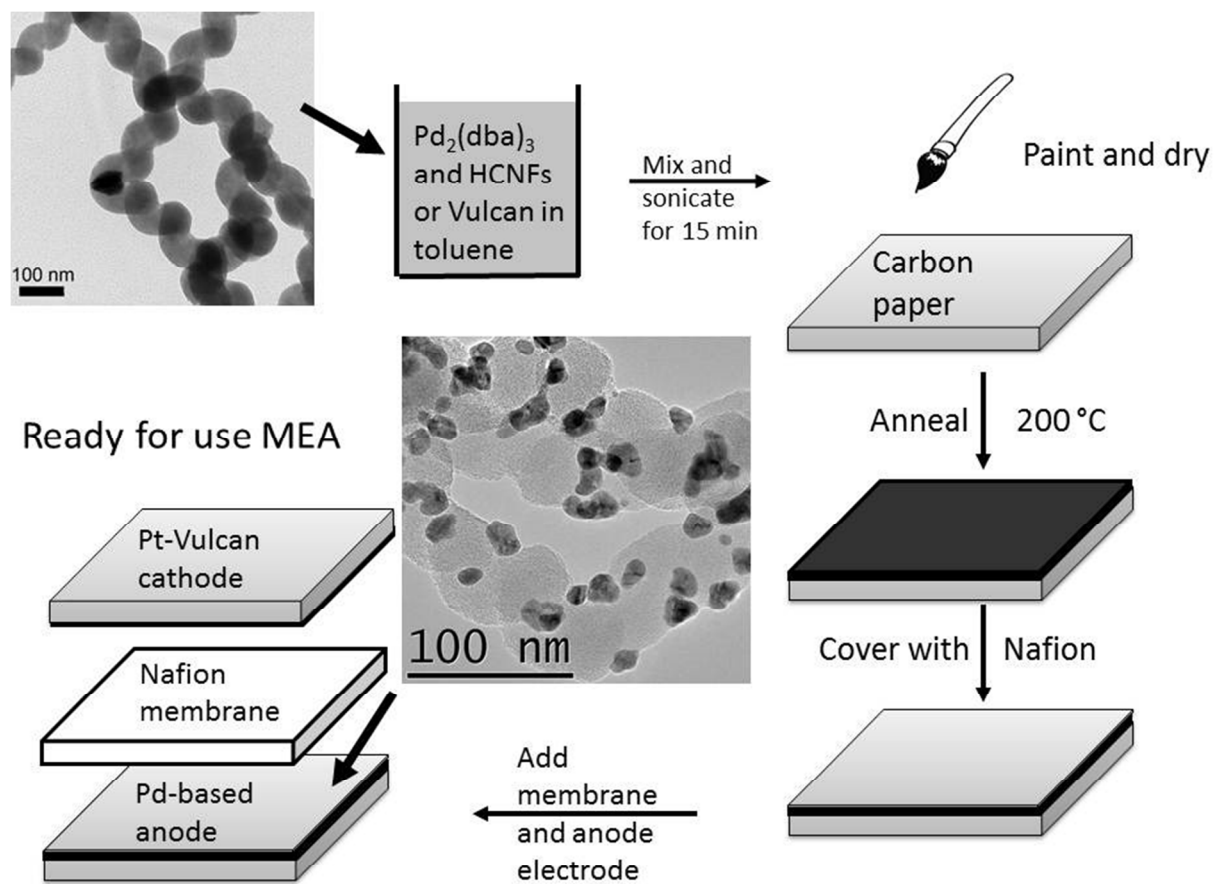
10 **Fig. 4** *a) Cyclic voltammetry curves of Pd-Vulcan (black line) and Pd-HCNFs (red line) before*
11 *(a) and after (b) adding 3 M formic acid. Electrolyte: 0.5 M PBS, scan rate: 0.05 V/s.*

12 **Fig. 5** *a) Power output and b) polarization curve of Pd decorated Vulcan and HCNFs in a direct*
13 *formic acid fuel cell. Black circles and red squares symbolize Vulcan and HCNFs, respectively.*
14 *Continuous and dotted lines represent the electrode before respectively after a complete*
15 *deactivation and regeneration by water purging.*

16 **Fig. 6** *Deactivation of prepared electrodes at 1000 mA. Black circles and red squares symbolize*
17 *Vulcan and HCNFs, respectively. Continuous and dotted lines represent the first respectively the*
18 *second deactivation.*

19 *Table 1: Comparison to other studies using different preparation methods for the catalyst.*

20 **Scheme 1**

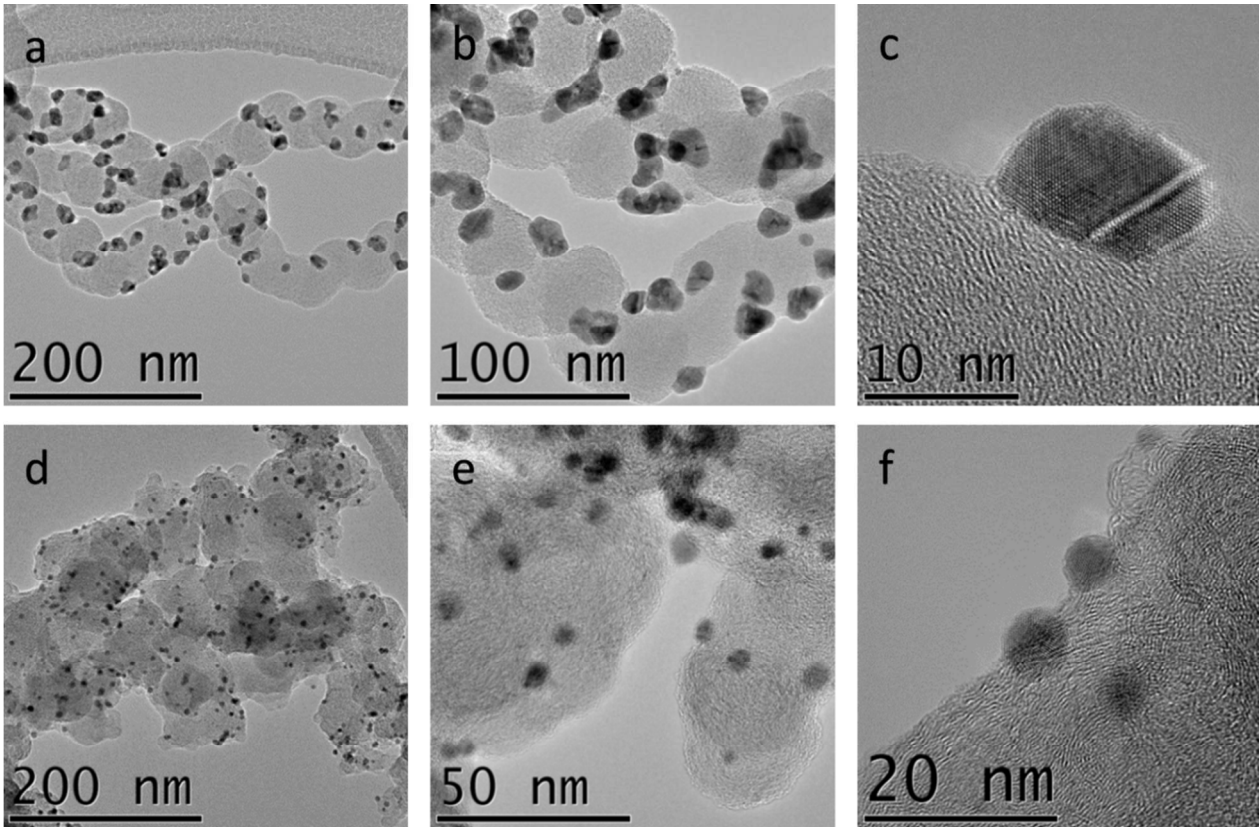


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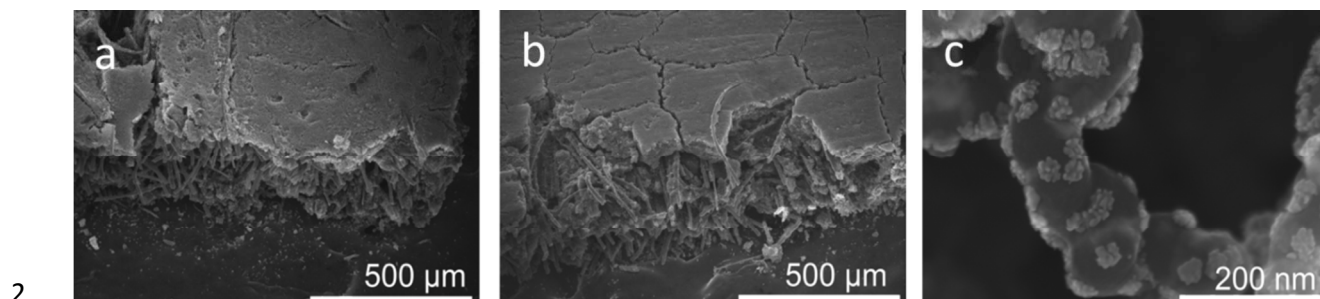
1 **Figure 1**



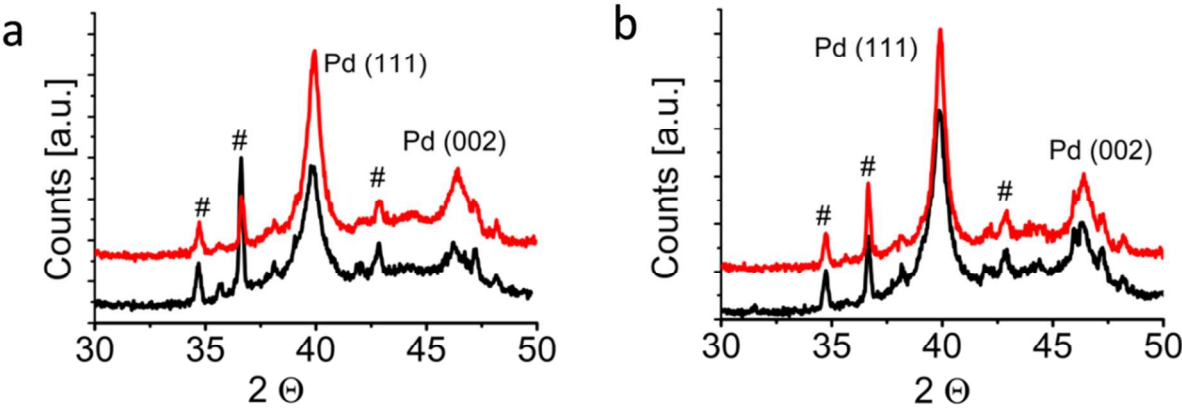
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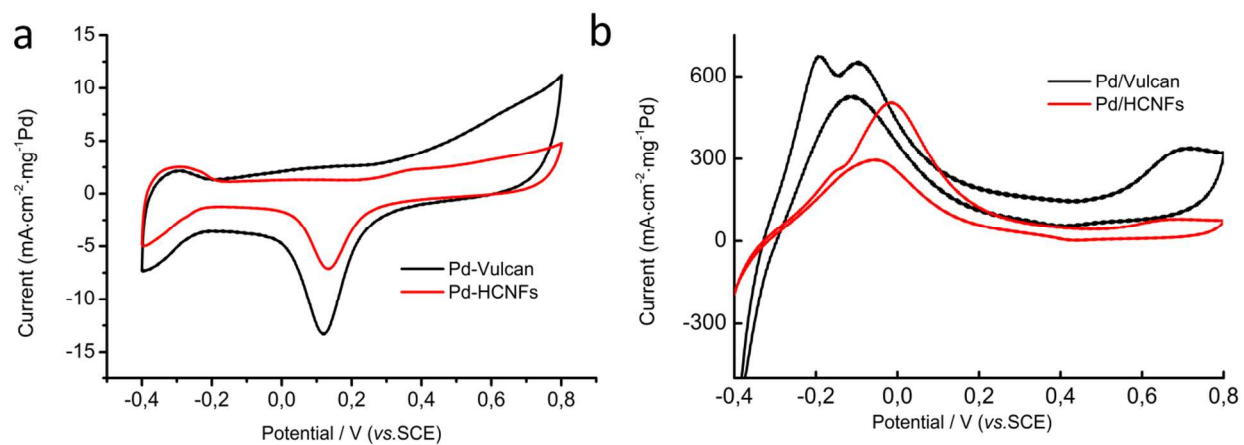
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1 **Figure 2**

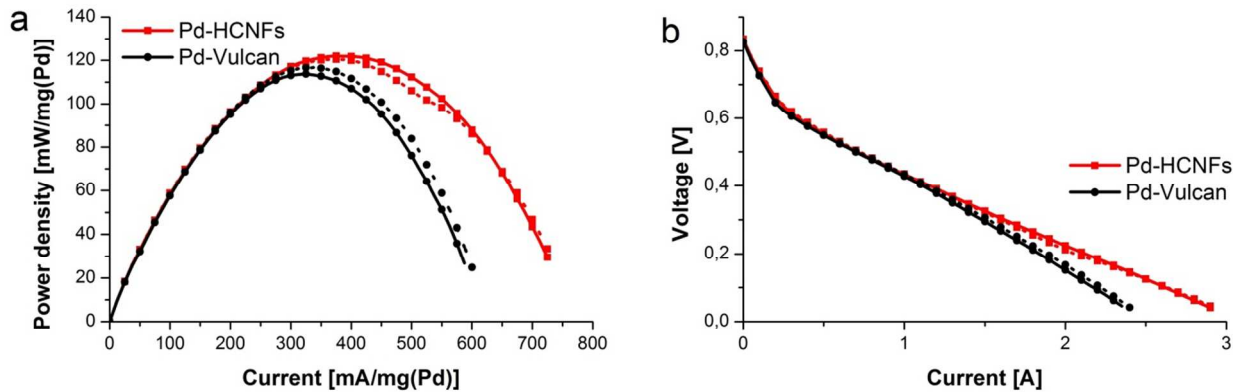


1 **Figure 3**

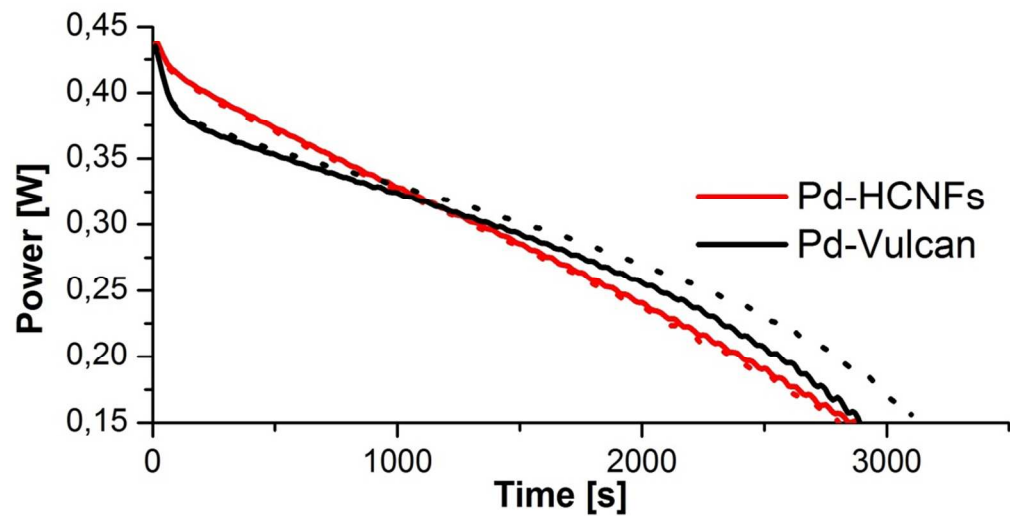


1 **Figure 4**

1 **Figure 5**



3 **Figure 6**



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2

Table 1

Method and support	Current CV	Power DFAFC [mW/mg(Pd)]	Particle size [nm]	Loading [wt%]
Polyol HCNFs [8]	300 mA mg(Pd) ⁻¹	62	15	18.6
Polyol MWCNTs [8]	130 mA mg(Pd) ⁻¹	42	-	28.4
Benzyl mercaptan HCNFs [9]	30 mA cm ⁻²	120	4.9	19
Commercial 20 wt% Pd/C [9]	15 mA cm ⁻²	125	5.7	21.5
This study HCNFs	500 mA cm ⁻² mg(Pd) ⁻¹	120	13.6/16 TEM/XRD	20*
This study Vulcan	650 mA cm ⁻² mg(Pd) ⁻¹	115	5.4/13 TEM/XRD	20*
Pd Carbon Medicinulis [10]	-	77	2.7/11 (2 size ranges)	10
Commercial 20 wt% Pd/C [10]	-	58	3.4	20

The table of contents entry:

Ready to use membrane electrode assembly are easily prepared by mixing and sonication of the chosen support in toluene with $\text{Pd}_2(\text{dba})_3$, painting of the resulting ink, followed by annealing at 200 °C. The method results in nicely decorated supports and the prepared electrodes show high potential in direct formic acid fuel cell.

Keywords: Fuel cell, electrode preparation, decoration, DFAFC, palladium.

