Ultrasonic-supported spraying process for coating of gas diffusion electrodes

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Introduction

High and low temperature fuel cells are planned to be used in a foreseeable future as energy converter for stationary and automotive applications. In the case of the middle temperature PEMFC, however, more robust systems and especially, more stable polymer membranes than pure PBI-based ones, which are still sensitive to water presence and phosphoric acid leaching that are able to work at 100-150°C are needed. This project aims together with nine other German institutes at the development of middle-temperature H_2 and methanol PEMFC. One of the working package focus on the development of highly reproducible coating process of Gas Diffusion Electrodes (GDE) for Direct Methanol Fuel Cell (DMFC) applications.

Catalyst material for the reaction layer

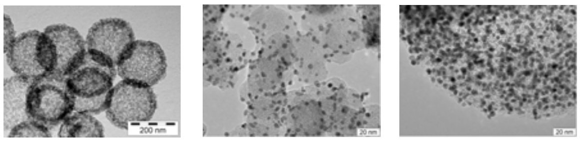


Fig. 1: TEM images of Hollow Graphitic Spheres (HGS), Pt-Vulcan & Pt-HGS

Hollow graphitic spheres were synthesized in MPI Mülheim. The average diameter was about 200 nm in comparison to 30-50 nm for carbon Vulcan; nice Pt distribution on C.

Ultrasonic-supported spraying technique

1) Ink formulation: 20-40wt% Pt/C + 10wt% Nafion +20wt% PTFE in H_2O/Isopropanol (1:1), see table on the bottom
2) Coating parameters; p=2psi, f=100Hz, d=10 mm, v=7cms^{-1} & T=50°C
3) 20-30 spraying steps on Gas Diffusion Layer until catalyst loading (2 - 4 mgcm^{-2}) is reached
4) Sintering of GDE for 1 h @ 80°C

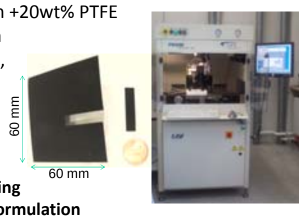
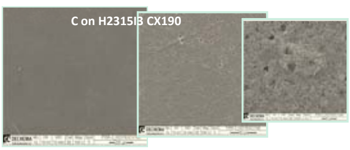


Fig. 2: Typical (left) GDE after catalyst spray coating with Prism 450 machine (USI) and (bottom) ink formulation

Catalyst + support	5wt% Nafion / Nafion	30wt% PTFE / PTFE	H_2O	2-Prop.	Ink	Solid material
0.5 g	1 g / 0,05 g	0,335g / 0,1 g	10 g	10 g	21,8 g	0,65 g
2,2%	4,6 % / 0,23%	1,5% /0,46%	45,9%	45,9%	100%	3%

SEM images of different GDE

Determination of layer thickness as well as quality of coating, especially regarding cracks, was investigated by SEM technique.



↑**Fig. 3: SEM images of same GDL with MPL at different magnitudes**

GDEs	MEAs	Pt-Beladung cm^2	Kat-Träger	Schichtdicke / ohne GDL µm
22	5	1,6	HGS	360 / 160
30	6	1,6	Vulcan	320 / 120
46	14	2	HGS	560 / 360
48	15	2	Vulcan	464 / 264
34	20	3,3	HGS	780 / 580
42	10	3,3	Vulcan	560 / 360
58	17	2	$HGS_{850°}$	400 / 200
H2315I3CX190	Kathode	MPL	unbekannt	200 (MPL: 40)

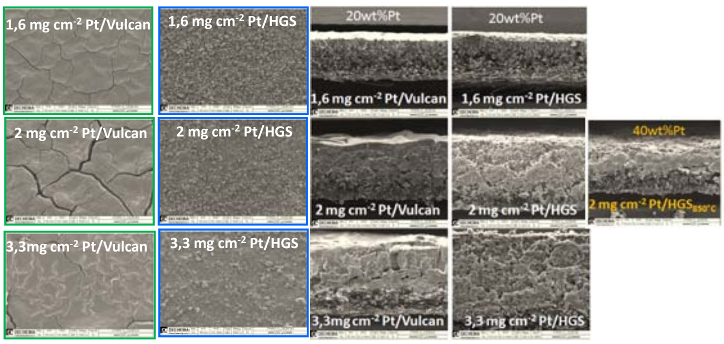
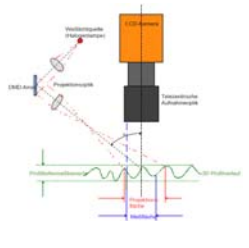


Fig. 4: SEM images of (left) surface & (right) cross-section of different GDE (see table)

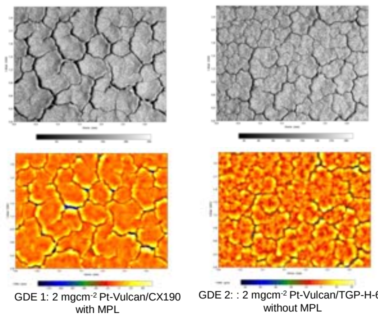
- Very uniform microporous layer (MPL) with 1-3µm holes.
- Fresh-coated HGS-based layers are 35-60% thicker than Vulcan-based ones.
- Numerous agglomerated clusters on HGS-based GDE surface.
- A 45% decrease in layer thickness from 360 down to 200 µm was reached by using 40wt% instead 20wt% Pt/HGS.
- More cracks are visible on Vulcan-based GDE surface.

Roughness evaluation by “Lichtstreifen” spectroscopy

The “Lichtstreifen” spectroscopy allow a contactless roughness evaluation of sample with a max. surface of 14x11cm (see fig. 5).



Dateiname	Ra	Rz	Wt
Einheit	(µm)	(µm)	(µm)
14x11 gde1.omc	15	99	20
14x11 gde2.omc	10	66	23
50x38 gde1.omc	8	42	23
50x38 gde2.omc	5	24	20
4x3 gde1.omc	8	63	40
4x3 gde2.omc	4	22	14



$$Ra = \frac{1}{lr}\int_0^{lr} |Z(x)|\,dx \qquad Rz = 1/n \sum_{i=1}^{n} Rz_i$$

Fig. 5: Images of different 4x3 cm Pt/Vulcan-based reaction layers on different GDL

- Higher roughness measured at GDE with MPL compared to that without MPL

Fuel Cell characterization

Results obtained in the 5 cm² DMFC @ 110°C/2bar are summarized in following table:

MEAs/Kathode-Kat.Träger	Pt-Beladung / mg_{Pt} cm^{-2}		P_{max} / mW cm^{-2}	
	Anode	Kathode	Sauerstoff	Luft
MEA5/HGS	2 (37,5wt%)	1.6 (30wt%)	223	110
MEA6/Vulcan	2 (37,5wt%)	1.6 (30wt%)	200	105
MEA14/HGS	2 (37,5wt%)	2.0 (30wt%)	200	110
MEA15/Vulcan	2 (37,5wt%)	2.0 (30wt%)	220	120
MEA20/HGS	2 (37,5wt%)	3.3 (30wt%)	160	100
MEA10/Vulcan	2 (37,5wt%)	3.3 (30wt%)	250	179
MEA17/ $HGS_{850°C}$	2* (50wt%)	2.0 (40wt%)	310	160
MEA16 /Vulcan	2* (50wt%)	2.0 (30wt%)	290	140

* MEA mit PtRu-HiSpec12100 als Anoden-Katalysator

- Obvious enhancement of MEA performance by increasing Pt concentration on carbon support up to 50% and 40% at the anode and cathode, respectively.
- Very promising performance of MEA17 with 850°C-treated HGS as catalyst support.

TEM images of cross-sectioned MEA

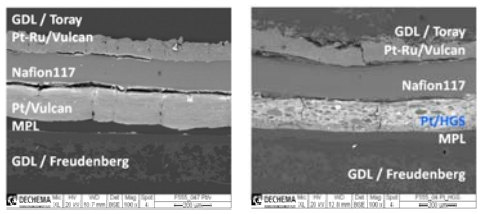


Fig. 6: TEM images of (left) MEA10 and (right) MEA9 with 3.3 mg_{Pt} cm^{-2} on Vulcan & HGS, respectively , as cathode catalyst

- Surprisingly, similar thickness of about 200 µm was measured for 3.3 mgcm^{-2} Pt/HGS and Pt/Vulcan cathode layers probably caused by compression effect.
- The thickness of the 2mg_{Pt} cm^{-2} PtRu/Vulcan layer and MPL is about 100 and 50 µm, respectively.
- HGS distribution in reaction layer is inhomogeneous: This may explain transport limitation of air & H_2O in MPL and reaction layer at high current densities.

Summary & Acknowledgements

- Ultrasonic-supported spraying is a powerful technique to get highly reproducible porous reaction and diffusion layers for DMFC application with very few loss of active material.
- Further efforts have to be done in order to reduce solvent content in the ink, optimize dispersion of special material such as HGS and minimize crack formation.

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