Effect of hollow graphitized spheres supported Pt cathode catalyst on MEA performance in a Middle Temperature DMFC

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Funded by: BMWi via AiF

Period: 01.06.2010 – 28.02.2013

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ALLIANZ INDUSTRIE FORSCHUNG

Gefördert durch:

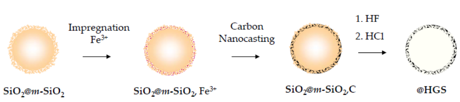
Bundesministerium für Wirtschaft und Technologie

Introduction & Motivation

In recent years, effort has been made in order to develop a middle temperature (100-150 C) PEM fuel cell. Therefore, more corrosion-resistant catalyst supports with mesoporous surface are needed as substitution material i.e. for Vulcan XC72R. In the framework of a research cluster project, Hollow Graphitized Spheres (HGS) material has been synthesized by the group of Prof. Schüth at MPI-Mülheim Germany (see fig. 1). This has an excellent corrosion resistance and is supposed to slow down agglomeration and depletion of Pt particles. The work investigates the influence of the HGS versus Vulcan as cathode material on the performance of the MEA in a 5 cm² laboratory direct methanol fuel cell (DMFC).

Experimental description of HGS & MEA preparation

HGS:



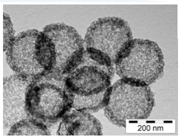


Fig. 1: (MPI Mülheim) HGS

Pt and Pt-Ru catalyst: $Pt_{50}Ru_{50}$ and Pt-catalysts were prepared by impregnation of H_2PtCl_6 and $RuCl_3$ in H_2O/CH_2O and CH_2O, respectively at 80°C on carbon support. Pt particle size is in the range of 4.5 and 4.1 +/- 1nm for Pt/HGS and Pt/Vulcan, respectively.
Anode & Cathode: Pt-Ru/Vulcan, Pt/HGS or Pt/Vulcan catalyst was mixed in water/isopropanol with 10%wt Nafion and 20%wt PTFE. The catalyst ink was sprayed with PRISM 450 (USI) device either on Toray TGP-H-60 or Freudenberg-CH2315CX190 with a microporous layer (MPL), respectively.
MEA: The anode and cathode gas diffusion electrodes were coated with 1mgcm^{-2} Nafion suspension before hot pressing at 130°C and 7bar with the Nafion117 membrane.
ADT: Accelerated Degradation Tests (ADT) were carried out at the air electrode by means of cyclic voltammetry at 80°C in N_2 (400 ml min^{-1}) whereas PtRu/Vulcan was flooded with H_2 (200 ml min^{-1}). The scan rate was 100 mV/s.
MeOH permeation: The cell was polarized in the electrolysis mode by using linear sweep voltammetry technique at 5mV/s. PtRu and Pt electrode was fed with 1 M MeOH and N_2, respectively.

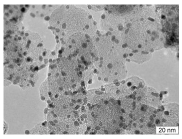


Fig. 2: Pt/vulcan

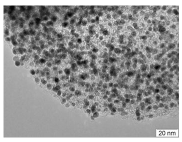


Fig. 3: Pt/HGS

Results

MEA composition & current-voltage curves of the MEAs

Anode: 2 mg $_{Pt}$ cm^{-2} (35%wt) Pt-Ru/Vulcan
Membrane: Nafion117
MEA-5: Cathode: **1,6** mg$_{Pt}$ cm^{-2} **Pt/HGS**
MEA-6: Cathode: **1,6** mg$_{Pt}$ cm^{-2} **Pt/Vulcan**
MEA-9: Cathode: **3,3** mg$_{Pt}$ cm^{-2} **Pt/HGS**
MEA-10: Cathode: **3,3** mg$_{Pt}$ cm^{-2} **Pt/Vulcan**
MEA-14: Cathode: **2** mg$_{Pt}$ cm^{-2} **Pt/HGS**
MEA-15: Cathode: **2** mg$_{Pt}$ cm^{-2} **Pt/Vulcan**
all 30%wt

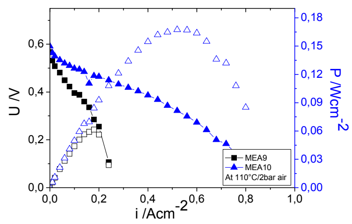
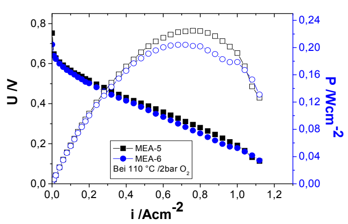


Fig. 4: MEA9 & MEA10 at 110 C/2bar with air



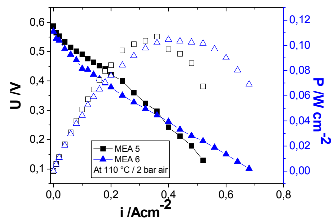
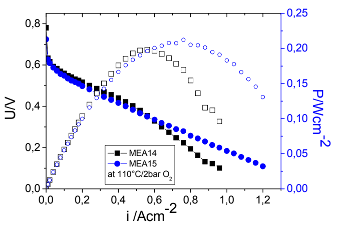


Fig. 5: MEA5 & MEA6 at 110 C/2bar (left) with oxygen and (right) with air



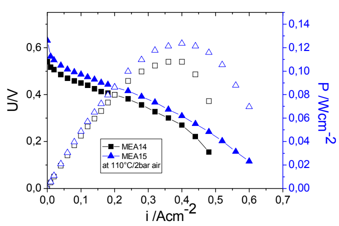


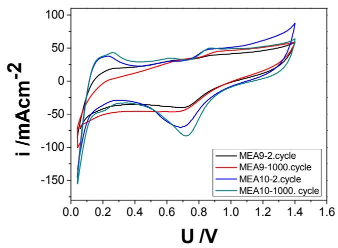
Fig. 6: MEA14 & MEA15 at 110°C/2bar (left) with oxygen and (right) with air

Table 1: Summary of max. measured power densities in DMFC at 110 C/2bar with O_2 and air

MEA/Support	Cathode cat. loading / mg $_{Pt}$ cm^{-2}	Oxygen / mW cm^{-2}	Air / mW cm^{-2}
MEA5/HGS	1.6	223	110
MEA6/Vulcan		200	105
MEA14 /HGS	2	200	110
MEA15/Vulcan		220	120
MEA9/HGS	3.3	-	55
MEA10/Vulcan		250	178

- MEA with low HGS-supported Pt catalyst loading exhibits higher performances compared to that of Pt/Vulcan
- At higher Pt loading than 2mg cm^{-2}, mass transport limitation in MEA with HGS-containing cathode is obvious.

ADT and methanol permeation tests



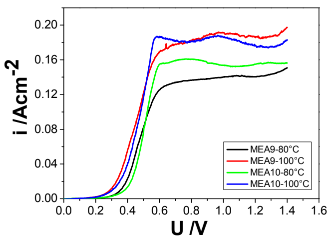


Fig. 7: (left) ADT and (right) methanol permeation experiments at MEA9 & 10

- No visible H_2 region for the HGS-supported Pt catalyst.
- Increase of H_2 ads./des. peak area after ADT in the case of MEA with Vulcan supported cathode catalyst!
- Methanol permeation increases with cell temperature.

SEM images of cross-sectioned MEA9 & 10

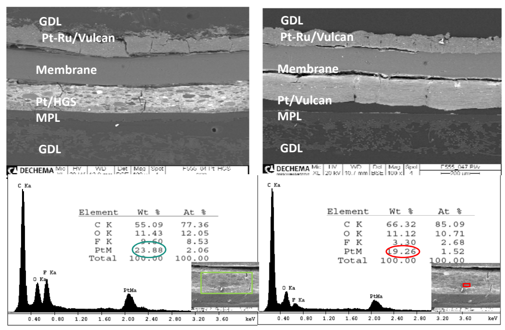


Fig. 7: Cross-sectional SEM images of (left) MEA9 and (right) MEA10 . Additional area and spot EDX spectra of MEA9 are presented below

- Similar thickness of about 200 µm was measured for 3.3 mgcm^{-2} Pt/HGS and Pt/Vulcan cathodes; The thickness of the 2mg$_{Pt}$ cm^{-2} PtRu layer and MPL is about 100 and 50 µm, respectively.
- Distribution of particles in HGS reaction layer is inhomogeneous: This could explain the lower performance during DMFC test in comparison to the MEA with the Vulcan-based cathode.
- The EDX spectra show an almost uniform Pt distribution throughout the reaction layer.

Conclusion

- A maximal power density of 178 mWcm^{-2} was achieved with a 3.3 mgcm^{-2} Vulcan-supported Pt cathode (MEA10) at 110 C and 2 bar.
- Better cell performances with HGS-based cathode was observed only for “low” catalyst loading of 1.6 mg$_{Pt}$ cm^{-2} (MEA5).
- At higher catalyst loading, MEA with Vulcan-based cathodes exhibit higher power densities.
- Inhomogeneous HGS-based catalyst layer observed by SEM could explain their relative low performances in the DMFC cell.
- Spraying procedure for HGS-based inks has to be improved
- No higher stability for HGS-based electrodes observed during ADT: Pt particle size has probably to be better fitted to mesoporous surface of HGS.
- ADT should be optimized for electrodes with catalyst loading > 2 mg$_{Pt}$ cm^{-2}.

We thank BMWi for financial support, project partners for excellent cooperation and our mechanical workshop for the technical support.