

Effect of carbon support on corrosion resistance of Pt-based GDE for MT-DMFC

M. Sakthivel, J.-F. Drillet
 e-mail: sakthivel@dechema.de
 Funded by: BMWi via AiF
 Period: 01.12.2013 - 31.05.2016

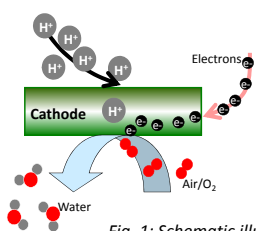


Introduction

The direct methanol fuel cell (DMFC) is a promising technology for energy supply for portable and stationary applications due to high energy density of methanol, compact design, easy fuel handling and storage. However, poor activity of Pt for methanol oxidation, methanol crossover that results on fuel loss and mixed potential formation at the cathode and low corrosion resistance of Pt/C at high cathodic voltage are technical challenges to overcome [1]. The long-term efficiency of the electrodes is strongly influenced by the nature of the catalyst support that should allow optimal distribution and stabilization of the catalyst nanoparticles, anchorage of functional groups and facile mass transport of reactants and products. It is also meanwhile well-known that mesoporous carbon is a well-adapted surface for hosting nanoparticles [2]. This work aims at the development of highly active, methanol-tolerant and corrosion-resistant catalyst for the middle-temperature (120-150°C) DMFC cathode. First results about preliminary screening of several as-prepared and commercial available carbon/graphite-supported 40wt% Pt catalysts regarding their activity for oxygen reduction reaction (ORR) and stability (accelerated degradation test) under half-cell conditions are presented.

[1] C. Lamy et al., Wiley-VCH, 257 (2009).
 [2] C. Galeano et al., J. Am. Chem. Soc. 134, 20457-20465, (2012).

Oxygen Reduction Reaction (ORR)



A suitable fuel cell catalyst should favor the “four-electron” reduction step of oxygen shown in (1) and not the “two-electron” reaction pathways (2) & (3) where H_2O_2 intermediate is involved.

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (E^0 = 1.229 \text{ V}) \quad (1)$$

$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 \quad (E^0 = 0.695 \text{ V}) \quad (2)$$

$$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (E^0 = 1.77 \text{ V}) \quad (3)$$

Fig. 1: Schematic illustration of oxygen reduction reaction (ORR) at Pt

Synthesis of 40 wt% Pt/C catalyst



The synthesis of 40wt% Pt was carried out on three commercially available carbon supports by formaldehyde reduction at 80°C for 1h under reflux condition. Based on relevant properties such as high surface area, porous structure and degree of graphitization, following products have been selected: carbon (Vulcan, 250 m²/g, Cabot corp.), ordered mesoporous carbon (OMC, 1000 m²/g, ACS Materials) and graphitized nanopowder (GNP500, 500 nm, 100 m²/g, Sigma Aldrich). The reaction products were washed with de-ionized water and filtered by using a 0.45 μm polycarbonate membrane, and finally dried for 4 h at 80°C and 50 mbar.

Fig. 2: Setup used for catalyst synthesis

Preparation of gas diffusion electrode (GDE)

Typical GDE fabrication was carried out as follows: first 100 mg catalyst/support, 20wt% PTFE and 10wt% Nafion were suspended in a H_2O + isopropanol (Carl Roth) solvent mixture, stirred for 30 min and then sprayed with a ultrasonic-supported coating machine (USI prism-450) onto either a microporous layer covered (equipped) gas diffusion layer (Freudenberg- H2315 IX91) for the cathode or onto a blank carbon paper (Toray-TGP-H-60) for the anode until reaching the desired catalyst loading value. Finally, as-coated GDE were sintered in an oven at 80°C for 1 hour.

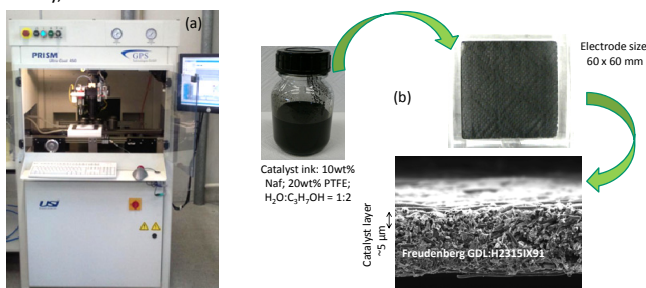


Fig. 3: GDE fabrication: (a) ultrasonic-assisted spray coating machine and (b) steps sequence from catalyst suspension to coated GDE (SEM image).

GDE cell setup

All electrochemical experiments were performed in an in-house made plexiglas® cell assembly (Fig4). Electrochemical tests were recorded by a potentiostat-galvanostat with integrated impedance module (Zahner-IM6eX). A Pt wire and a saturated calomel electrode (SCE) was employed as counter and reference electrode, respectively. Freshly prepared working electrodes (0.5 cm² geometric area) were inserted in the GDE cell.

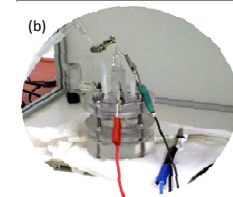
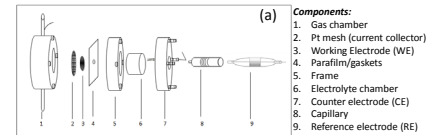


Fig. 4: (a) Schematic exploded view and (b) photo of the plexiglas® GDE cell setup

Characterisation of 40wt% Pt/C in half-cell

Electrochemical behavior of Pt/C catalysts was studied in de-aerated and O_2 -saturated 0.5 M H_2SO_4 electrolyte by means of GDE measurements. Catalyst and PTFE loading was 1 mg_{pt} cm⁻² and 20 wt.%, respectively. Electrochemical surface area (ECSA) of the catalyst was calculated by integrating the hydrogen desorption region in the CV at 40 mV s⁻¹. Accelerated degradation tests (ADT) consisted of 5000 cycles and were carried out within potential range of 0.4 to 1.4 V in a N_2 -saturated 0.5 M H_2SO_4 electrolyte at 1 V s⁻¹.

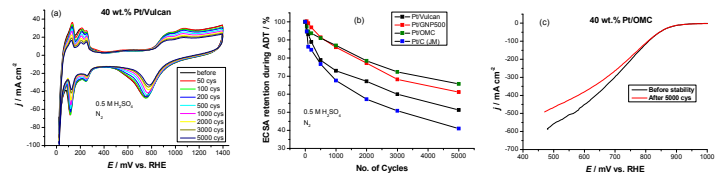


Fig. 5: Characterization of Pt/C catalysts by:

- CV in N_2
- ECSA loss during ADT
- ORR activity, 1600 rpm, before and after ADT (5000 cycles)

System	Spec. Activity* mA cm ⁻²	Mass activity* mA mg _{pt} ⁻¹	ECSA % §
Pt/Vulcan	43.01	154	51.2
Pt/OMC	64.13	118	67
Pt/GNP500	95.79	205	61.2
Pt/C (JM)	32.11	97	40.1

Table 1: Summary of the results obtained from GDE half-cell measurements.

* Specific and Mass activity values are calculated for ORR @ 0.8 V, 0 rpm

§ ECSA retention after 5000 cycles (0.4 – 1.4 V @ 1.0 V s⁻¹)

- High ECSA loss for Pt/C after 5000 cycles.
- Highest ECSA retention of 70% for Pt/OMC.
- No altering of Pt/OMC performance until 150 mA/cm² after 5000 cycles.
- Highest specific and mass activity for ORR achieved by GNP500-supported system.

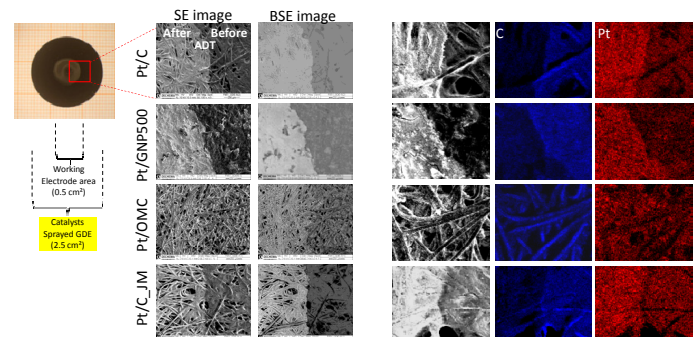


Fig. 6: SEM and WDX images of 1.0 mg_{pt} cm⁻² Pt/C GDE before and after ADT

- After ADT, less Pt particles segregation at GDE surface was concluded for Pt/OMC GDE due to slight color change of SE images & WDX data compared to other systems.

Summary & Acknowledgements

- From GDE investigated systems, Pt/GNP500 catalyst exhibited highest ORR activity and Pt/OMC the best corrosion resistance during electrochemical ADT test.
- Further works will focus on preparation and characterisation of Pt₃Pd and Pt₃Ni.

BMW are greatly acknowledged for financial support (17955 BG/3), project partners from ZSW Ulm and ICVT university of Stuttgart as well as members of industrial committee for excellent cooperation.