Effect of carbon support on corrosion resistance of Pt-based catalysts

M. S. Kalthivel, J.-F. Drillet

E-mail: s.kalthivel@dechema.de

Funded by: BMWi via AiF


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 in 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 catalysts for the middle-temperature (100-150°C) DMFC cathode. First results about preliminary screening of several as-prepared and commercial available carbon/graphite-supported 20wt% Pt catalysts regarding their activity for oxygen reduction reaction (ORR) and stability (accelerated degradation test) under half-cell conditions are presented.

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 H2O2 intermediate is involved.

\[
\begin{align*}
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow 2\text{H}_2\text{O} \quad (E^\ddagger = 1.229 \text{ V}) \\
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- \\
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow 2\text{H}_2\text{O} \quad (E^\ddagger = 1.77 \text{ V})
\end{align*}
\]

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

Synthesis and Characterisation of 20 wt% Pt/C

The synthesis of 20wt% Pt was carried out on five 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.), high surface area graphite (TIMCAL-HSAG300, 250 m²/g), ordered mesoporous carbon (OMC, 1000 m²/g, ACS Materials), graphite nanoparticles (GNP10, 10 nm, 720 m²/g, ACS Materials) and graphitized nanopowder (GNP500, 500 nm, 100 m²/g, Sigma Aldrich). The reaction products were washed with deionized 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

Fig. 3: (a) XRD patterns of different carbon-supported Pt catalysts and (b) thermogravimetric analysis of different commercial carbon supports.

- Diffraction peaks at 2θ=39.5°, 46.09°, 67.55°, and 81.25° match well standard Pt pattern (JCPDS, 04-0802).
- Similar fcc Pt peaks were measured for all as-prepared Pt/C catalysts.
- Large and narrow peak at 2θ=26.45° observed at Timcal and GNP materials is an indication for highly graphitized domains in carbon structure.
- TGA results:
  - negligible weight loss for GNP500 until 500°C
  - Pt loading estimation closed to nominal value of 20wt%: Pt/Vulcan (19.91%), Pt/Timcal (21.7%), Pt/OMC (20.8%), Pt/GNP10 (20.85%) and Pt/GNP500 (20.6%)

TEM Characterisation

Fig. 4: TEM images and particle size distribution histogram of different 20wt% Pt/C catalysts

- Well-ordered crystalline structure only recognizable at OMC material
- Quality of Pt particle distribution: OMC > Vulcan > GNP 500 > Timcal ~ GNP10
- Pt particles size distribution was found to be in the range of 3.0 – 8.0 nm.

Half Cell Characterisation of 20wt% Pt/C Catalyst

Electrochemical behavior of Pt/C catalysts was studied in O2-saturated 0.5 M H2SO4 electrolyte by means of rotating ring disk electrode (RRDE) measurements. The catalyst and Nafion loading was 40-50 μg cm² and 1 wt.% (excepted for ADT 10wt%), respectively. The electrochemical surface area (ECSA) of the catalyst was calculated by integrating the hydrogen desorption region in the CV at 40 mV s⁻¹. The accelerated degradation tests (ADT) consisted of 7000 cycles and were carried out within the potential range of 0.4 to 1.4 V in a nitrogen-saturated 0.5 M H2SO4 electrolyte at 1 V s⁻¹.

Fig. 5: Characterization of Pt/C catalysts by: a) CV in N2, b) ORR activity, 1600 rpm, c) tafel plots, d) H2O2 formation, e) ECSA loss during ADT

- Highest double layer capacity for OMC > GNP10 > Timcal > Vulcan > GNP 500
- O2 reduction activity, 6000 rpm: Pt/GNP10, Pt/Timcal < Pt/V < Pt/GNP500
- Typical two slopes regions of 60 and 120 mV dec⁻¹ observed for all Pt/C catalysts
- Very low H2O2 production < 0.1%
- Highest stability achieved by OMC-supported system during ADT

Fig. 6: Activity and stability performance of 20wt% Pt/C catalysts

Summary & Acknowledgements

- The large surface area of OMC (1000 m²/g) allowed uniform dispersion of Pt within mesoporous structure.
- From all investigated systems, 20wt% Pt/OMC catalyst exhibited highest ORR activity and corrosion resistance during ADT procedure.
- Further work will focus on preparation of higher Pt loading (40wt%) and fabrication of gas diffusion electrode tests.

BMWi, project partners from ZSW Ulm and ICBT university of Stuttgart as well as members of industrial committee are greatly acknowledged for financial support (37955 BG/3) and excellent cooperation, respectively.