

# Activity and stability of bimetallic Pt<sub>3</sub>Pd/C catalysts for ORR in DMFC

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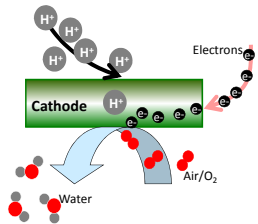


## Introduction

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]. Pt-bimetallic catalyst alloys such as PtCo, PtNi, PtCu, PtCr and PtFe have already shown an improved activity for the oxygen reduction (ORR) in phosphoric acid compared to that of pure Pt [2]. Both, the electronic (shift of d-band center) and geometric (tensile/compressive strain) effects are supposed to be responsible for the increase in activity of Pt after the alloying process. Addition of a second transition metal causes also changes of local bond, active site distribution and reactivity of Pt surface atoms for oxygen reduction reaction (ORR). It is also meanwhile well-known that mesoporous carbon is a well-adapted surface for hosting nanoparticles [3]. This work aims at the development of highly active and corrosion-resistant bi-metal catalyst for the middle-temperature (90-130°C) DMFC with a unpressurized cathode. First results about as-prepared and commercial available carbon/graphite nanoparticle-supported 40 wt% Pt<sub>3</sub>M (M = Cr & Pd) 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] Janan et al., J Electrochem. Soc. 130 (11) (1983) 2299-2302  
[3] 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<sub>2</sub>O<sub>2</sub> 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 and characterisation of 40 wt% Pt<sub>3</sub>M/C



Fig. 2: Setup used for catalyst synthesis

The synthesis of 40wt% Pt, Pt<sub>3</sub>M was carried out on commercially available carbon supports by formaldehyde reduction at 80°C for 1h under reflux condition. Pt<sub>3</sub>Cr synthesis was carried out by co-reduction of hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O) and chromium(III) nitrate hydrate (CrN<sub>3</sub>O<sub>9</sub>·xH<sub>2</sub>O) in formaldehyde. Similarly, Pt<sub>3</sub>Pd was synthesized using Pd(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O precursor. Based on relevant properties such as high surface area, porous structure and degree of graphitization, following commercially available carbons were selected: carbon black (Vulcan XC-72, 50 nm, 250 m<sup>2</sup>g<sup>-1</sup>, Cabot) and graphitized nanopowder (GNP<sub>500</sub>, 500 nm, 100 m<sup>2</sup>g<sup>-1</sup>, 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.

## XRD analysis

- Diffraction peaks at 2θ=39.5°, 46.09°, 67.55°, and 81.25° match well with fcc Pt & Pd standard and patterns.
- A small shift in diffraction angle of about 0.7 to 0.96° is associated with the change in Pt-Pt interatomic distance after alloying with Cr and Pd elements.
- Peak at 2θ=26.45° observed at GNP materials is an indication for highly graphitized domains.

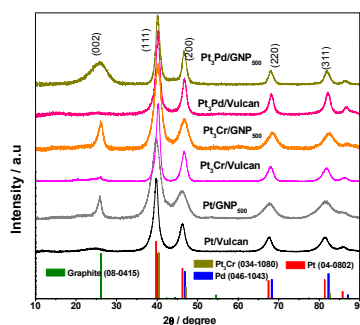


Fig. 3: (a) XRD patterns of different carbon-supported 40 wt% Pt-based catalysts

## TEM images

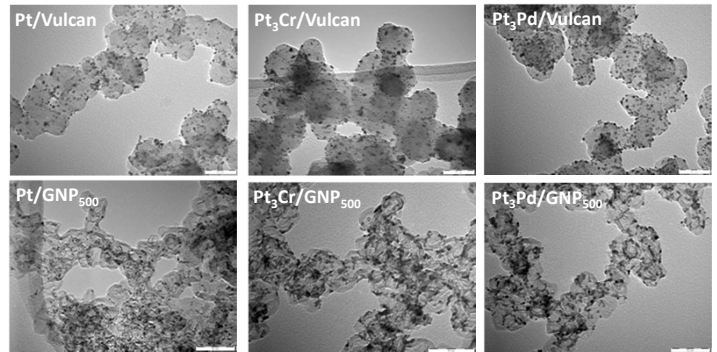


Fig. 4: TEM images of different 40 wt% Pt/C and Pt<sub>3</sub>M/C catalysts

- Better catalyst dispersion on Vulcan than on GNP<sub>500</sub>
- Pt particles size distribution was found to be in the range of 3.0 – 8.0 nm.

## Half Cell characterisation of 40 wt% Pt<sub>3</sub>M/C catalyst

Electrochemical behavior of Pt/C catalysts was studied in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte by means of rotating disk electrode (RDE) and gas diffusion electrode (GDE) measurements. The catalyst and Nafion loading was 40-50 μg<sub>Pt</sub> cm<sup>-2</sup> 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<sup>-1</sup>. The accelerated degradation tests (ADT) were carried out within the potential range of 0.4 to 1.4 V in a nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte at 1 V s<sup>-1</sup>.

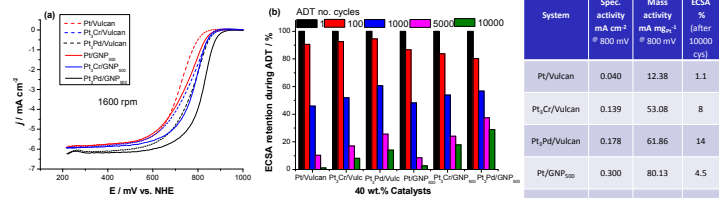


Fig. 5: Characterization of 40-50 μg<sub>Pt</sub>cm<sup>-2</sup> catalysts under RDE conditions by a) LSV in O<sub>2</sub>-sat. solution and b) ECSA loss during ADT

- Positive influence of alloying and use of mesoporous carbon on Pt activity for ORR: 9 times increase in spec. activity<sub>@800mV</sub> for Pt<sub>3</sub>Cr/GNP<sub>500</sub> compared to Pt/Vulcan.
- Best results in terms of overpotential @ 2.5 mA cm<sup>-2</sup> were obtained at Pt<sub>3</sub>Pd/GNP<sub>500</sub> (100 mV less than at Pt/Vulcan) following by Pt<sub>3</sub>Cr/GNP<sub>500</sub> (59 mV), Pt<sub>3</sub>Pd/Vulcan (58 mV); Pt<sub>3</sub>Cr/Vulcan (40 mV) and Pt/GNP<sub>500</sub> (28 mV).
- Highest ECSA retention of 30% for Pt<sub>3</sub>Pd/GNP<sub>500</sub> after 10000 cycles.

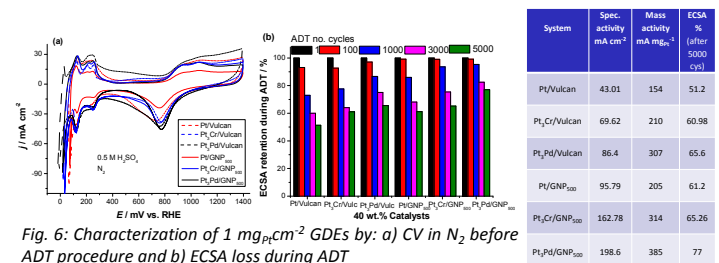


Fig. 6: Characterization of 1 mg<sub>Pt</sub>cm<sup>-2</sup> GDEs before ADT procedure and b) ECSA loss during ADT

- Huge increase of ECSA retention for all systems due to addition of 20wt% PTFE binder to usual 10wt% Nafion under RDE condition; Highest ECSA retention of 77% for Pt<sub>3</sub>Pd/GNP<sub>500</sub>
- Confirmation of beneficial effect of alloying and use of mesoporous carbon on both activity for ORR and stability.

## Summary

- 40 wt% Pt<sub>3</sub>Cr & Pt<sub>3</sub>Pd were developed by facile co-reduction route in formaldehyde.
- Large enhancement in activity for ORR was achieved by alloying Pt with Pd and using mesoporous carbon as support.
- Highest ECSA retention of 77% for Pt<sub>3</sub>Pd/GNP<sub>500</sub> after 5000 ADT cycles.