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, PtIr and PtFe have already shown an improved activity for the oxygen reduction reaction (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 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% Pt3M (M = Cr & Pd) catalysts regarding their activity for oxygen reduction reaction (ORR) and stability (accelerated degradation test) under half-cell conditions are presented.

**Introduction**

The synthesis of 40 wt% Pt, Pt3M was carried out on commercially available carbon supports by formaldehyde reduction at 80°C for 1 h under reflux condition. PtCr synthesis was carried out by co-reduction of hexachloroplatinic acid (H2PtCl6), HCHO and chromium(III) nitrate hydrate (Cr(NO3)3·9H2O) in formaldehyde. Similarly, PtPd was synthesized using Pd(NO3)2·2H2O precursor. Based on relevant properties such as high surface area, porous structure and degree of graphitization, following commercially available carbons were selected: carbon graphite (08-0415) and mesoporous carbon as support. First TEM images of different 40 wt% Pt/C and Pt3M/C catalysts (Fig. 4).

**Synthesis and characterisation of 40 wt% Pt3M/C**

![Fig. 1: Schematic illustration of oxygen reduction reaction (ORR) at Pt](image)

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.

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

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

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

**XRD analysis**

- Diffraction peaks at 2θ of 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 0.9° is associated with the change in Pt-Pt interatomic distance after alloying with Cr and Pd elements.
- Peak at 2θ of 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](image)

**Half Cell characterisation of 40 wt% Pt3M/C catalyst**

![Fig. 5: Characterization of 40-50 μg·cm⁻² catalysts under ORR conditions by a) LSV in O₂-saturated 0.5 M H₂SO₄, and b) ECSA loss during ADT](image)

Electrochemical behavior of Pt/C catalysts was studied in O₂-saturated 0.5 M H₂SO₄ electrolyte by means of rotating disk electrode (RDE) and gas diffusion electrode (GDE) measurements. The catalyst and Nafion loading was 40-50 μg·cm⁻² 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 0.6 V vs. RHE.

**Summary**

- 40 wt% Pt3Cr & Pt3Pd 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 PtPd/GNP after 5000 ADT cycles.

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**Figures**

- **Fig. 1:** Schematic illustration of oxygen reduction reaction (ORR) at Pt
- **Fig. 4:** TEM images of different 40 wt% Pt/C and Pt3M/C catalysts
- **Fig. 5:** Characterization of 40-50 μg·cm⁻² catalysts under ORR conditions by a) LSV in O₂-saturated 0.5 M H₂SO₄, and b) ECSA loss during ADT.
- **Fig. 6:** Characterization of 1 mg·cm⁻² GDEs by: a) CV in N₂ before ADT procedure and b) ECSA loss during ADT.