

# Activity of Pt-Au electrocatalyst for the oxygen reduction in methanol containing solution

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## Introduction

The direct methanol fuel cell (DMFC) is recognized as a promising technology for energy supply of portable and stationary applications due to high energy density of methanol, compact design, easy fuel handling and storage. Despite considerable advantages, the DMFC still has drawbacks such as poor activity of Pt for methanol oxidation compared to that for hydrogen oxidation, methanol crossover that results on fuel loss and mixed potential formation at the cathode and low corrosion resistance of the catalyst support [1]. Some Pt-based alloy catalysts such as PtCo, PtCu and PtFe [2] already showed improved methanol tolerance but unfortunately poor long-term stability due to the dissolution of the non-noble metal [3]. Therefore, the development of core-shell architected catalysts by arranging thin Pt monolayer shell on metal core appears to be an interesting strategy to significantly enhance their corrosion resistance and catalytic activity [4]. One important drawback is still the segregation of the core material to the surface. This work focuses to develop methanol-tolerant and corrosion-resistant catalysts for the middle-temperature (120-150°C) DMFC cathode.

- [1] C. Lamy, C. Coutanceau, N.A. Vante, *Electrocatalysis of Direct Methanol Fuel Cells: From Fundamentals to Applications*, H. Liu, J. Zhang (Ed.), Wiley-VCH, (2009) 257  
[2] V. Baglio, A. Stassi, A. Di Blasi, C. D'Urso, V. Antonucci, A.S. Arico, *Electrochim. Acta* **53** (2007) 1360  
[3] M. Oezaslan, P. Strasser, *J. Power Sources* **196** (2011) 5240  
[4] K. Hartl, K.J.J. Mayrhofer, M. Lopez, D. Goia, M. Aren, *Electrochem. Commun.* **12** (2010) 1487

## Working Principle of DMFC

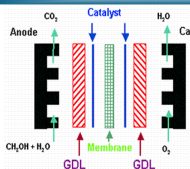


Fig.1: Operation of DMFC single cell

### Electrolyte: Solid Polymer Membrane

Anode Reaction:  
 $\text{CH}_3\text{OH} + \text{H}_2\text{O} \Rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$   
Cathode Reaction:  
 $\frac{3}{2} \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \Rightarrow 3 \text{H}_2\text{O}$   
Overall Net Reaction:  
 $\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \Rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$

## Objectives

This project aims at the development of a bi-metal Pt catalyst for the middle temperature fuel cell (100-150 °C, PEMFC and DMFC) cathode together with the research group of Prof. Dr. F. Schüth, Max-Planck-Institute in Mülheim. This project is part of an AiF/DFG cluster project.

The individual tasks of this project are:

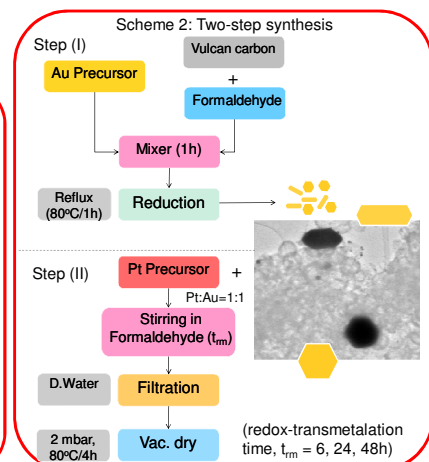
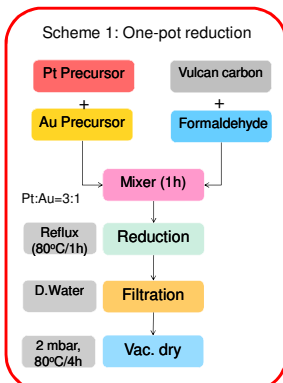
**KWI:** Synthesis of high active Pt based bi-metal alloy with early and late transition metal elements • Optimization of carbon supported catalyst structure, particle size, dispersion, composition and stability through physicochemical characterization, electrochemical (rotating (ring) disk electrode - RDE/RRDE) and fuel cell testing • Investigation of new catalyst architecture (Core-Shell) • Study of influence on the thermal treatment.

**MPI:** Synthesis of high graphitized carbon supports (hollow spheres) as alternative to carbon Vulcan • The encapsulation of the catalytic metals within the hollow spheres • Estimation of the physical shape, size, structure and chemical composition.

Supply of high active catalysts for the cluster partners (TP3 & TP4)

## Synthesis of Catalysts

Synthesis of the Pt-Au bimetal catalysts were carried out in two different approaches: (1) one-pot reduction, namely both Au and Pt ion precursors were reduced simultaneously in a formaldehyde solution (scheme 1); (2) two-step synthesis, first formation of gold nano particles on Carbon and subsequent deposition of Pt particles on gold surface by redox-transmetalation (scheme 2). The nominal Pt mass ratio was related in both cases to Pt/C and amounted to 20wt%.



## UV-Vis and XRD spectra of Pt-Au catalysts

Au particles with hexagonal shape were preferentially formed, whereas particles with spherical and elongated hexagonal shape have also been detected by TEM (see scheme 2). The average particle size amounts to about 500 nm. Au(111), high number of facets and large particle size are usually preferred as core material to host high active Pt nanoparticles.

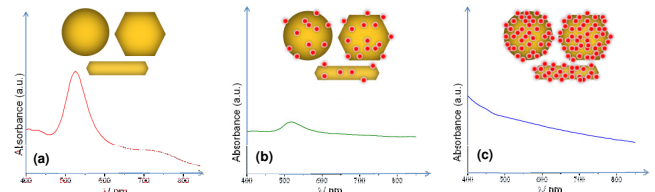


Fig.2: UV-Vis spectra of catalysts from Scheme 2: (a) Au/C, (b) Pt/Au/C ( $t_m=6\text{h}$ ) and (c) Pt/Au/C ( $t_m=48\text{h}$ )

- The surface plasmon resonance (SPR) peak of Au decreases with redox-transmetalation reaction time (Fig.2).
- The XRD peaks of Au/C matches with standard (JCPDS 04-0784) (Fig.3 b).
- Approchement of Pt and Au peaks in Fig.3 is an indication for Pt-Au alloy formation
- Distinctive Pt and Au peaks, broad Pt peaks of Pt/Au reveal formation of small Pt nanoparticles on Au substrate (Fig.3 c).

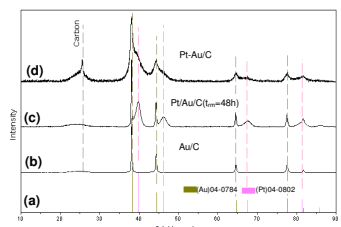


Fig.3: XRD patterns of Au and Pt-Au catalysts

## Electrochemical Performance of Pt-Au Catalysts

Electrochemical behavior of the AuPt/C catalysts was studied in  $\text{N}_2$  (Fig.5),  $\text{O}_2$  and methanol (Fig.6) containing 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte by means of cyclic Voltammetry (CV) using a rotating ring disk electrode (RRDE).

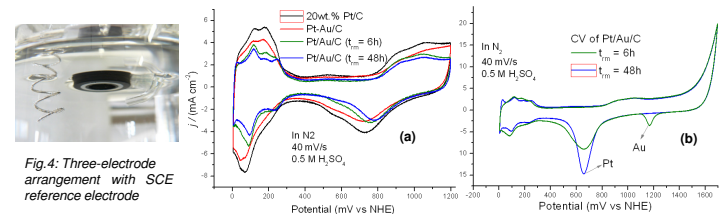


Fig.4: (a) Cv of different catalyst in  $\text{N}_2$ . (b) Influence of reduction time on electrochemical behaviour of Pt and Au.

- Typical behaviour is observed for Pt-Au alloy in Fig.5a
- Smaller Pt active surface for Pt/Au/C compared to that of pure Pt.
- Positive shifts of PtO formation/reduction to more positive values at Pt/Au/C
- AuO reduction peak visible at Pt/Au/C ( $t_m=6\text{h}$ ): incomplete coverage of Au with Pt
- 43 mV less overpotential (@ 2 mA  $\text{cm}^{-2}$ ) at Au/Pt/Cr ( $t_m=48\text{h}$ ) for ORR
- Pt/Au/C ( $t_m=48\text{h}$ ) catalyst shows high methanol tolerance during ORR

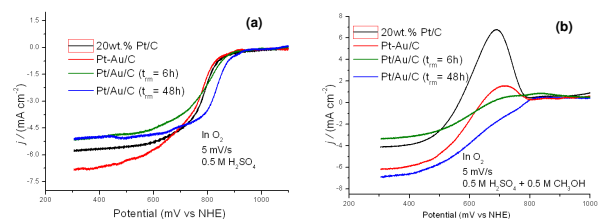


Fig.6: Activity of Pt/C, Pt/Au/C and Pt/Au/C for ORR in (a) oxygen and (b) oxygen and methanol containing electrolyte.

## Conclusions & Outlook

- One-pot reduction resulted in Pt-Au alloy formation.
- Full coverage of Au with Pt after  $t_m=48\text{h}$  confirmed by UV-Vis and CV.
- Pt/Au/C ( $t_m=48\text{h}$ ) synthesized with the two-step reduction method shows highest activity for ORR and methanol tolerance compared to the one-pot reduction method.
- Electrochemical characterizations of Pt/Au/C ( $t_m=24$  &  $36\text{h}$ ) have to be carried out.
- TEM and XPS investigations are in progress.

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