

# Activity and stability study of PtCr/C catalysts for ORR

M. Sakthivel, J.-F. Drillet  
e-mail: sakthivel@dechema.de  
Funded by: DFG  
Period: 01.05.2010 - 30.07.2013



## Introduction

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 [1]. 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). However, dissolution or/and segregation to the surface of the non-noble metal in the case of an alloy and core-shell structure, respectively affect the long-term activity of these systems. In this work, different Pt-bimetal catalysts were tested regarding ORR activity, chemical and electrochemical corrosion resistance as well as performance under fuel cell conditions in case of PtCr/C.

[1] Jalan et al., J Electrochem. Soc. 130 (11) (1983) 2299-2302

## Oxygen Reduction Reaction (ORR)

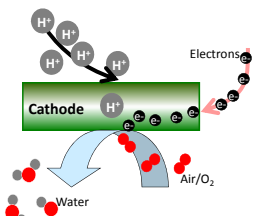
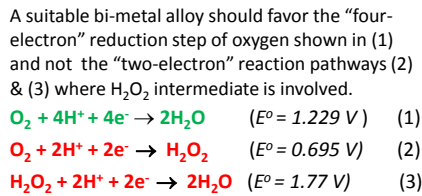


Fig. 1: Schematic illustration of oxygen reduction reaction (ORR) at Pt



## Half Cell Characterisation of 40wt% PtCr/C catalyst

Electrochemical behavior of PtCr/C catalyst was studied in  $O_2$ -saturated 0.5 M  $H_2SO_4$  electrolyte (Fig.) by means of Linear Sweep Voltammetry (LSV) using a rotating disk electrode (RDE) cell. The total catalyst/support loading was about  $80 \mu g \text{ cm}^{-2}$ . The electrochemical surface area (ECSA) of the catalyst was calculated by integrating the hydrogen desorption region in the CV at  $40 \text{ mV s}^{-1}$ . For comparison, a commercial 40wt% Pt/C catalyst from Johnson Matthey (JM) was also tested. The accelerated degradation tests (ADT) consisted of 7000 cycles that were carried out within the potential range of 0.4 to 1.4 V in a nitrogen-saturated 0.5 M  $H_2SO_4$  electrolyte at  $1 \text{ V s}^{-1}$ .

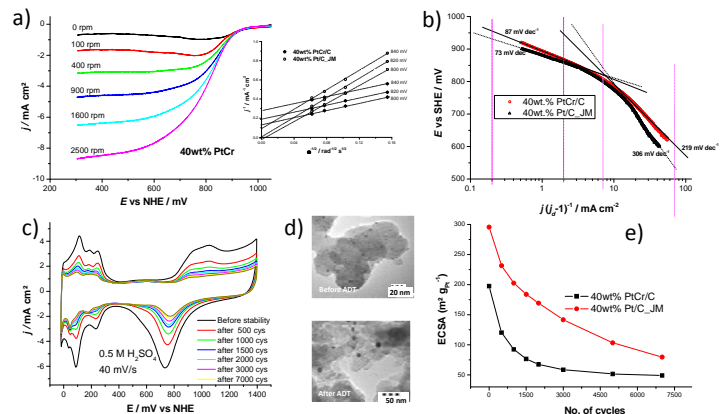


Fig. 5: a) ORR on 40wt% PtCr/C mit Levich-koutecky plots of both PtCr/C & Pt/C(JM); b) Tafel plots of ORR activity @1600rpm; c) CV controls during ADT test, d) TEM images of PtCr/C before and after ADT; e) ECSA behavior during ADT test

- Higher Tafel slope for PtCr/C (87 mV) compared to 73 mV for commercial Pt/C
- Huge ECSA loss observed during first 500 cycles: 23% for PtCr/C and 38% for Pt/C
- Lower ECSA values and similar degradation rate for PtCr/C system compared to Pt/C
- Increase of average PtCr particle size from 4.5 nm up to 8-9 nm after 7000 CVs

## Preliminary screening of 20 wt% PtM/C catalysts (Pt:M 60:40)

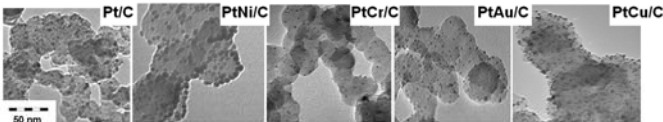


Fig. 2: TEM images of the different PtM/C Table 1: results from TEM, TGA, AAS & RDE

Catalyst	Metal content Gew. %	Size nm	$C_{M}$ $mg \text{ l}^{-1}$	Spec. activity $\text{mA cm}^{-2}$	Mass activity $\text{mA mg}^{-1}$	Tot. Mass activity $\text{mA mg}_{\text{total}}^{-1}$
Pt/C	19.79	3-4	0.2	0.327	89.32	89.32
Pt <sub>60</sub> Ni <sub>40</sub> /C	13.04	7-8	0.045 (Ni)	0.447	147.83	88.43
Pt <sub>60</sub> Cr <sub>40</sub> /C	13.75	4-4.5	0.022 (Cr)	0.619	178.56	107.26
Pt <sub>60</sub> Au <sub>40</sub> /C	19.11	5	-	0.133	30.97	18.11
Pt <sub>60</sub> Cu <sub>40</sub> /C	13.26	4.5-5	5.374 (Cu)	0.232	76.26	45.75

## Synthesis and Characterisation of 40 wt% Pt-Cr/C

Since PtCr was found to be the more effective catalyst for ORR as well as the more stable against corrosion ( $C_M$  value in tab. 1), further investigation were focused only on 40wt% PtCr. Its synthesis were carried out by co-reduction of hexachloroplatinic acid ( $H_2PtCl_6 \cdot 6H_2O$ ) and chromium(III) nitrate hydrate ( $CrN_3O_9 \cdot xH_2O$ ) in formaldehyde. The reaction was carried out at  $80^\circ C$  for 1h under reflux condition (see fig 3). The nominal mass ratio of Pt:Cr was 3:1 and total metal loading on carbon Vulcan (C) was 40wt%.

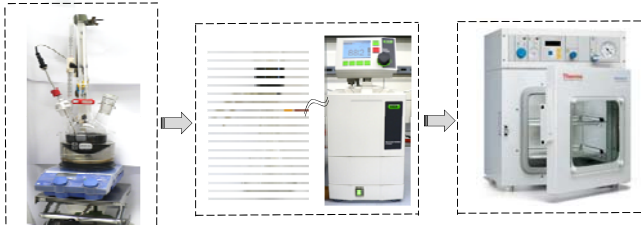


Fig. 3: Instrument setup used for catalyst synthesis

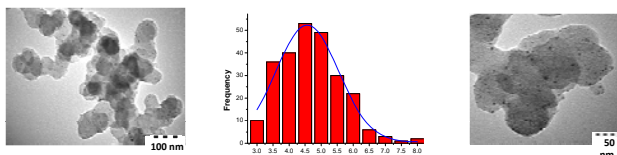


Fig. 4: TEM images and particle size distribution histogram of 40wt% PtCr/C catalyst

- Average PtCr/C production was 0.8-1 g
- Scale-up to obtain larger catalyst mass (5g) was not successful
- Well-defined PtCr distribution on carbon support was confirmed by TEM
- The average particle size from histogram is about 4.6 nm

## Fuel Cell Characterisation

Behavior of PtCr/C cathode catalyst was studied at ZBT Duisburg under  $H_2$ /air PEM fuel cell conditions at  $80^\circ C$ . The results obtained at MEA with cathode Pt loading of  $0.177 \text{ mg cm}^{-2}$  are presented in Fig. 6. Each 1-5<sup>th</sup> aging cycle include 100 CVs between 0.4 V and 1.4 V @  $1 \text{ V s}^{-1}$  whereas the 6<sup>th</sup> one is more severe and composed of 500 CVs between 0.05 and 1.4 V @  $1 \text{ V s}^{-1}$ .

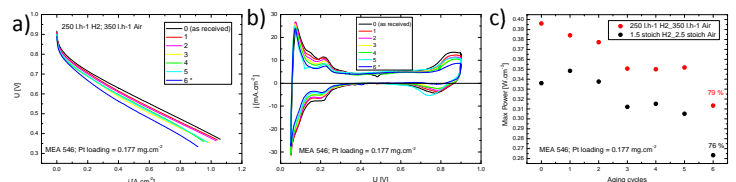


Fig. 6: Activity of PtCr/C in  $H_2$  fuel cell; a) Polarization plots & b) CV's during stability test. c) Function of max. power density vs. aging cycles for 2 different  $H_2$ /air feeds

- MEA tests reveal high activity and stability of 40wt% PtCr/C as cathode material
- Max. power density after ADT was about 76-79% of initial value
- High  $H_2$ /air feed rates are needed to reach highest catalyst utilization ( $P_{\text{max}}$ )

## Summary & Acknowledgements

- Feasibility of PtCr/C as performing and corrosion-resistant bi-metal cathode catalyst was demonstrated in this work.
- PtCr exhibited highest activity towards ORR and better corrosion resistance during preliminary screening test compared to 20 wt% PtCu/C, PtAu/C, PtNi/C and Pt/C (JM).
- Uniform and narrow distribution of PtCr particles on carbon was confirmed by TEM.
- Similar trend was observed during half-cell and full-cell experiments at DFI and ZBT, respectively.
- Further works on PtCr/C are planned in a new AIF project with ZSW Ulm.

DFG is greatly acknowledged for financial support (DR 812/1-1). We gratefully thank Dr. I. Radev and Dr. V. Peinecke from ZBT Duisburg for full-cell measurements as well as all DFG/AIF cluster partners for excellent cooperation.