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Chemical Technology

Activity of HGS-supported Pt-Au catalysts for ORR in absence and presence of methanol

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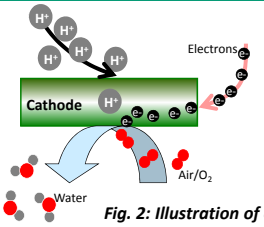
Introduction

Pt-bimetallic catalyst alloys such as PtCo, PtNi, PtCu and PtFe have already shown an improved activity for the oxygen reduction (ORR) in acid electrolyte compared to that of pure Pt. Both, the electronic (d-band center) and geometric (tensile/compressive strain) effects appears to be responsible for the increase in activity of Pt after the alloying process. The addition of a second metal causes changes of local bond, active site distribution and reactivity of Pt surface atoms for oxygen reduction reaction (ORR). In most cases, however, the second metal is unstable and tends to segregate to the surface in the case of a core-shell configuration [1]. However, by increasing the core size up to 30 nm, the solubility of Pt particle can be decreased; such systems exhibit additionally high mass activity and turnover frequency [2]. Addition of less active Au atoms for ORR can reduce the local coverage of Pt with O atoms at high potentials and also stabilize the Pt surface [3]. According to the Au-Pt phase diagram, the catalyst microstructure also accounts the problem of phase segregation which alters electronic structure and catalytic properties. The large miscibility gap can be reduced by using a two-phase synthesis nano-alloying protocol that implicates the use of surfactant for core encapsulation. However, removal of these organics necessitates thermal treatment that usually severely affects the structure/size and catalytic properties. Therefore, in this work, synthesis of large Pt-Au bimetallic system was carried out on carbon VulcanXC72R (C) and hollow graphitic spheres (HGS) without using any organic surfactants.

*[1] K.J.J. Mayrhofer, K. Hartl, V. Juhart, and M. Arenz, J. Am. Chem. Soc., **2009**, 131, 16348*
*[2] H.A. Gasteiger and N.M. Markovic, Science **2009**, 324, 48*
*[3] Y.-H. Fang and Z.-P. Liu, J. Phys. Chem. Lett., **2011**, 115, 17508*

Oxygen Reduction Reaction (ORR)



A suitable bi-metal alloy should favor the "four-electron" reduction step of oxygen as shown in the eq. (1). And not eq. (2) where H_2O_2 intermediate is involved.

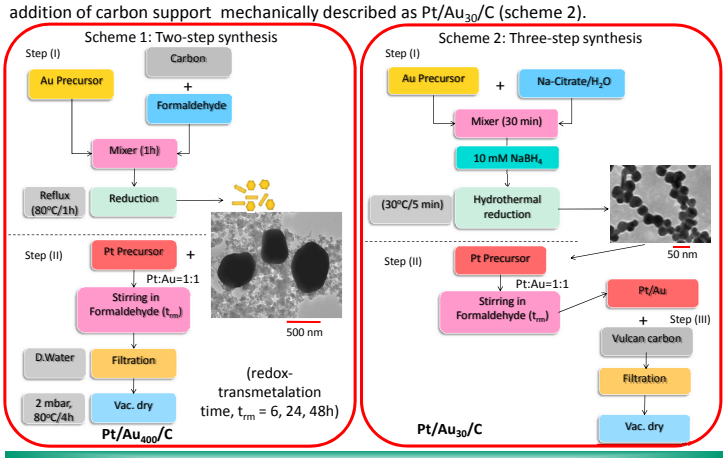
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($E^o = 1.229\ V$) --- eq. 1

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ ($E^o = 0.695\ V$)
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ ($E^o = 1.77\ V$) --- eq. 2

Fig. 2: Illustration of oxygen reduction reaction (ORR) at platinum

Synthesis of Pt-Au Catalysts on Carbon Supports

Synthesis of the bimetal catalysts were carried out in three different approaches: (1) one-pot reduction, namely both Au and Pt ion precursors were reduced simultaneously on carbon in a formaldehyde solution giving Pt_3Au/C (3nm); (2) two-step synthesis, first formation of gold nano particles on carbon and subsequent deposition of Pt particles on gold surface by redox-transmetalation $Pt/Au_{400}/C$ (scheme 1); (3) three step synthesis, formation of gold nano particles, subsequent deposition of Pt particles on gold surface by redox-transmetalation and addition of carbon support mechanically described as $Pt/Au_{30}/C$ (scheme 2).



UV-Vis 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 1). The average particle size amounts to about 500 nm.

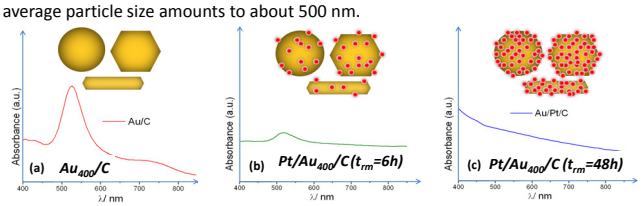


Fig.3: UV-Vis of catalysts from Scheme 2

•The surface plasmon resonance (SPR) peak of Au decreases with redox-transmetalation reaction time and was not visible for t_{rm} =48h (Fig3).

XRD and TEM of Pt-Au catalysts

• Pt_3Au alloy formation is not obvious and should be investigated more in details by e.g. XPS.
• Distinctive Pt and Au peaks, broad Pt peaks reveal formation of small Pt nanoparticles on Au substrate (Fig 4b,c).
• TEM images reflect the small uniform size (30 nm) of Au (Fig 5a) and Pt particle coverage on Au (Fig 5b) and SEM-EDX elemental mapping also confirms the Pt skin on Au particle.

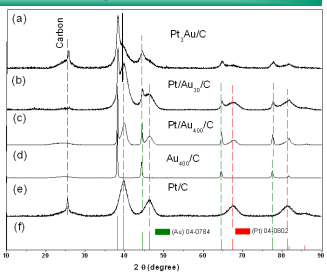


Fig.4: XRD spectra of Au and Pt-Au

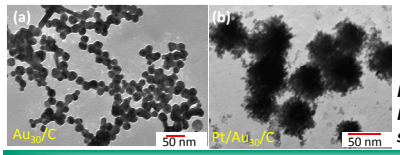


Fig. 5: TEM images of (a) Au_{30} and (b) Pt/Au_{30} nanoparticles obtained from the synthesis rout described in scheme2.

Electrochemical Characterisation of Pt-Au catalysts

Electrochemical behavior of the bimetal catalysts was studied in N_2 (Fig.6), O_2 and methanol containing 0.5 M H_2SO_4 electrolyte (Fig.7), by means of cyclic Voltammetry (CV) using a rotating ring disk electrode (RRDE).

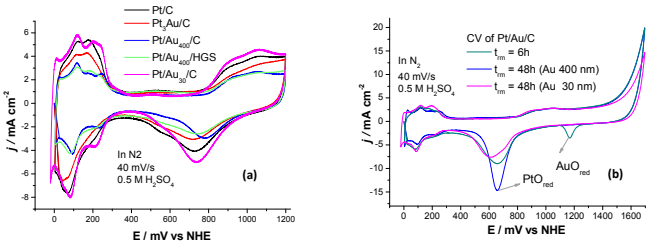


Fig.6: (a) CV of different catalysts in N_2. (b) Influence of reduction time on electrochemical behaviour of Pt and Au.

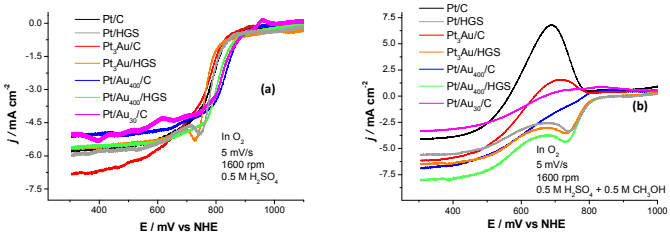


Fig.7: Activity of Pt and Pt-Au supported on carbon and HGS for ORR in (a) oxygen and (b) oxygen and methanol containing electrolyte.

- Higher Pt active surface for Pt/Au compared to that of pure Pt
- AuO reduction peak visible at Pt/Au/C*(t_{rm}=6h)*: incomplete coverage of Au with Pt
- 33 mV less overpotential (@ 2 mA cm^{-2}) at $Pt/Au_{30}/C$ for ORR compared to Pt/C
- 43 mV less overpotential (@ 2 mA cm^{-2}) at $Pt/Au_{400}/C$ for ORR compared to Pt/C
- 23 mV less overpotential (@ 2 mA cm^{-2}) at $Pt/Au_{400}/HGS$ for ORR compared to Pt/C
- $Pt/Au_{400}/HGS$ catalyst shows highest methanol tolerance during ORR
- $Pt/Au_{30,400}/C$ *(t_{rm}=48h)* catalysts show highest specific and mass activity for ORR @800 mV

Table 1: Summary of the results for ORR

System	Pt wt%	Au wt%	Metal Loading +/- 5µg/cm²	Pt/ECSA H_2 des. cm²	Spec. activity @800mV mA/cm²$_{ECSA}$	Mass activity @800mV mA/mg$_{Pt}$	Mass activity @800mV mA/mg$_{Pt+Au}$
Pt/C	20	-	34	55.4	0.0173	56.33	-
Pt/HGS	20	-	34	57.5	0.0163	55.06	-
Pt_3Au/C	15	5	25.5:8.5	40.8	0.0187	59.84	44.88
Pt_3Au/HGS	15	5	25.5:8.5	42.1	0.0139	45.88	34.41
$Pt/Au_{400}/C$	20	20	34:34	67	0.0262	103.71	51.85
$Pt/Au_{400}/HGS$	20	20	34:34	67	0.0222	87.74	43.87
$Pt/Au_{30}/C$	20	20	34:34	69	0.0233	95.7	47.55

Conclusions

- One-pot reduction resulted in Pt_3Au formation
- By using two-step route, full coverage of Au with Pt after t_{rm}=48h confirmed by UV-Vis & CV but deposition of Pt on C was observed as well.
- With the three-step reduction method, Au particle size in the range of 30nm and good distribution of Pt particles (Pt skin) on Au was obtained.
- Higher specific and mass activity was achieved for ORR at $Pt/Au_{30}/C$ compared to Pt/C.
- Pt/Au nanoparticles supported on HGS show highest methanol tolerance than Vulcan carbon
- Feasibility of Pt skin on Au core by surfactant-free route synthesis was demonstrated

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