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, PdNi, 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 particle can be decreased; such systems exhibit additionally high mass activity and turnover frequency [2].

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 \( H_2O \) intermediate is involved.

\[
\begin{align*}
O_2 + 4H^+ + 4e^- & \rightarrow 2H_2O, \quad (E^* = 1.229 \text{ V}) \tag{1}
\end{align*}
\]

\[
\begin{align*}
O_2 + 2H^+ + 2e^- & \rightarrow H_2O, \quad (E^* = 0.695 \text{ V}) \tag{2}
\end{align*}
\]

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/Au400/C (3nm); (2) two-step synthesis, first formation of gold nanoparticles on carbon and subsequent deposition of Pt particles on gold surface by redox-transmetalation Pt/Au30/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/Au0.5C (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.

XRD and TEM of Pt-Au catalysts

• PtAu 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.

Electrochemical Characterisation of Pt-Au Catalysts

Electrochemical behavior of the bimetal catalysts was studied in N2 (Fig.6), O2 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).

Table 1: Summary of the results for ORR

<table>
<thead>
<tr>
<th>System</th>
<th>Pt wt%</th>
<th>Au wt%</th>
<th>Metal Loading (mg/cm²)</th>
<th>Voltammetry Results</th>
<th>Mass Activity @800mV (mA/mgPt)</th>
<th>Mass Activity @800mV (mA/mgPt+Au)</th>
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<tbody>
<tr>
<td>Pt/C</td>
<td>20</td>
<td>-</td>
<td>34</td>
<td>55.4</td>
<td>0.0173</td>
<td>56.33</td>
</tr>
<tr>
<td>Pt/HGS</td>
<td>20</td>
<td>-</td>
<td>34</td>
<td>57.5</td>
<td>0.0163</td>
<td>55.06</td>
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<tr>
<td>Pt/Au/C</td>
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<td>5</td>
<td>25-5.8</td>
<td>40.8</td>
<td>0.0187</td>
<td>59.84</td>
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<tr>
<td>Pt/Au/HGS</td>
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<td>5</td>
<td>25-5.8</td>
<td>42.1</td>
<td>0.0192</td>
<td>45.88</td>
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<tr>
<td>Pt/Au30/C</td>
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<td>20</td>
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<td>67</td>
<td>0.0262</td>
<td>103.71</td>
</tr>
<tr>
<td>Pt/Au0.5HGS</td>
<td>20</td>
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<td>34</td>
<td>67</td>
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<td>20</td>
<td>34</td>
<td>69</td>
<td>0.0233</td>
<td>95.7</td>
</tr>
</tbody>
</table>

Conclusions

- One-pot reduction resulted in PtAu formation
- By using two-step route, full coverage of Au with Pt after \( t_{trm}=48h \) 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 PtAu0.5C compared to Pt/C.
- Pt/Au nanoparticles supported on HGS show highest methanol tolerance than Vulcan carbon.

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

Fig.6: (a) CV of different catalysts in N2. (b) Influence of reduction time on electrochemical behaviour of Pt and Au.

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

Fig.5: TEM images of (a) Au0.5HGS and (b) PtAu0.5HGS nanoparticles obtained from the synthesis rout described in scheme2.