Electrochemical Stability of Au sub-ML on Pt/QC Electrode

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Introduction

Form of the next-generation energy

Conventional large-scale power generation

Next-generation energy device for smart grid society

Smart grid society

- Nuclear power generation
- Hydraulic power generation
- Thermal power generation

- Solar power
- Wind generation
- Accumulator
- Fuel cell

It is a next-generation energy device including the Fuel cell to support smart grid society.
Introduction

Energy conversion

- Chemical Energy
- Thermal energy
  - Burn
  - Rotation (heat-engine)

- Direct conversion

- Kinetic energy

- Electrical Energy
- Generation

Thermal power generation

The battery can convert chemical energy into electrical energy without having the carneau limitation.
Polymer Electrolyte Fuel Cells (PEFCs)

Anode reaction
\[ H_2 \rightarrow 2H^+ + 2e^- \]

Cathode reaction
\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]

Total reaction
\[ 2H_2 + O_2 \rightarrow 2H_2O \]

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Introduction

Fig. 1 Schematic illustration for PEFCs.

Fig. 2 Schematic illustration for Pt/C catalyst.
Pt dissolution is one of the most important issue for the commercialization in PEFCs. Gold is most stable material in noble metals. Adzic et. al. reported that Au sub-ML suppress the Pt dissolution.

In this study, we focused the effect of Au role for the suppression of Pt dissolution, and investigated by the EQCM and RRDE technique.
Sauerbrey equation

\[ \Delta m = \frac{S \cdot \sqrt{\rho \cdot \mu}}{2 \cdot N \cdot F^2} \cdot (\Delta F) \]

- \( \Delta m \): Mass change (g)
- \( \Delta F \): Frequency change (Hz)
- \( \mu \): Shear stress of the quartz crystal (2.95 \times 10^{11} \text{ g/cm \cdot sec}^2)
- \( S \): Surface area [\( \phi = 3 \text{mm} \)]
- \( \rho \): Density of the quartz crystal (2.65 \text{ g/cm}^3)
- \( N \): Overtone order \( (N = 1) \)
- \( F \): Nominal frequency (10,000,000Hz)

\[ \therefore \frac{1 \text{Hz}}{cm^2_{geo}} = 4.42 \text{ng/cm}^2_{geo} \]

Experimental

EQCM technique

- Electrolyte: 0.05 M H_2SO_4
- Working electrodes: Au on QC (10MHz, \( \phi = 3 \text{mm} \))
- Counter electrode: Pt
- Reference: RHE
- Temperature: 25°C

Fig. 4 Three-electrode glass cell for ORR measurements.
Fig. 4 Three-electrode glass cell for ORR measurements.

- Electrolyte: 0.1 M HClO₄
- Working electrodes: RDE
  Disk: catalyst (Pt/C TKK, 46.8 wt.%) on GC ($S_{GC} = 0.28 \text{cm}^2$, $Pt$ loadings: $14.1\ \mu g/cm^2$)
- Counter electrode: Pt-wire
- Reference: RHE
- Temperature: 25°C
- Rotating rate: 400 – 3600 rpm

Fig. 5 Hydrodynamic voltammograms of oxygen reduction current at disk. Rotating rate: 400 – 3600 rpm.

Koutecky—Levich equation

\[
\frac{1}{I_D} = \frac{1}{I_K} + \frac{1}{I_L} = \frac{1}{I_K} + \frac{1}{0.62nFAC_0^*D_0^{\frac{2}{3}}v^{-\frac{1}{6}}\omega^2}
\]

$I_L$: the diffusion limiting current
$n$: the number of electron involved in ORR
$F$: the Faraday constant
$A$: the geometric surface area of the electrode
$C_0^*$: the equilibrium concentration of dissolve O₂ in the solution
$D_0$: the diffusion coefficient of dissolve O₂ in the solution
$\nu$: the kinematic viscosity of the solution
$\omega$: the angular frequency of rotation
Under Potential Deposition (UPD) method

Cu monolayer (ML) was UPDed on Pt at 0.328 V for 10 min.

Experimental

0.05 M $\text{H}_2\text{SO}_4$ + 2 mM CuSO$_4$

2 mM HAuCl$_4$

Au ML/Pt/C catalyst was prepared by replacement of Cu$_{\text{UPD}}$ atoms with Au atoms.

$3\text{Cu}_0 + 2\text{Au}^{3+} \rightarrow 3\text{Cu}^{2+} + 2\text{Au}_0$

Fig. 6 Schematic illustration for Au ML/Pt/C preparation.
Results and Discussion

Durability of Pt/QC and Au 1ML/Pt/QC Electrode

Square durability on Pt/QC electrode

Fig. 7 CV and EQCM measurements on Pt on QC electrode. Scan rate: 50mVs⁻¹.

- Typical, Pt peaks (e.g., Hydrogen adsorption/desorption and PtOx formation/reduction) were observed in CV and EQCM measurements.
Table 1. The mass of Pt dissolutions per step calculated.

<table>
<thead>
<tr>
<th>Voltage Range</th>
<th>Pt Dissolution Δm cycle⁻¹ (ng cm⁻²Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 V</td>
<td>-0.2874</td>
</tr>
<tr>
<td>1.1 V</td>
<td>0.0898</td>
</tr>
<tr>
<td>1.2 V</td>
<td>0.6818</td>
</tr>
</tbody>
</table>

Fig. 8 The mass change of Pt measured by EQCM technique during square wave durability tests.

- Pt dissolved into electrolyte above 1.1 V.
- The amount of dissolved Pt increased with the increase of upper limit potential.
Results and Discussion

Durability of Pt/QC and Au 1ML/Pt/QC Electrode

Preparation of Au ML on Pt/QC electrode

Fig. 9 The frequency change during the preparation of Au ML on Pt/QC electrode.

Fig. 10 CVs on Bare Pt and Au ML on Pt/QC electrodes. Scan rate: 50mVs⁻¹.

Pt coverage calculated from ECSA was ca. 80%.

Atomic ratio
EQCM: \( \frac{\Delta f_{Au}}{\Delta f_{Cu}} = 0.971 \)

Theoretical: \( \frac{Au}{Cu} = 0.667 \)

- The atomic ratio calculated from EQCM measurement was larger than theoretically estimated atomic ratio. In addition, surface coverage of Au ML was larger than this ratio. Therefore, Au atoms displaced not only to UPD-Cu but also to surface Pt??
Results and Discussion

Durability of Pt/QC and Au 1ML/Pt/QC Electrode

Square durability on Au ML/Pt/QC electrode

Fig. 11 The mass change on Au ML/Pt/QC measured by EQCM technique during square wave durability tests.

Table 2 The mass of Pt dissolutions per step calculated.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Pt/QC</th>
<th>Au ML/Pt/QC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 V</td>
<td>-0.2874</td>
<td>-0.3188</td>
</tr>
<tr>
<td>1.1 V</td>
<td>0.0898</td>
<td>-0.0713</td>
</tr>
<tr>
<td>1.2 V</td>
<td>0.6818</td>
<td>0.0327</td>
</tr>
</tbody>
</table>

- Pt and/or Au dissolution occurred above 1.2V upper potential than on Pt/QC.
- Au ML/Pt/QC dissolved on 1.2 V, but the amount of dissolved Pt was suppressed by Au ML.

The durability of Pt dissolution was enhanced by Au 1ML?
The coverage of Au sub-monolayer on Pt/C lower than that on Pt/QC.
Results and Discussion

Effects of Au ML on Activity and Durability in Oxygen Reduction Reaction

Durability test

Pt/C

Au 1ML/Pt/C
[\theta_{Au} = 28\%]

- ECSA decreased with increase of potential step.
- Au ML/Pt/C had better durability than Pt/C.

Fig. 13 CVs on Au ML/Pt/C and Pt/C on GC electrodes during durability tests. Scan rate: 50mVs\textsuperscript{-1}.

Fig. 14 CVs of Pt/C on GC electrode plotted against cycle number. Scan rate: 50mVs\textsuperscript{-1}.
Results and Discussion

Effects of Au ML on Activity and Durability in Oxygen Reduction Reaction

ORR activity

Fig. 15 Activites of Pt/C, Au 1ML/Pt/C at 0.9 V for ORR in 0.1 M HClO₄.

- Au ML had larger durability than Pt/C, and SA increased after durability test.
Conclusions

- Au ML/Pt/QC and Au XML(x=1 or 2)/Pt/C electrodes were successfully prepared by UPD technique.
- Au displacement not only to UPD-Cu, but also to surface Pt was observed in EQCM measurement.
- However, the coverage of Au XML(x=1, 2)/Pt/C was much lower than that of Au ML/Pt/QC electrode.
- It shows that Au suppressed Pt dissolution during durability test by EQCM and RDE studies.
- The durability of Au XML/Pt/C has greater than that of Pt/C in $I_K$.
- This means that Au might suppressed Pt dissolution, and enhanced the SA for ORR after the durability test.