ガルバニック交換反応による1値原子層成長の偏光全反射蛍光XAFSによるその場観測

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What is Galvanic Replacement Reaction and UPD?

\[ M \text{ (solid)} + M^{2+} \text{(sol)} \rightarrow M^{+} \text{(solid)} + M^{2+} \text{(sol)} \]

If the \( M^{+} \) is more noble.

\[ \text{Ag (solid)} + \text{Au}^{+} \text{(sol)} \rightarrow \text{Au (solid)} + \text{Ag}^{+} \text{(sol)} \]
\[ \text{Zn (solid)} + \text{Cu}^{2+} \text{(sol)} \rightarrow \text{Cu (solid)} + \text{Zn}^{2+} \text{(sol)} \]

UPD (underpotential deposition)

Due to the strong interaction of substrate, deposition occurs at more positive potential than the deposition potential.
Background: galvanic replacement reaction

Morphology comparison:

Polarization Total Reflection Fluorescence X-Ray Absorption Fine Structure

**XANES**  
**EXAFS**

\[ \chi(k) = 3 \sum_{i} \cos^2 \theta_i \chi_i(k) \]

\[ \chi(k) = \frac{1}{2} \sum_{i=1}^{N} \chi_i(k)(1.2 + 2.4 \cos^2 \theta_i) \]

**K-edge:**

**L\textsubscript{3}-edge:**

Fluorescence XAFS: diluted/thin  
Total Reflection: X-ray depth is only a few nm  
PTRF-XAFS: highly dispersed sample on atomically flat surface

Asakura, K. In Catalysis Spivey, J. J., Gupta, M., Eds.; RSC publishing: Cambridge
**Experimental setup**

**Glovebox: N₂**

- 0.1 M HClO₄ + 1mM Cu(ClO₄)₂
  - Full Cu UPD ML

- 0.1 M HClO₄ + 1mM H₂PtCl₆
  - SLRR for 30s

**Flow in**

**Flow out**

- During XAFS measurement
- During EC reaction

**CE**

**Sample**

**RE**

**X**

**S-pol**

**P-pol**
Pt was not fully reduced to metal state after replacement reaction.
Pt complex structure = PtCl$_4^{2-}$

Figure 2. EXAFS comparison between the experimental data and FEFF calculation for the Pt/Au(111) at $E = 0.45$ V. a) s-Polarization and b) p-polarization.

Figure 3. A PtCl$_4$ complex model on Au(111) used in the FEFF simulation. Yellow, green, and blue balls are Au, Cl, and Pt atoms, respectively. The Pt–Cl complex preserved the square planar [PtCl$_4$]$^{2-}$ structure with Pt on top of the Au atom. The Pt–Cl bond length is 0.226 nm for all four bonds, while the Pt–Au distance is 0.270 nm.
EXAFS simulation using FEFF code – Mixed model of PtCl$_4$ and Pt-Pt bond

F-test for PtCl$_4$ and Pt metal mixture model

\[
R_{avg}^2 = \frac{R_s^2/\varepsilon_s^2 + R_p^2/\varepsilon_p^2}{1/\varepsilon_s^2 + 1/\varepsilon_p^2}
\]

\( R_{2.88} < R_{2.77} \)

Pt-Pt bond length: 2.88 Å

Acceptable range for PtCl$_4$ complex: 100% to 57%

FEFF simulation for PtCl$_4$ model with comparison of the 60% mixed model.
Ex-situ methods: XPS and STM

Pt coverage:

\[ 0.34 \pm 0.04 \text{ ML} \]

40 \pm 6 \%

\[ \text{PtCl}_4^{2-} = \pm 0.22 \]

\[ \text{Pt}^0 = 0.12 \]
Reaction stoichiometry

\[ Pt^{2+} + 2e^- \rightarrow Pt \]

<table>
<thead>
<tr>
<th>PtCl\textsubscript{4} percentage</th>
<th>CV</th>
<th>EXAFS</th>
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<tbody>
<tr>
<td>60%</td>
<td></td>
<td>100 to 57%</td>
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\[
\begin{align*}
\text{[PtCl}_6\text{]}^{2-} + Cu^0 & \rightarrow \text{[PtCl}_4\text{]}^{2-} + Cu^{2+} + 2Cl^- \\
\text{[PtCl}_6\text{]}^{2-} + 2Cu^0 & \rightarrow Pt^{0} + 2Cu^{2+} + 6Cl^- \\
\text{[PtCl}_6\text{]}^{2-} + 4Cu^0 + 2Cl^- & \rightarrow Pt^{0} + 4[CuCl}_2\text{]}^{-} \\
\end{align*}
\]

Slope: 0.23 ± 0.04

PtCl\textsubscript{4} percentage: 59%

0.62 ML Cu oxidation: 136.5 \(\mu\text{C/cm}^2\)

Reduction of [PtCl\textsubscript{6}]\textsuperscript{2-} to Pt\textsuperscript{0}: 126 \(\mu\text{C/cm}^2\) Pt 0.14 ML
Proposed model

\[ [\text{PtCl}_2] = 0.60 \]

\[ \text{Pt}^0 = 0.40 \]
Conclusion

◆ Pt-Cl complex was observed after SLRR of Cu UPD layer, using *in-situ* PTRF-XAFS.
◆ PtCl₄ model was proposed based on FEFF calculation.
◆ The oxidation state of Pt was nearly 2+ based on XANES analysis.
◆ This Pt-Cl complex represented a shorter bond length comparing to [PtCl₄]²⁻, which may coming from the charge transfer from Pt to Au substrate. Pt-Pt bond distance of 2.88 Å showed smaller R factor.
◆ 60% [PtCl₄]²⁻ + 40% Pt metal model was proposed based on XAFS, XPS and CV.

\[ \mu_{\text{unpol}} = \frac{(2\mu_{s,\text{PtCl}_4} + \mu_{p,\text{PtCl}_4})}{3} \]

\[ [\text{PtCl}_4]^{2-} \text{ percentage: 59%} \]

+ spontaneous deposition of Pt on Au(111)
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Thank you for your attention!