

***ELECTROLESS DEPOSITION
OF METAL COATINGS FOR
ELECTROCATALYSIS OF FUEL
CELL REACTIONS***

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FUEL CELL ELECTROCATALYSIS

Improvement of the catalytic activity of Pt for fuel cell electrocatalysis.

☐ *Modification with ad-atoms Š Modes of action*

- 1) The third-body mechanism
- 2) The prevention of poison formation
- 3) The bifunctional mechanism
- 4) The modification of the electronic properties of the electrode surface.

☐ *Increase the catalyst utilization*

Dispersion of micro- and nano-structured metal particles on porous materials.

- ↗ Electrocrystallization
- ↗ Electroless deposition
- ‰ Two-step Procedure (electrodeposition of non-precious metal and electroless replacement by a precious metal)

ELECTROLESS DEPOSITION OF Pt ON Ti

Immersion of Ti in an aqueous 0.1 M HClO₄ solution containing 2x10⁻³ M K₂PtCl₆



Fig. 2. TEM image and the corresponding diffraction pattern of electroless deposited Pt crystals on freshly polished Ti after immersing it in 0.1 M HClO₄ + 2x10⁻³ M K₂PtCl₆ solution for 60 s.



Fig. 3. XPS spectra for Pt 4f obtained from Pt/Ti samples prepared by immersing a freshly polished Ti plate in 0.1 M $\text{HClO}_4 + 2 \times 10^{-4}$ M K_2PtCl_6 solution for: (1) 5 s; (2) 10 s; (3) 60 s. A and B: original platinum peaks; A1 and B1: deconvoluted platinum peaks; A2 and B2: deconvoluted platinum oxide (PtO) peaks.

HYDROGEN EVOLUTION ON Pt/Ti ELECTRODES

Cyclic voltammogram of the Pt/Ti electrode in 0.1 M HClO₄ and the $I(E)$ quasi-stationary polarization curve for the HER in the same solution.



Fig. 4. Quasi stationary $I(E)$ voltammogram for the HER on Pt($t_d = 10$ s)/Ti in aqueous 0.1 M HClO₄ solution. $dE/dt = 5$ mV s⁻¹.

The inset shows the cyclic voltammogram of the Pt/Ti electrode in 0.1 M HClO₄ ($v = 50$ mV s⁻¹).

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Fig. 5. Tafel plots for HER on Pt/Ti and smooth Pt electrodes in aqueous 0.1 M HClO₄ solution.

- (1) Pt ($t_d = 2$ s)/Ti
- (2) Pt ($t_d = 4$ s)/Ti
- (3) Pt ($t_d = 10$ s)/Ti
- (4) Pt ($t_d = 60$ s)/Ti
- (5) Smooth Pt.

Note

The smaller the platinum particles the higher the catalytic activity is

OXYGEN REDUCTION ON Pt/Ti ELECTRODES

The next system studied was the reduction of oxygen on Ti covered by electroless-deposited Pt in 0.1 M HClO₄ aqueous solution.



Fig. 6. Averaged current–potential curves for oxygen reduction on a Pt/Ti rotating-disc electrode in O₂-saturated 0.1 M HClO₄ ($dE/dt = 20 \text{ mV s}^{-1}$). Rotation frequency $f = 18.33 \text{ Hz}$.

- (1) Pt($t_d = 5 \text{ s}$)/Ti
- (2) Pt($t_d = 15 \text{ s}$)/Ti
- (3) Pt($t_d = 20 \text{ s}$)/Ti
- (4) Pt($t_d = 35 \text{ s}$)/Ti
- (5) Pt($t_d = 60 \text{ s}$)/Ti
- (5) Smooth Pt

GOLD SUPPORTED Pt ELECTROCATALYSTS FOR O₂ REDUCTION

Two-step procedure:

- ↘ Deposition of a less noble metal (*i.e.* Cu, Pb etc.) electrochemically
- ↘ Displacement by platinum at open-circuit potential



- ☐ The time of copper deposition was changed from 3 s to 120 s
- ☐ The displacement time with Pt was kept constant equal to 180 s.

OutTime™ and a
TRF (LZW) decompressor
are needed to see this picture.

Fig. 8. AES spectra for the system Pt/(Cu_{60s})/Au at different immersion times. (A) 0 s; (B) 60 s; (C) 120 s; (D) 180 s.

Note

Even at immersion time of 180 s the Cu amount was not fully displaced by Pt

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TIFF (LZW) decompressor
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Fig. 9. AFM contact mode images of (A) bare Au and (B) Au covered by Pt deposit.

$$t_{\text{Cu, dep}} = 60 \text{ s}$$

$$t_{\text{Pt, repl}} = 180 \text{ s}$$

- The metallic particles are almost uniformly spread on the Au substrate.
- The size of the particles is about 50 Š 100 nm in diameter and consists of agglomerated crystallites of much smaller dimensions.

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Fig. 10. Cyclic voltammogram of a Pt(Cu)/Au modified electrode in oxygen-free 0.1 M HClO₄ ($dE/dt = 50 \text{ mV s}^{-1}$).

$$t_{\text{Cu, dep}} = 60 \text{ s}$$

$$t_{\text{Pt, repl}} = 180 \text{ s}$$

➔ The cyclic voltammogram shows typical features for both polycrystalline gold and platinum.



Fig. 11. Current–potential curves for oxygen reduction on Pt(Cu_{xs})/Au rotating-disc electrodes in O₂-saturated 0.1 M HClO₄ ($dE/dt = 20 \text{ mV s}^{-1}$). Rotation rate $f = 1100 \text{ rpm}$.
 $t_{\text{Cu, dep}}$: (1) 3 s; (2) 10 s; (3) 40 s; (4) 60 s; (5) 120 s
 $t_{\text{Pt, repl}} = 180 \text{ s}$
The insets show mass-transport corrected Tafel plots.

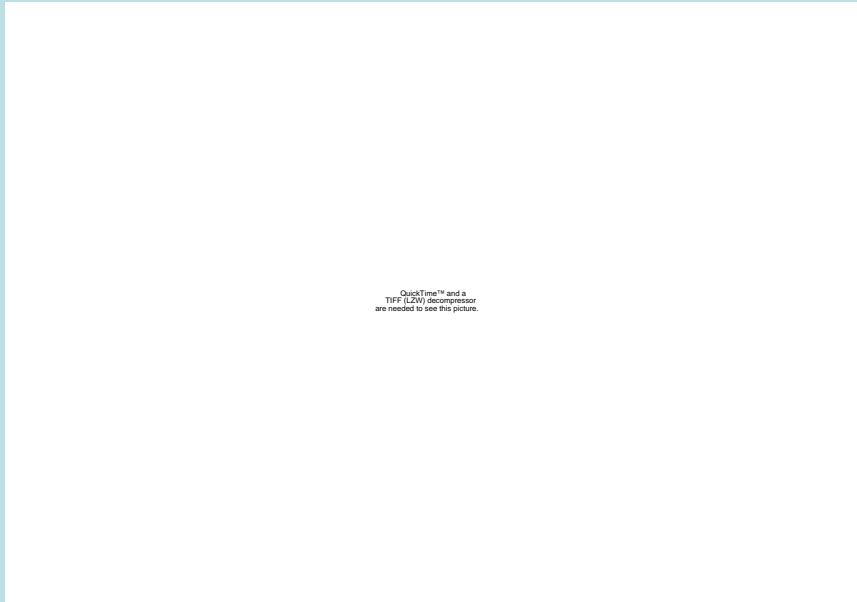


Fig. 12. Current-potential curves for oxygen reduction on Pt(Cu)/Au rotating-disc electrodes in O₂-saturated 0.1 M HClO₄ ($dE/dt = 20 \text{ mV s}^{-1}$). Rotation frequency: $f = (1) 8.33; (2) 12.5; (3) 18.33; (4) 25; (5) 33.33; (6) 50 \text{ Hz}$.

$$t_{\text{Cu, dep}} = 60 \text{ s}$$

$$t_{\text{Pt, repl}} = 180 \text{ s}$$

The inset shows plot of j_L vs. $\omega^{1/2}$.

- ❑ The catalytic activity of the Pt(Cu)/Au electrode for oxygen reduction depends on the amount of copper deposited and exchanged by Pt.

The half-wave potential increases as the amount of copper is increased, until it reaches a maximum value for 60 s of copper deposition.

- ❑ A remarkable hysteresis was observed between the forward (negative) and the backward (positive) potential scan.

Reduced platinum clusters exhibit higher catalytic activity than oxidized platinum clusters.

- ❑ The catalytic activity of reduced Pt(Cu)/Au surface is significantly higher than the activity of reduced smooth polycrystalline Pt surface.

