Dissolution Rates of Precious Metal Compounds in Acid

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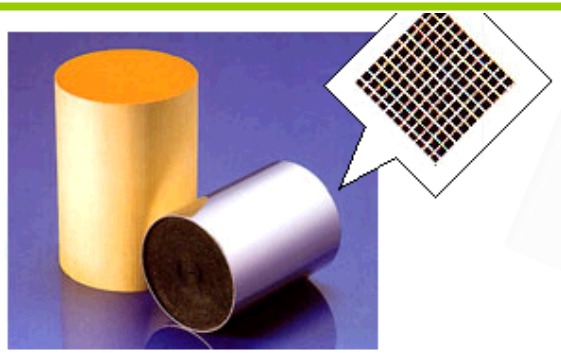
Introduction

Precious metals (Pt, Pd, Rh, Au .....) in industry

Recovery from used products ···· economically important



Pt, Pd, Rh
in automotive catalyst

Au, Pd, Ag
in electronic device

Recovery involves a large environmental load because of chemical stability
ex. Leaching requires a large amount of strong acid

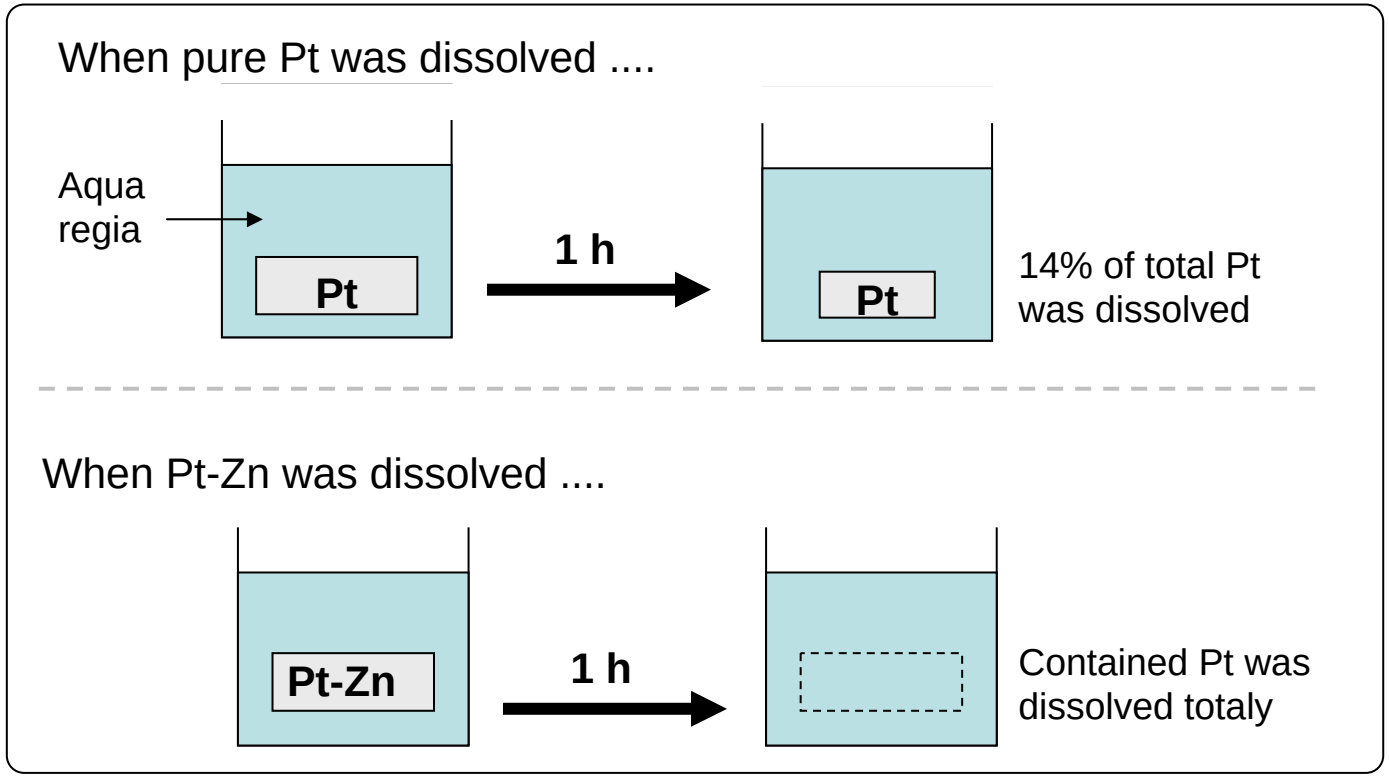
Investigative purpose

Development of a method to dissolve precious metal in aqueous solution easily

Previous work

Some precious metal compounds dissolved at higher rate than pure precious metals in aqua regia.[Ref. 1]

Compounds consisted of Pt, Pd or Rh and Ca, Mg or Zn



Ref. 1 T. H. Okabe et al., *J. Mater. Res.*, Vol. 18, 8 (2003)
T. H. Okabe et al., *Materials Transactions*, Vol. 44, No. 7 (2003)
Y. Kayanuma et al., *Journal of Alloys and Compounds* 365 (2004)
Y. Kayanuma et al.,*Metallurgical and Materiaks Transactions*, 35B (2004)

Novel recovery process

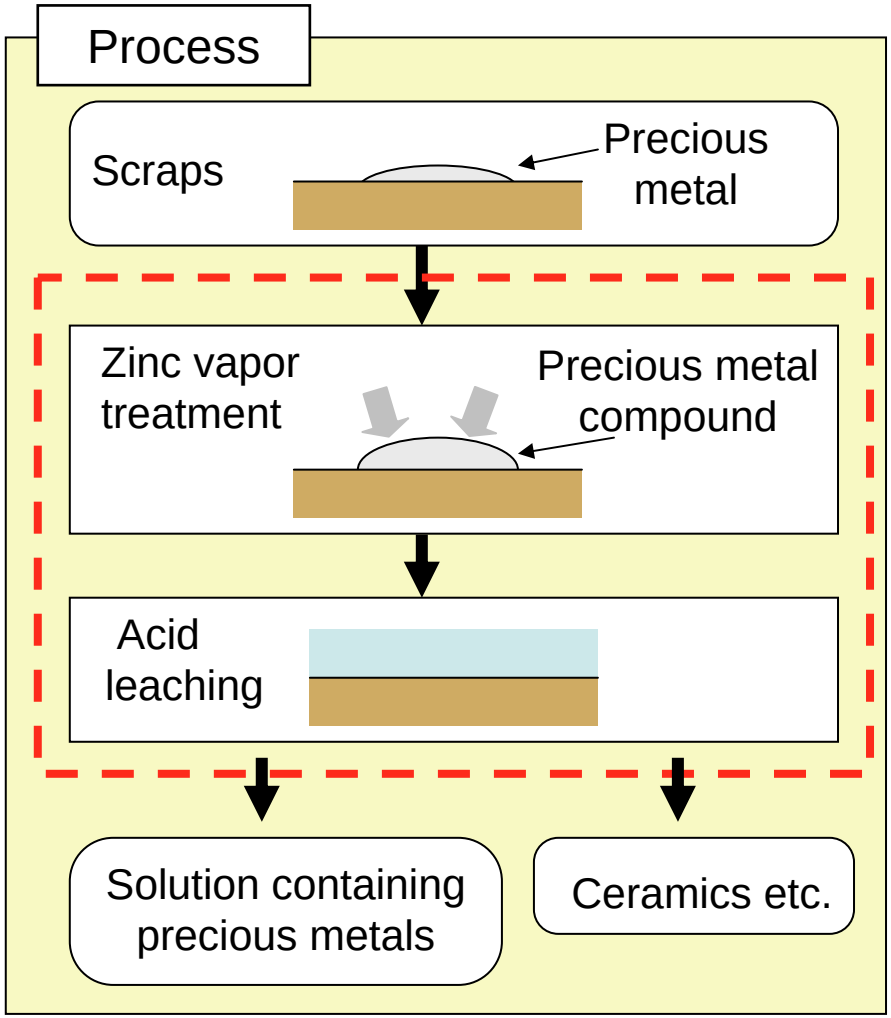


Fig. Novel recovery process for precious metal using Zn vapor

In the pretreatment Precious metals and zinc form compounds which dissolve easily

⇩

The use of acid and processing time can be reduced

Dissolution mechanism of the compounds has not been clarified.

Further investigation is required.

What compounds should be formed to dissolve precious metals easily ?

Experimental

- Compounds synthesis by exposing precious metals to Zn vapor
- Electrochemical measurement of dissolution rates of compounds

Compound synthesis

Isopiestic vapor pressure method Ref. 1

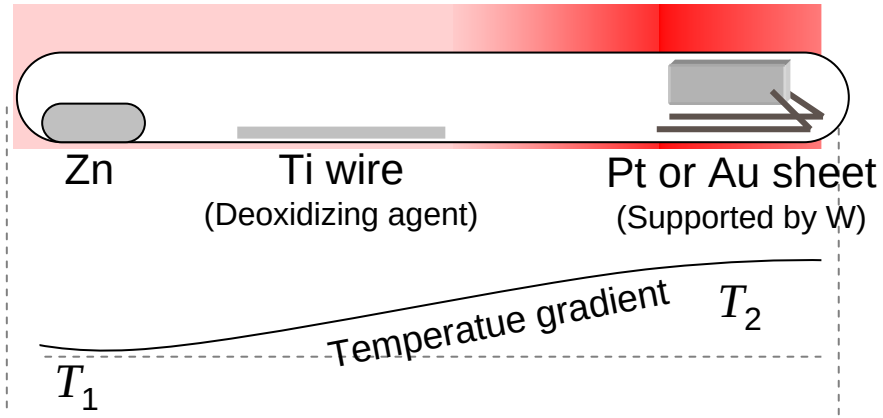


Fig. Schematic representation of synthesis method

Activity of Zn in formed compound can be controlled by temperature gradient

$$a_{Zn} = p_{Zn \text{ at } T_1} / p_{Zn \text{ at } T_2}$$

Ref. 1 S. Thimmaiah et al.; *Solid State Science*, 5, 1309-1317 (2003)

Specimens

Table List of obtained compounds

	Obtained compound	
	composition	structure
Pt-Zn	Pt-50%Zn	υ
	Pt-75%Zn	γ_1
Au-Zn	Au-40%Zn	β'
	Au-75%Zn	γ_2

Estimated from gain in weight (Homogeneity was confirmed by SEM observation)

Confirmed by XRD

Specimens

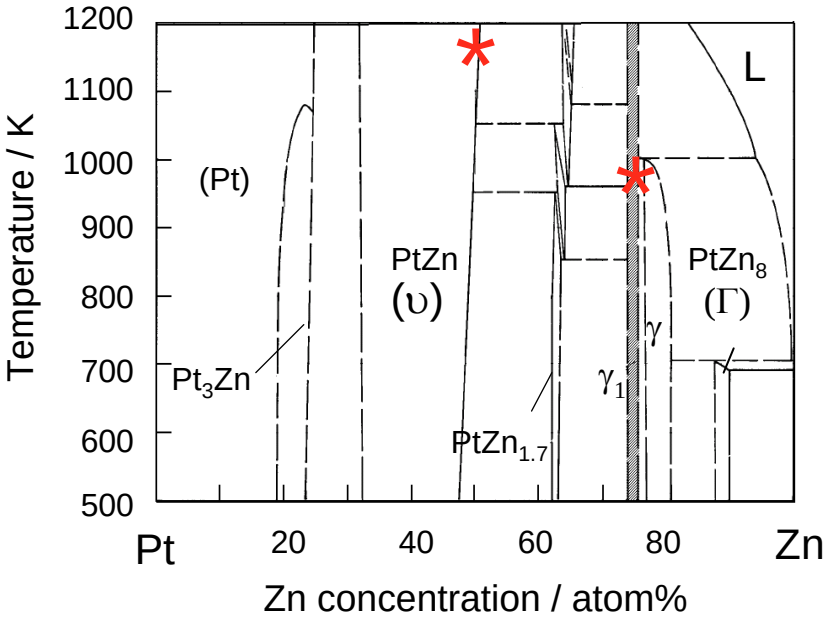


Fig. Phase diagram for Pt-Zn system [Ref .1]

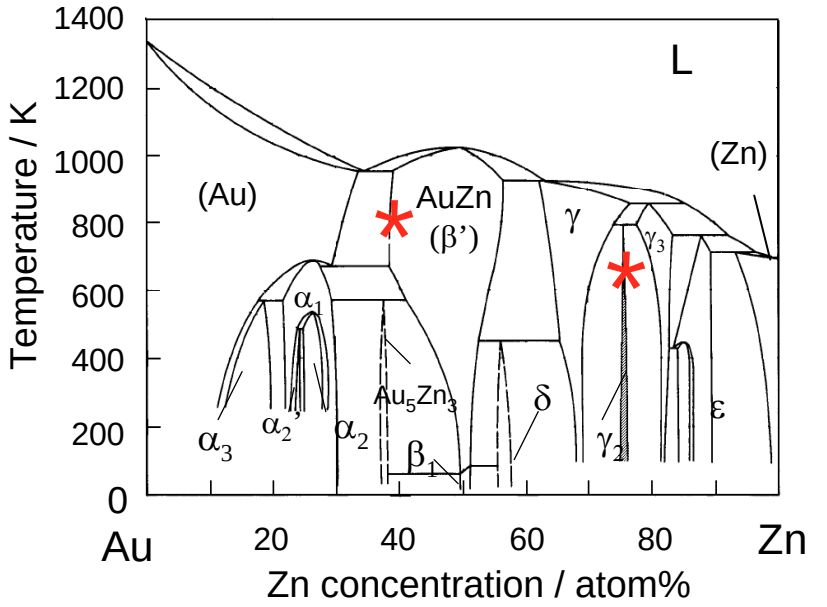


Fig. Phase diagram for Au-Zn system [Ref. 1]

Ref. 1 T. B. Massalski et al. "*BINARY ALLOY PHASE DIAGRAMS*", ASM (1986)

Channel flow double electrode (CFDE)

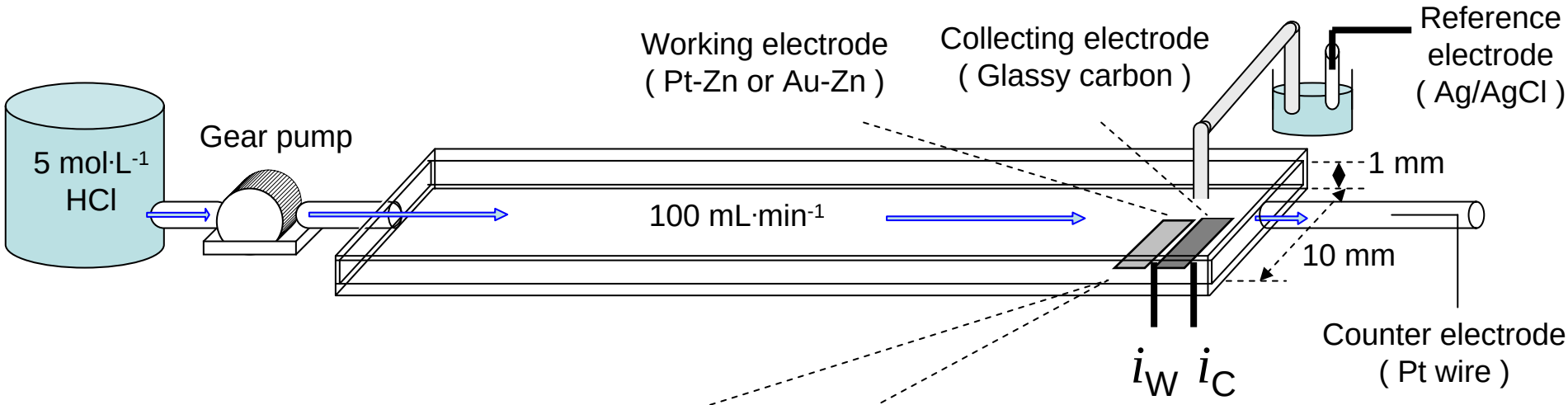


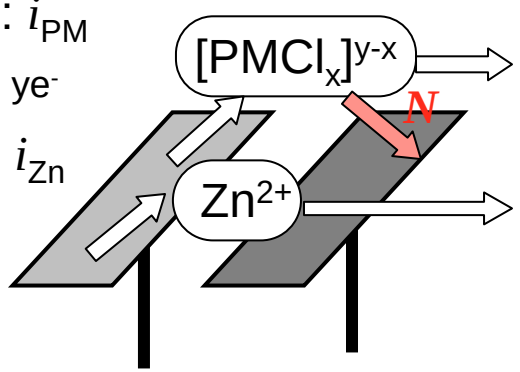
Fig. Schematic representation of CFDE

Dissolution current of PM : i_{PM}

$PM + xCl^- \rightarrow [PMCl_x]^{y-x} + ye^-$

Dissolution current of Zn : i_{Zn}

$Zn \rightarrow Zn^{2+} + 2e^-$



$i_W = i_{Zn} + i_{PM}$ $i_C = - i_{PM} \times N$

Collection efficiency (N) can be calculated theoretically from geometric parameters of electrodes Ref. 1

$$i_{PM} = - i_C / N$$

$$i_{Zn} = i_W - i_{PM}$$

(In following parts, i_{Pt}, i_{Au} and i_{Zn} represent dissolution currents of Pt, Au and Zn determined using equations above)

Ref. 1 K. Aoki et al., *J. Electroanal. Chem.*, 195, 229-249 (1985)

Potential of collecting electrode

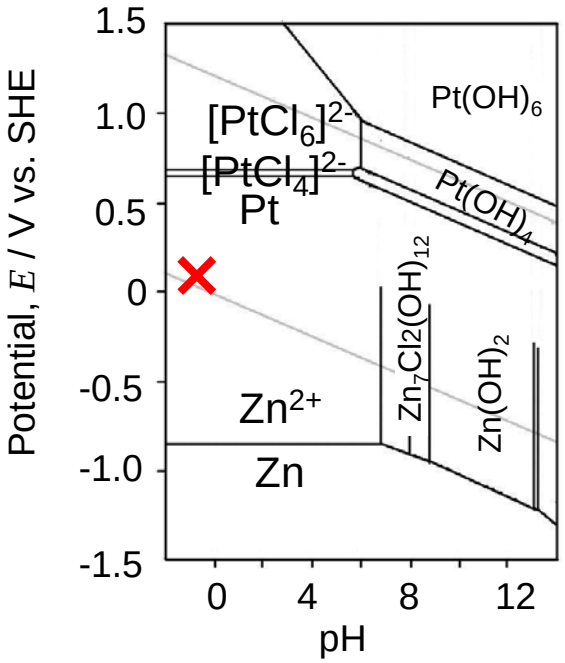


Fig. Potential-pH diagram for platinum-chloride-Water system at 298.15 K. $a_{\text{of dissolved metals}} = 10^{-3}$ and a_{Cl^-}=5. That for Zn-chloride-water system is shown together

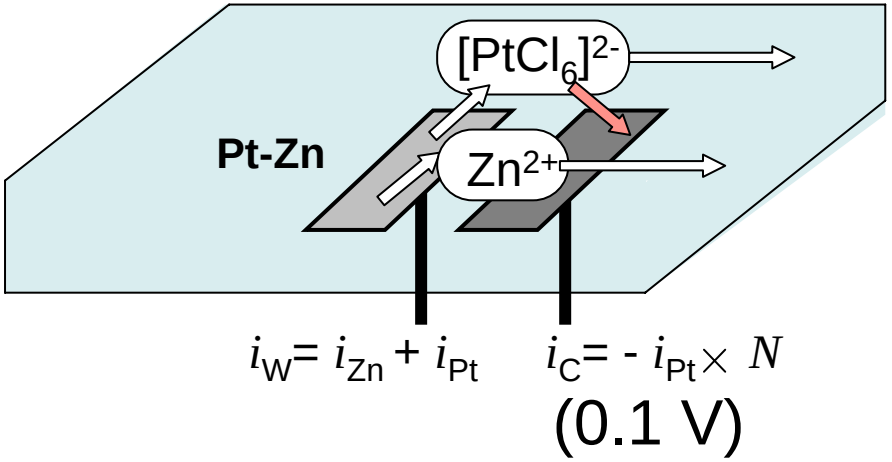


Fig. Reactions on two electrode. The collecting electrode was set at 0.1 V in order to reduce platinum ions generated on the working electrode

Dissolution of pure Pt (Preliminary examination)

Verification of the calculated collection efficiency

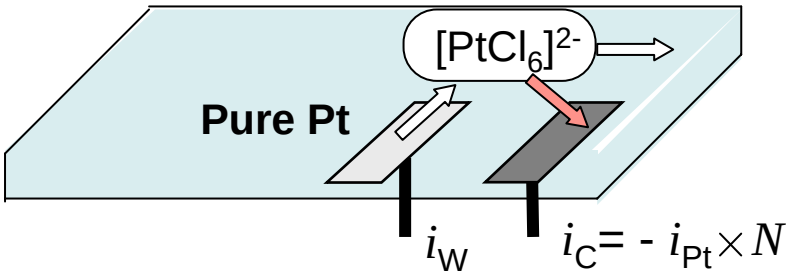


Fig. Reactions on two electrodes

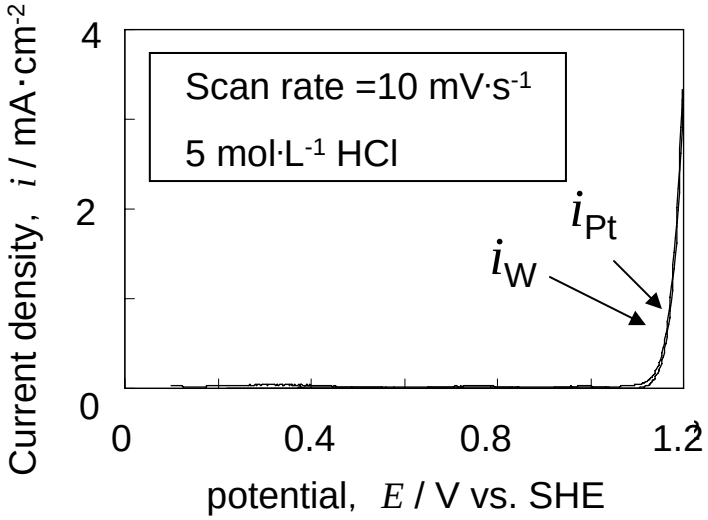


Fig. Linear sweep voltammogram obtained by Pt working electrode.

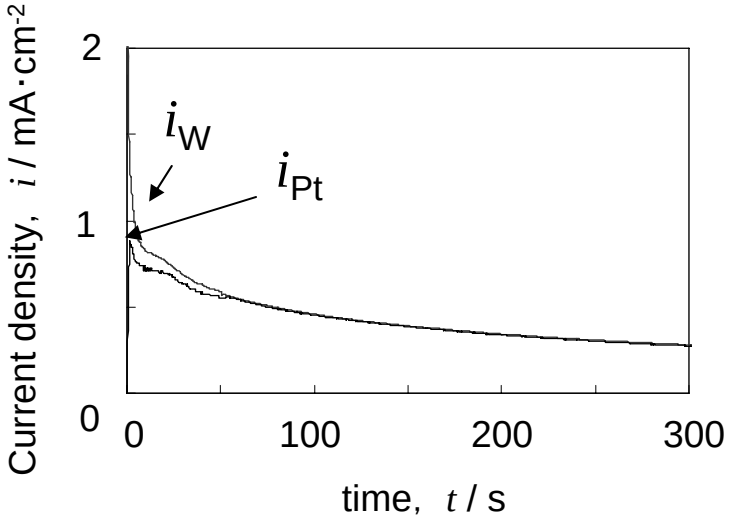


Fig. Time variations of i_W and i_{Pt} at 1.2 V.

i_W and i_{Pt} were in good agreement

⇨ Anodic current at Pt-Zn electrode can be separated into i_{Pt} and i_{Zn}

Measurement for Au-Zn

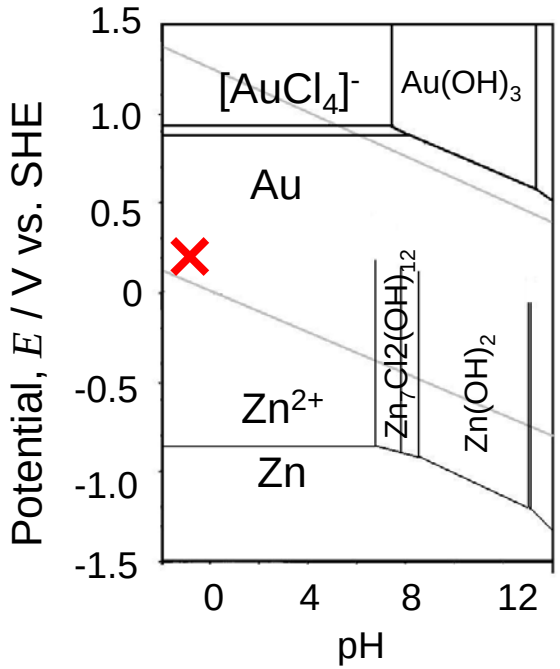


Fig. Potential-pH diagram for a gold-chloride-water system at 298.15 K. $a_{\text{of dissolved metals}}$ = 10^{-3} and a_{Cl^-}=5 [Ref. 1]. That for Zn-chloride-water system is shown together.

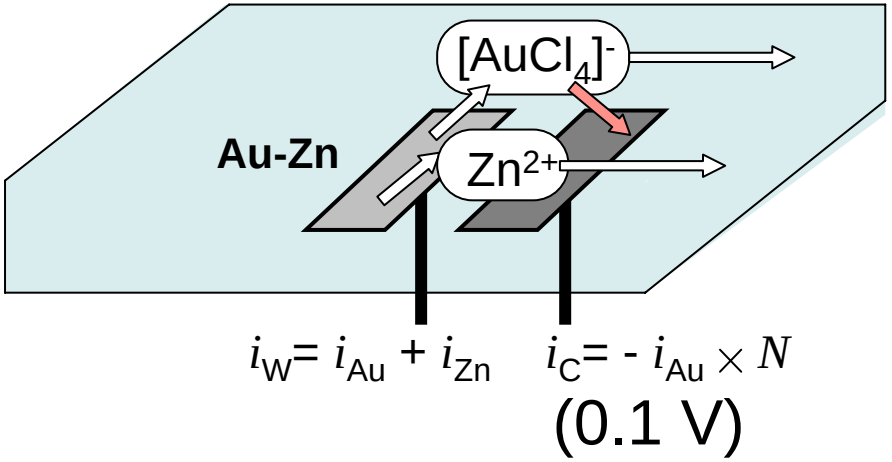


Fig. Reactions on two electrode. The collecting electrode was set at 0.1 V in order to reduce gold ions generated on the working electrode

Ref. 1 G.H. Kelsall et al.,*Journal of Electroanalytical Chemistry*, 361, 13-24 (1993)

Dissolution of pure Au (Preliminary examination)

Verification of the calculated collection efficiency

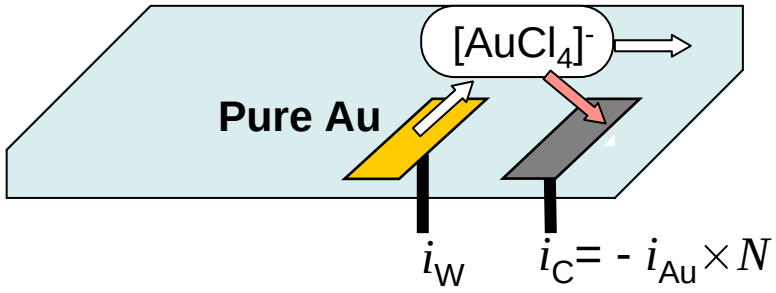


Fig. Reactions on two electrodes

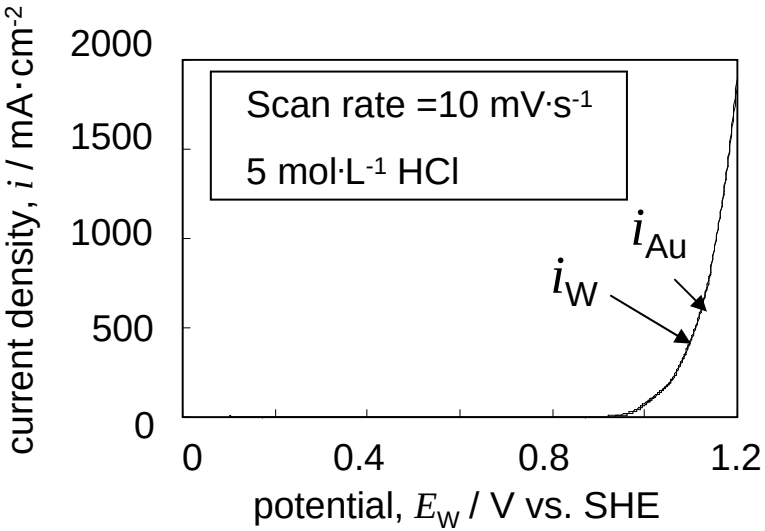


Fig. Linear sweep voltammogram obtained by Au working electrode

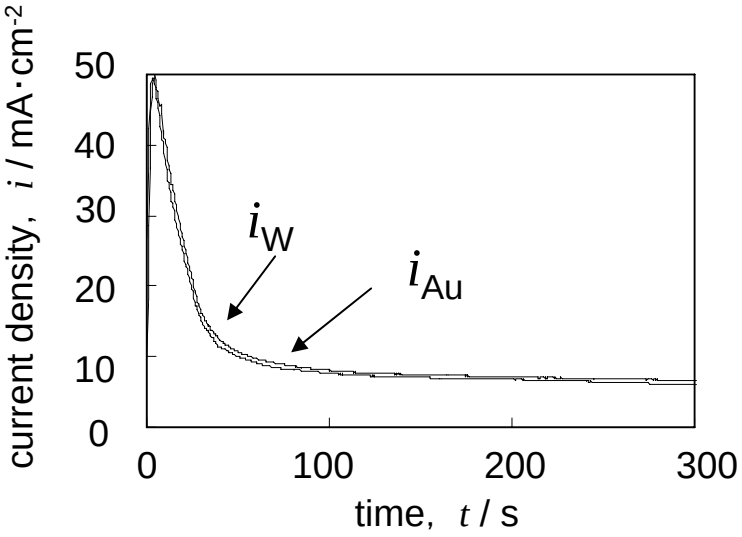


Fig. Time variations of i_W and i_{Au} at 1.0 V.

i_W and i_{Au} were in good agreement

⇨ Anodic current at Au-Zn electrode can be separated into i_{Au} and i_{Zn}

Results

Dissolution behaviors of Pt-50%Zn and Au-40%Zn

From a linear sweep voltammogram...

- Zn didn't dissolve preferentially at low potentials
- Zn and precious metals dissolved simultaneously at high potentials

During dissolution at fixed potential...

- i_{Zn} from the compounds increased with time
- i_{Pt} and i_{Au} were higher than from pure precious metals

Dissolution behaviors of Pt-75%Zn and Au-75%Zn

From a linear sweep voltammogram...

- Zn dissolved from compounds preferentially even at low potentials

During dissolution at fixed potential...

- i_{Zn} from the compounds decayed with time
- i_{Pt} and i_{Au} increased with time
  - i_{Pt} was much higher than from Pt-50%Zn.
  - i_{Au} was smaller than from Au-40%Zn.

Summary and future work

Pt-50%Zn, Pt-75%Zn, Au-40%Zn and Au-75%Zn was synthesized by exposing precious metals to Zn vapor.

Dissolution rates of precious metals from the compounds were measured by CFDE method.

- Dissolution rate of Pt was the highest from Pt-75%Zn.
- Dissolution rate of Au was the highest from Au-40%Zn.