Dissolution Rates of Pt-Zn Intermetallic Compounds in Acid

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Novel recovery process using Zn vapor

The demand for platinum as autocatalyst and its price is increasing.

The extraction of Pt from scrap is not easy

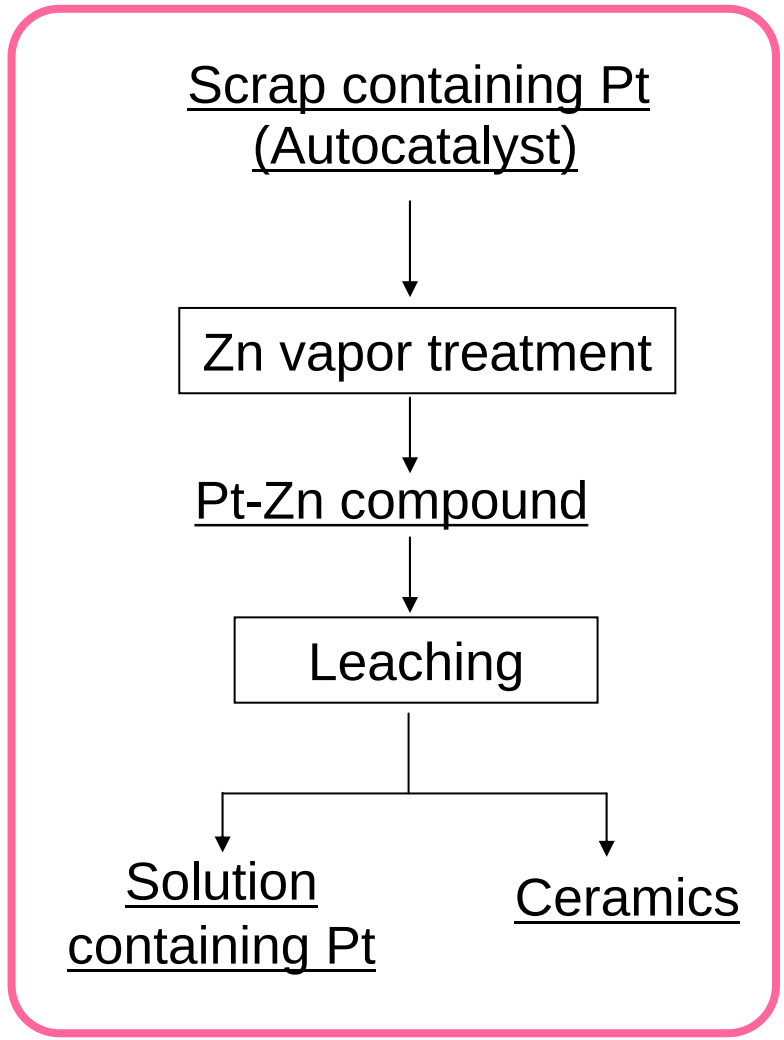
Leaching of Pt requires...

Strong acid
and
Long time

Large environmental load

We proposed a new recovery process

The processing time and use of acid in the leaching process can be reduced



Previous study

The dissolution behaviors of compounds was studied so far.
(Pt, Pd, Rh reacted with vapor of Zn, Mg, Ca [1][2][3][4])

Pt-Zn compound

The compounds were synthesized from Pt and zinc vapor, and dissolved in aqua regia.
After reaction time of 1 hour, percentage of dissolved Pt was determined by chemical analysis.

Pure Pt	14% of total Pt dissolved
Pt-Zn	Contained Pt dissolved completely

High dissolution rate of compound — Due to an increase in surface area ?

The mechanism of the dissolution of compounds has not been clarified.

→ **Further research is required (This study)**

[1] T. H. Okabe et al., J. MAter. Res., Vol. 18, 8 (2003)
[2] T. H. Okabe et al., Materials Transactions, Vol. 44, No. 7 (2003)
[3] Y. Kayanuma et al., Journal of Alloys and Compounds 365 (2004)
[4] Y. Kayanuma et al.,Metallurgical and Materiaks Transactions, 35B (2004)

This study

Investigation of the dissolution behavior of Pt from Pt-Zn compounds using electrochemical method

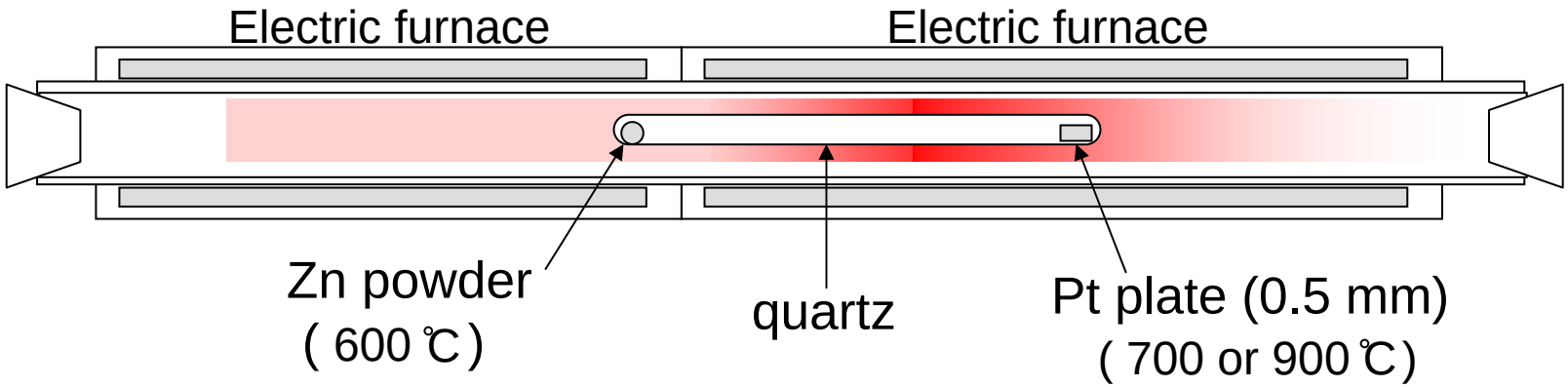
(Dependence on potential and composition)

Experimental

1. Synthesis of Pt-Zn using Zinc vapor.
2. Electrochemical measurement of dissolution rate of Pt-Zn using channel flow double electrode.

Synthesis

Isopiestic vapor pressure method

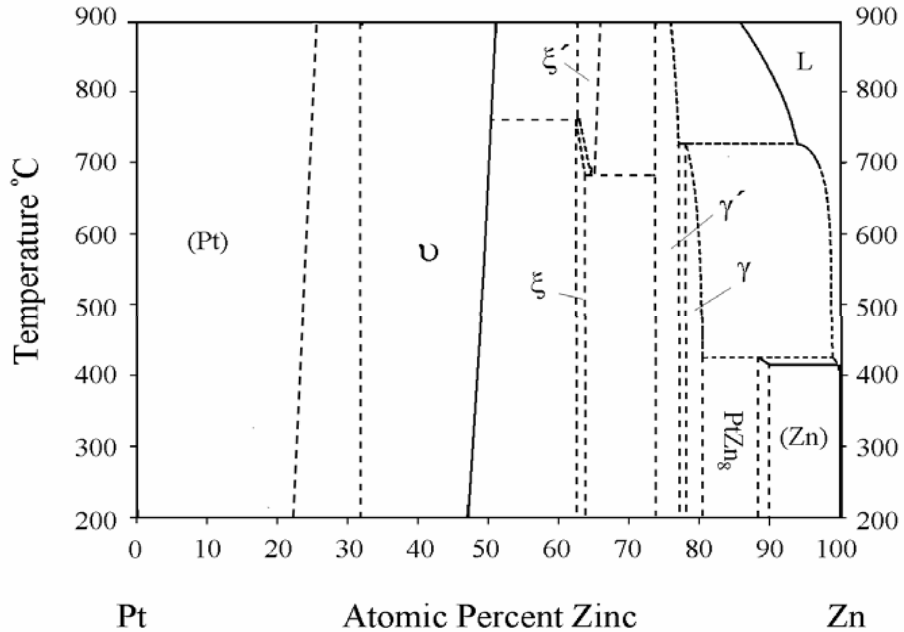


Zn vapor source ---- 600 ℃
Pt plate ---- **900** ℃
Reaction time ---- 17 days

→ Pt-52%Zn (υ phase)

Zn vapor source ---- 600 ℃
Pt plate ---- **700** ℃
Reaction time ---- 1 day

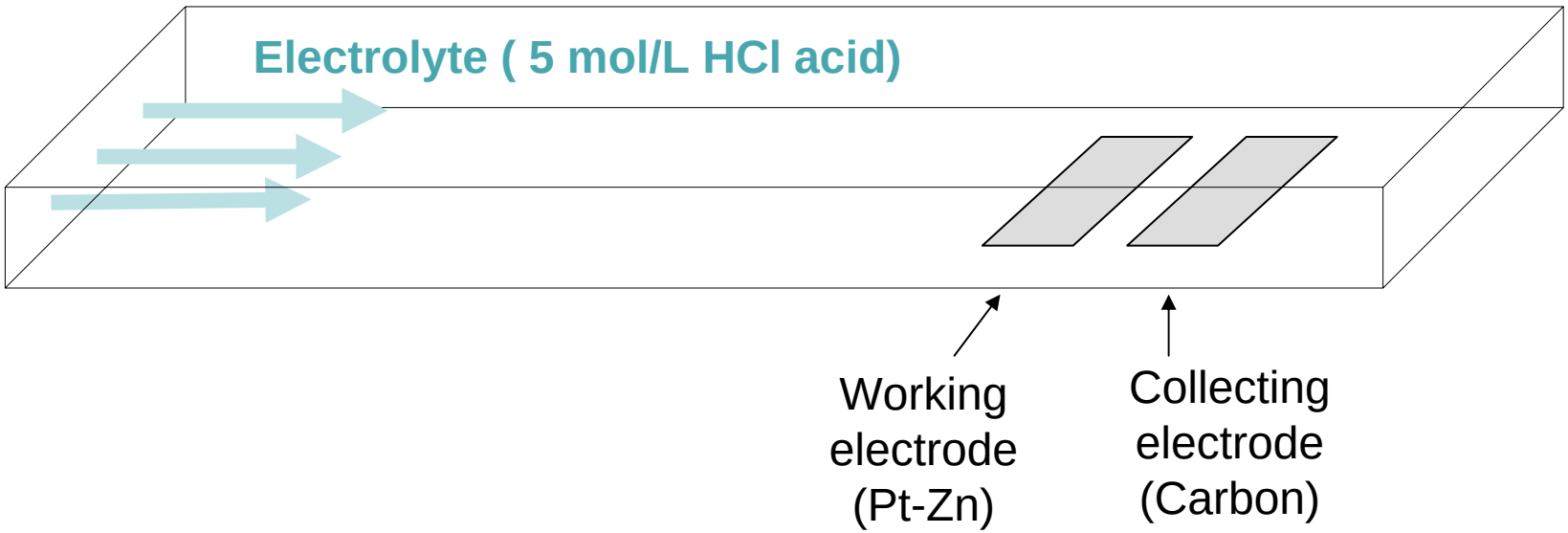
→ Pt-75%Zn (γ‘ phase)



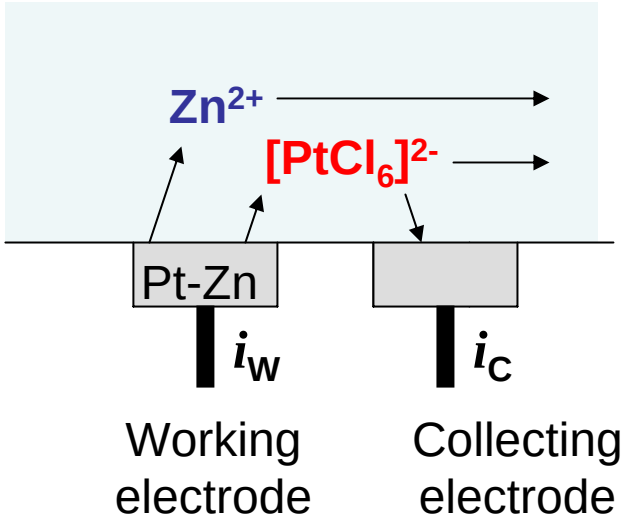
Electrochemical measurement

Channel flow double electrode（CFDE）

Schematic representation



Electrochemical measurement



$i_W = i_{Pt} + i_{Zn}$

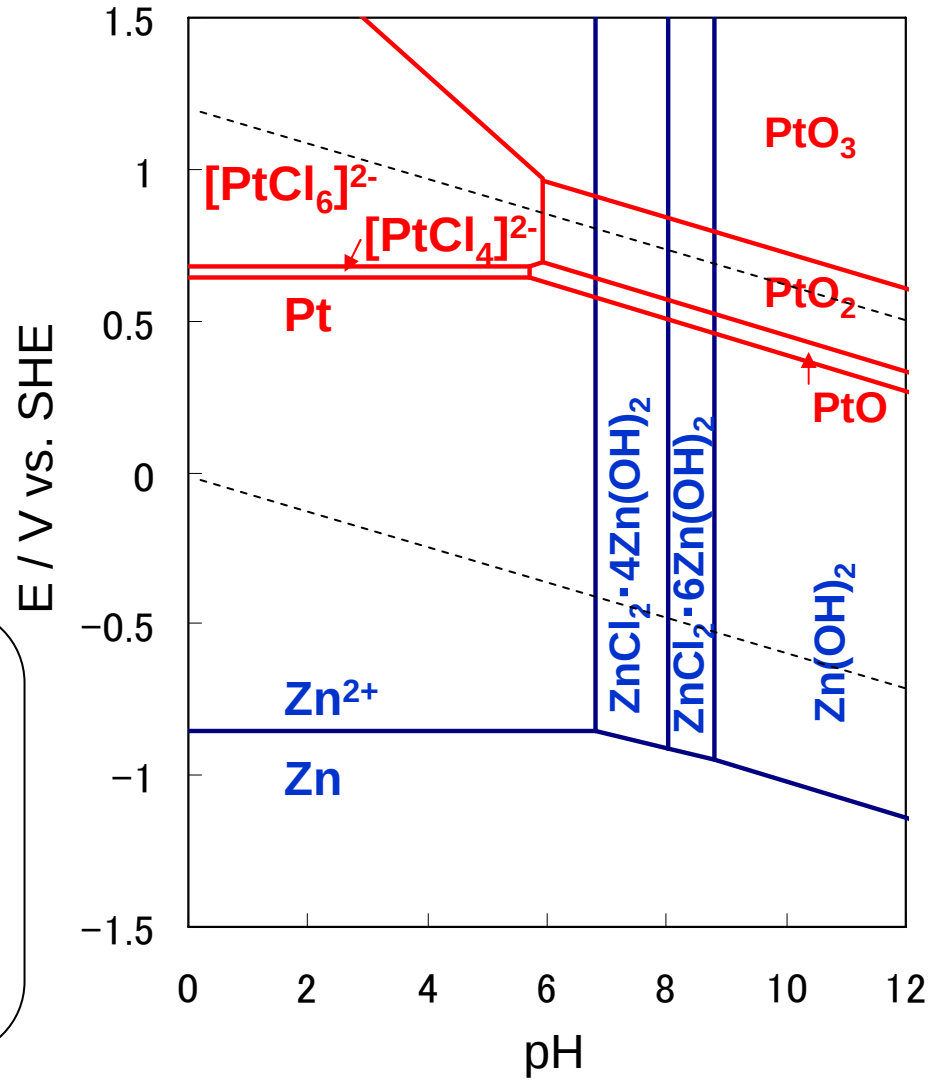
$Zn \rightarrow Zn^{2+} + 2e^-$

$Pt + 6Cl^- \rightarrow [PtCl_6]^{2-} + 4e^-$

$i_C = -N \times i_{Pt}$

Collection efficiency, N

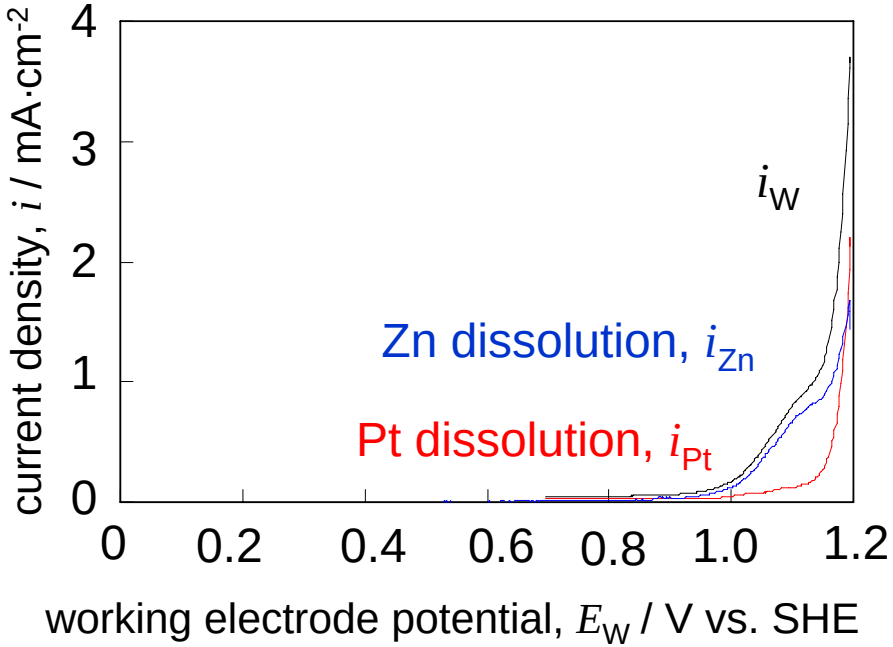
$[PtCl_6]^{2-} + 4e^- \rightarrow Pt + 6Cl^-$



Anodic dissolution of Pt-52% (υ phase)

A linear scan stripping voltammogram

Working electrode : 0.1 V →1.2 V
(10 mV·s^{-1})

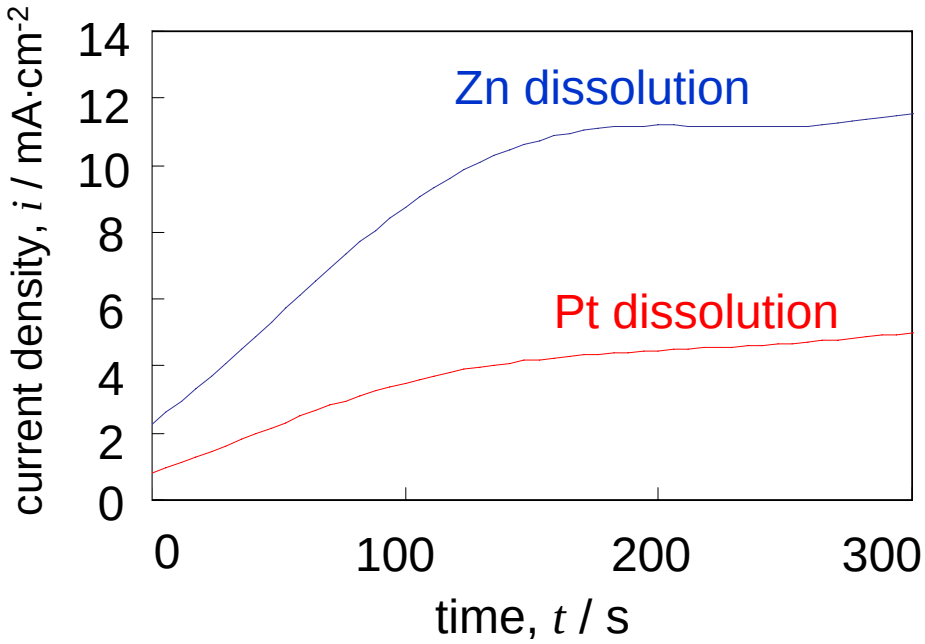


Pt dissolution current was comparable in magnitude with that of pure Pt.

Zn dissolution current was generated at the potential at which Pt dissolves（0.9 V ～ ）.

Potentiostatic measurement

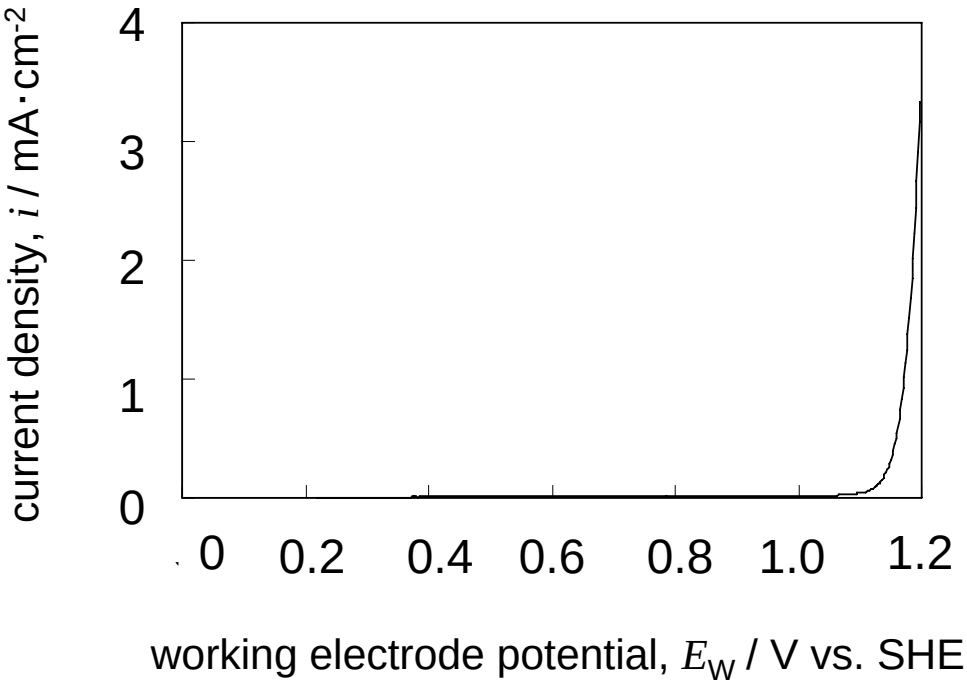
Working electrode : 1.2 V



Dissolution currents of Pt and Zn increase with time.

Pt dissolution current was about 4 mA·cm^{-2} after reaction time of 5 minutes.

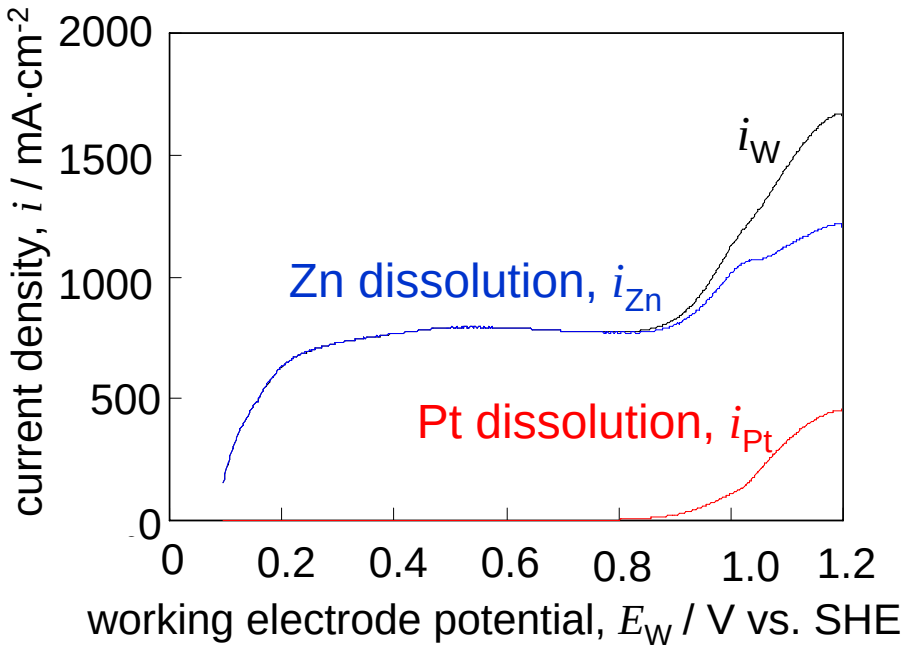
Anodic dissolution of Pure Pt



Anodic dissolution of Pt-75%Zn (γ' phase)

A linear scan stripping voltammogram

Working electrode : 0.1 V →1.2 V
(10 mV·s^{-1})

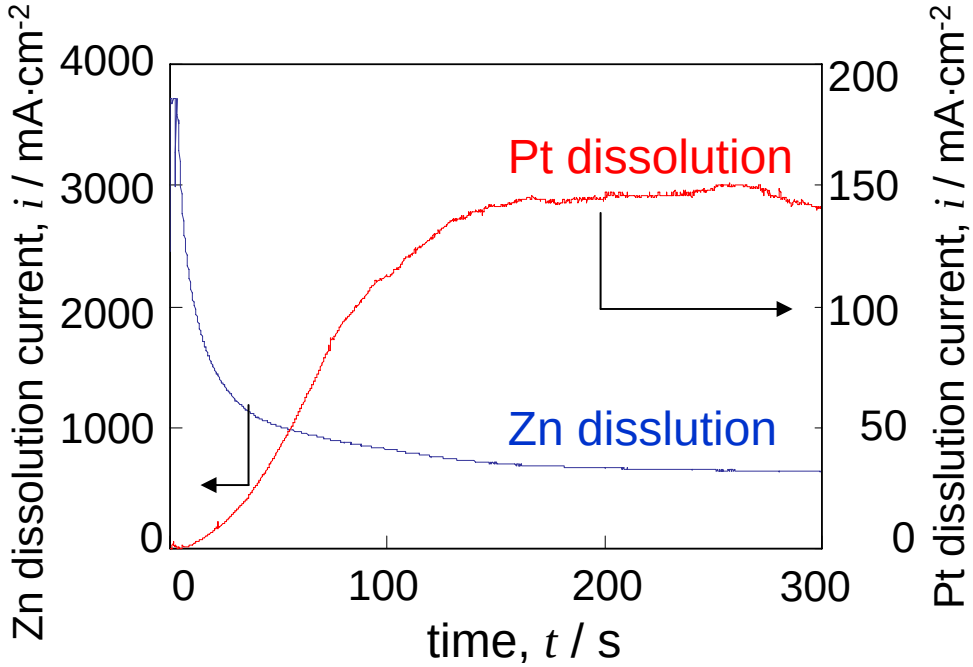


Pt dissolution current was about two orders of magnitude higher than that from υ (or pure Pt)

Zn dissolution current was generated even at the potential at which Pt doesn't dissolve.

Potentiostatic measurement

Working electrode : 1.0 V

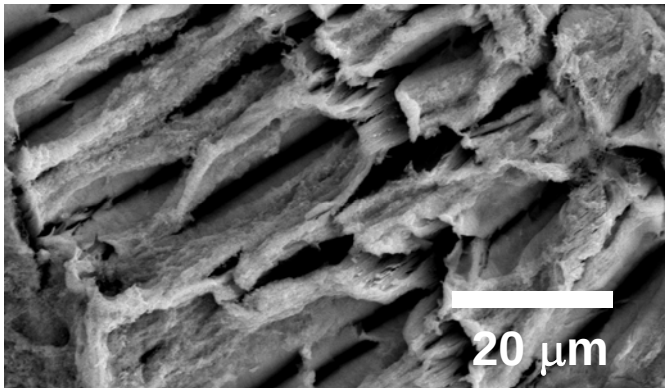


Pt dissolution current increased with time and reached about 120 mA·cm^{-2} after the reaction time of 5 minutes

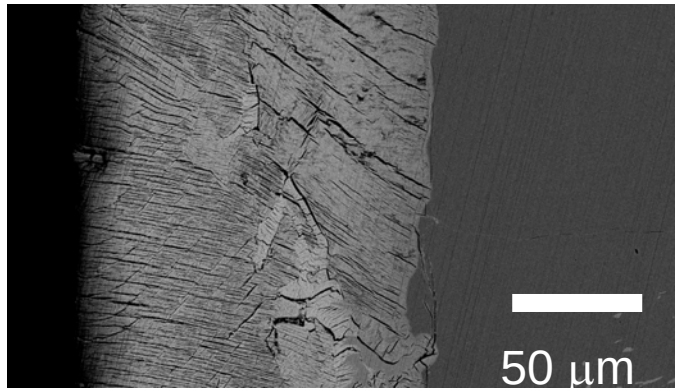
Zn dissolution current decayed with time

Changes in γ' phase caused by dissolution

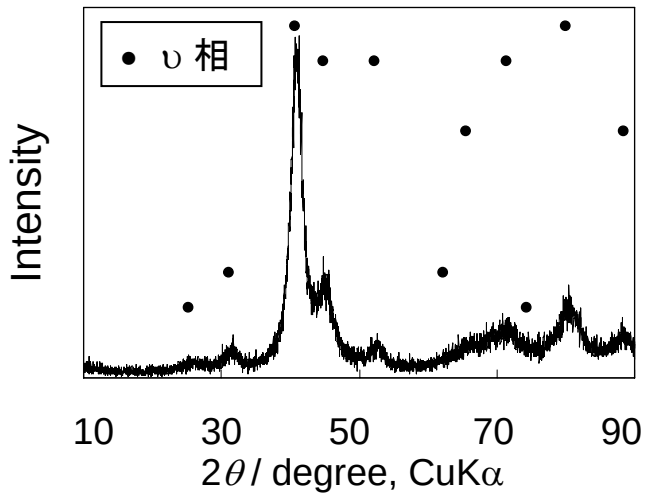
Surface morphology after 5 minute dissolution at 1.0 V



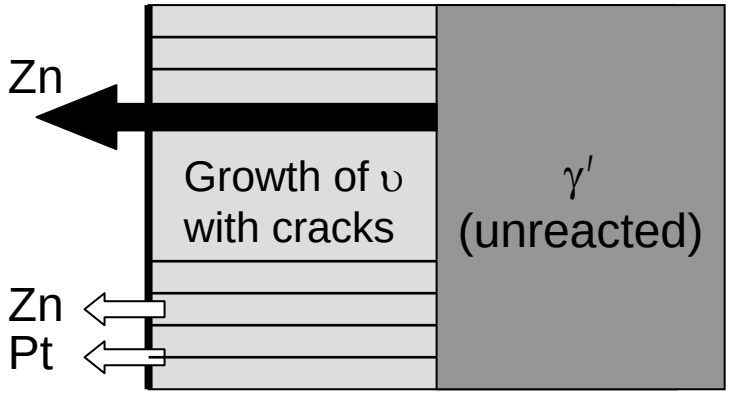
Cross-sectional surface of γ' electrode after dissolution



XRD pattern of γ' electrode after dissolution



crystallite size = 4 nm
(Estimated by Scherrer equation)



Summary

Pt-Zn intermetallic compounds（υ phase and γ′ phase）were synthesized, and the dissolution rates of Pt and Zn from these compounds were measured by CFDE.

The dissolution rate of Pt from υ electrode increased with time, probably due to increase in surface area.

The dissolution rate of Pt from γ′ electrode increased with time, as much as probably due to cracking and nanocrystallization by preferential dissolution of Zn.