

In situ Potentiometric, Resistance and Dilatometric Measurements of Palladium Electrodes during Repeated Electrochemical

Hydrogen Absorption

東京工業大学大学院 材料工学専攻

沼田 博雄

1. 目的

本研究は、Pd 棒に電解法で水素を吸蔵させ、その際の電位、抵抗および伸びの同時測定から、Pd 棒内部の組織変化を検討した。

次に、繰り返水素吸蔵・脱蔵を行い、その組織変化への影響を検討した。

1. 単一モード電解による電位、抵抗および伸び

2. Cモード電解による電位、抵抗および伸び

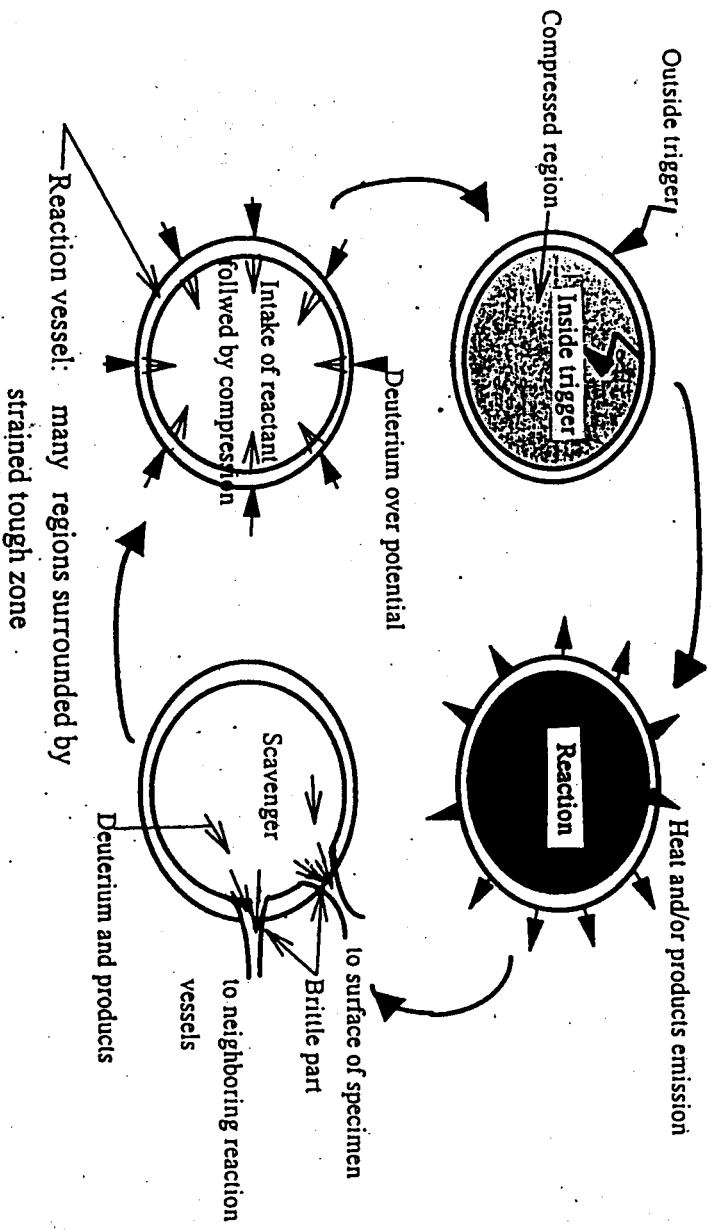
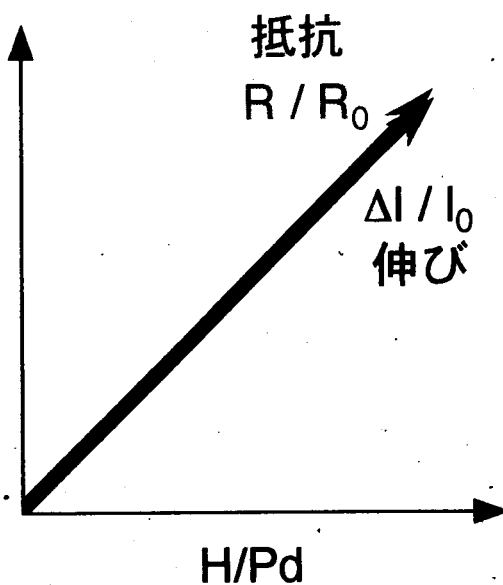
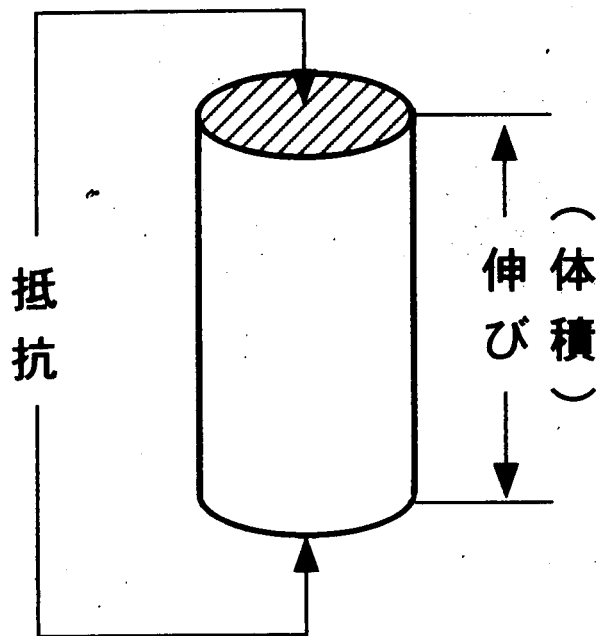
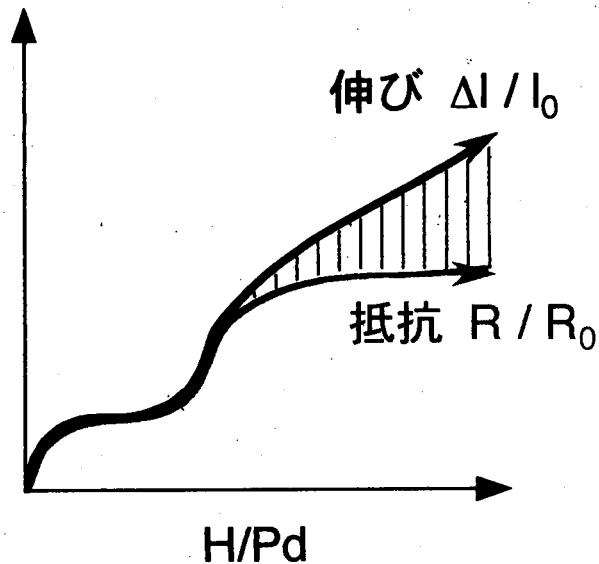
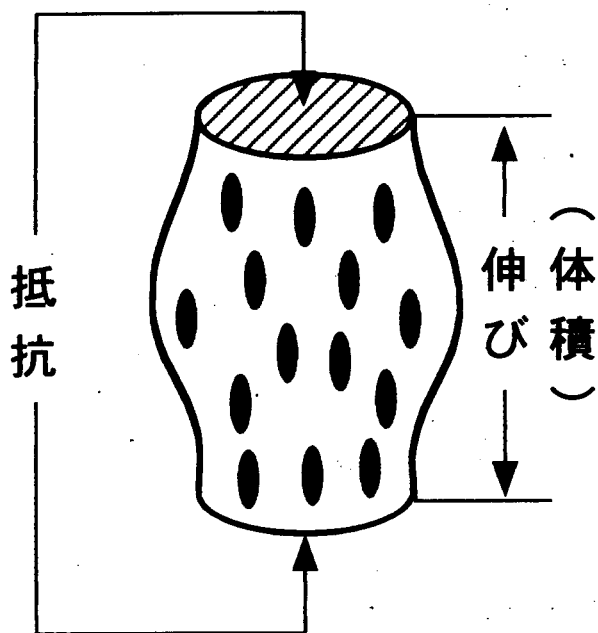


Fig. 2 Cold fusion reaction in condensed matter(Pd-D)

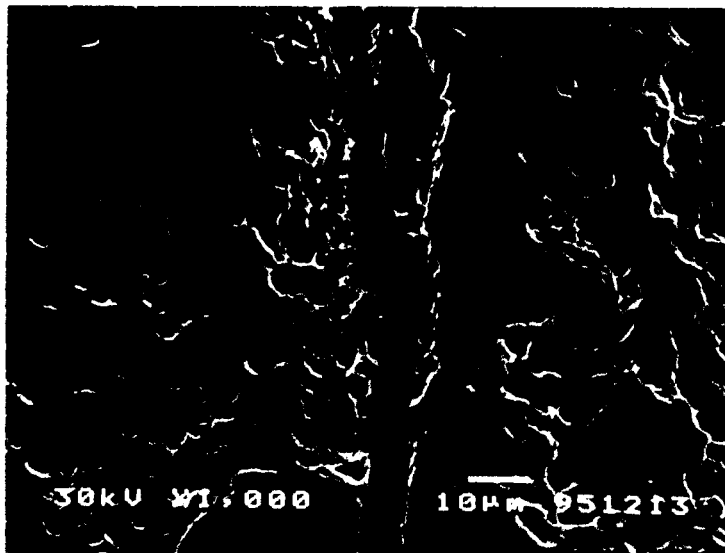
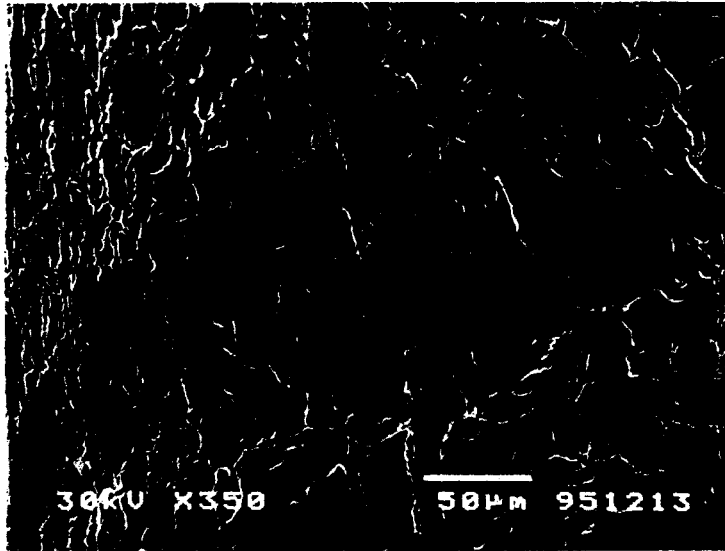
低い吸蔵比

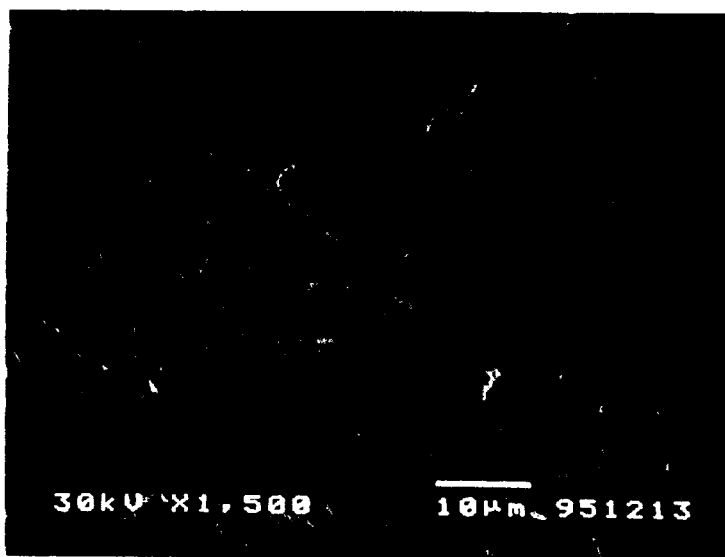
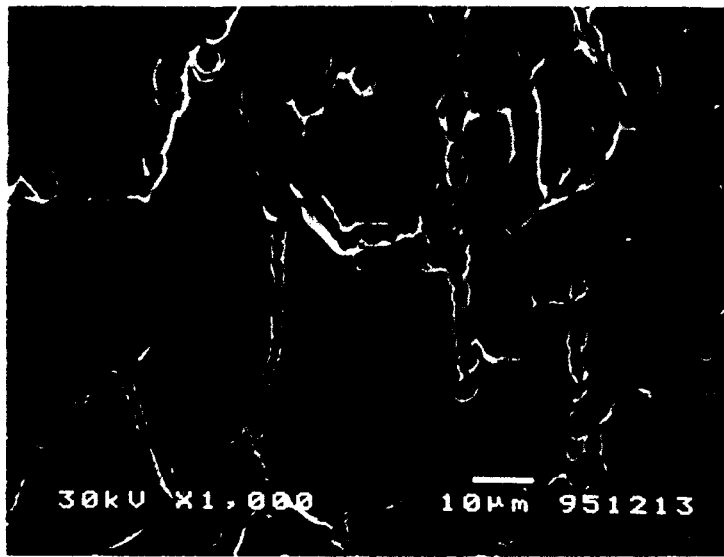


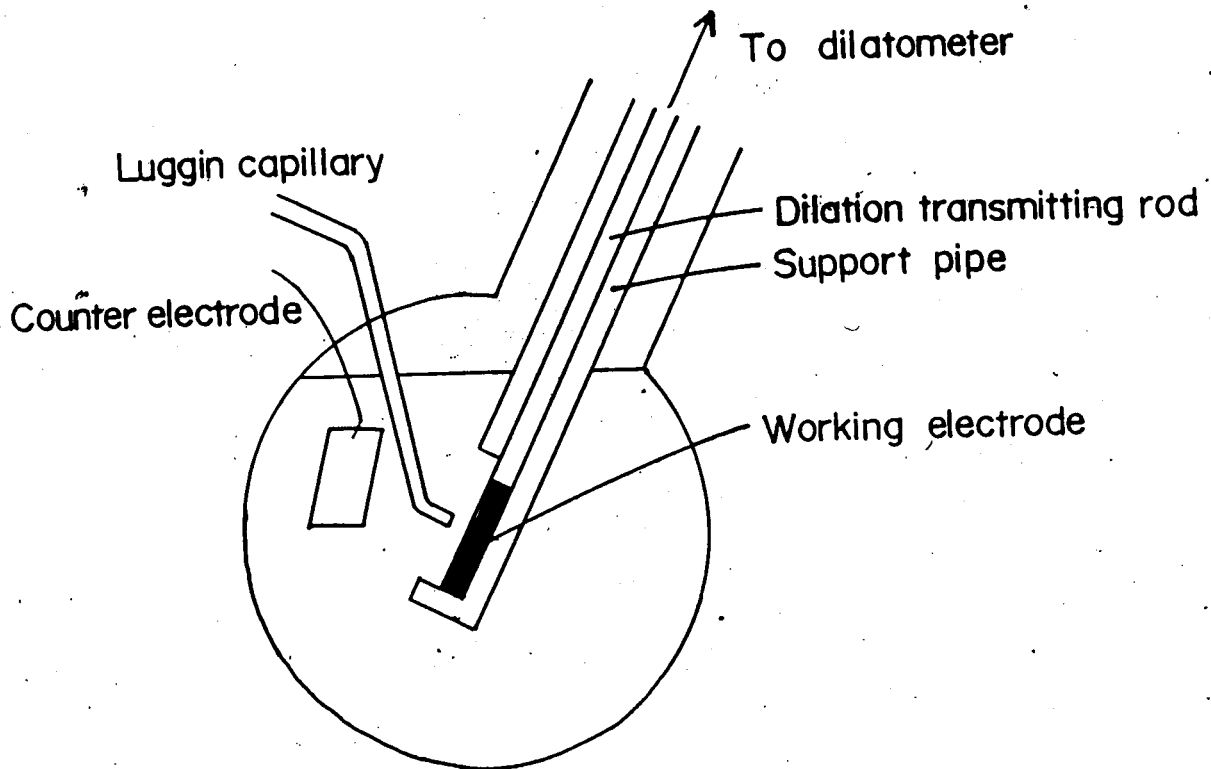
高い吸蔵比



Cモード繰り返し電解時の
電気抵抗と伸び







Schematic diagram of electrolysis cell.

Pd electrode

Dimension: 50 mm length, 2 ϕ mm Rod

Heat treatment: 3 h annealing at 800°C

Electrolyte

600 ml, Glycerin and phosphoric acid
(2:1 weight ratio)

Counter electrode

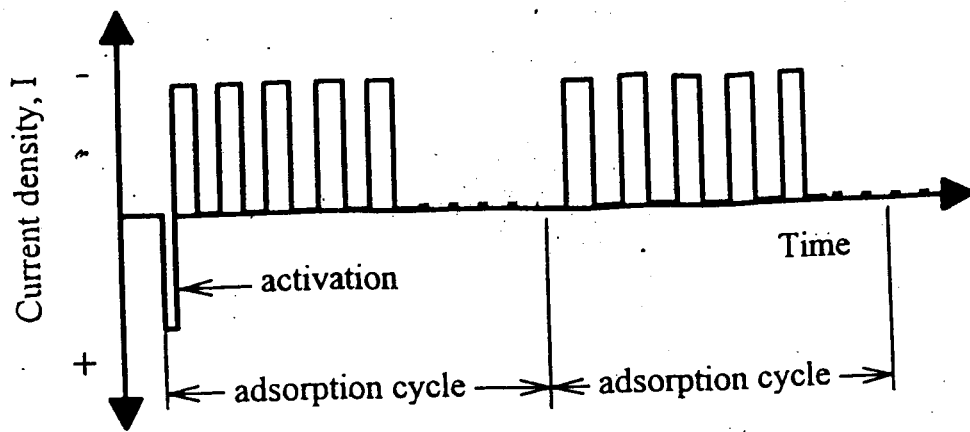
Platinized Pt 3cm²

Reference electrode

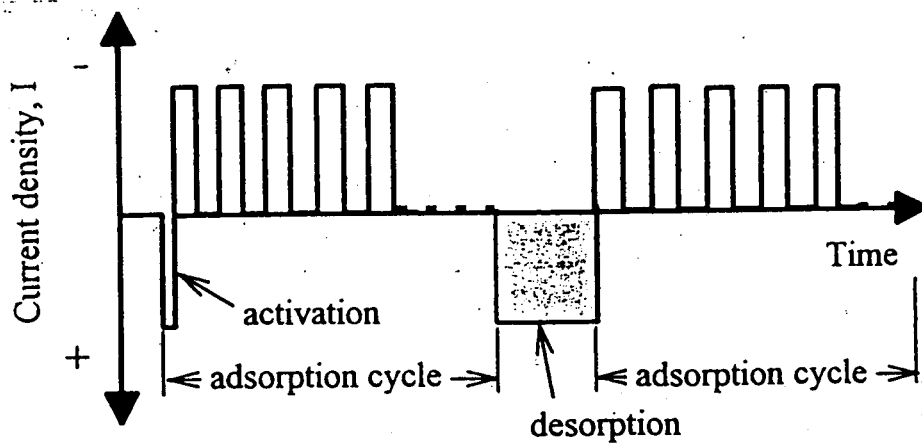
SCE

Electrolysis

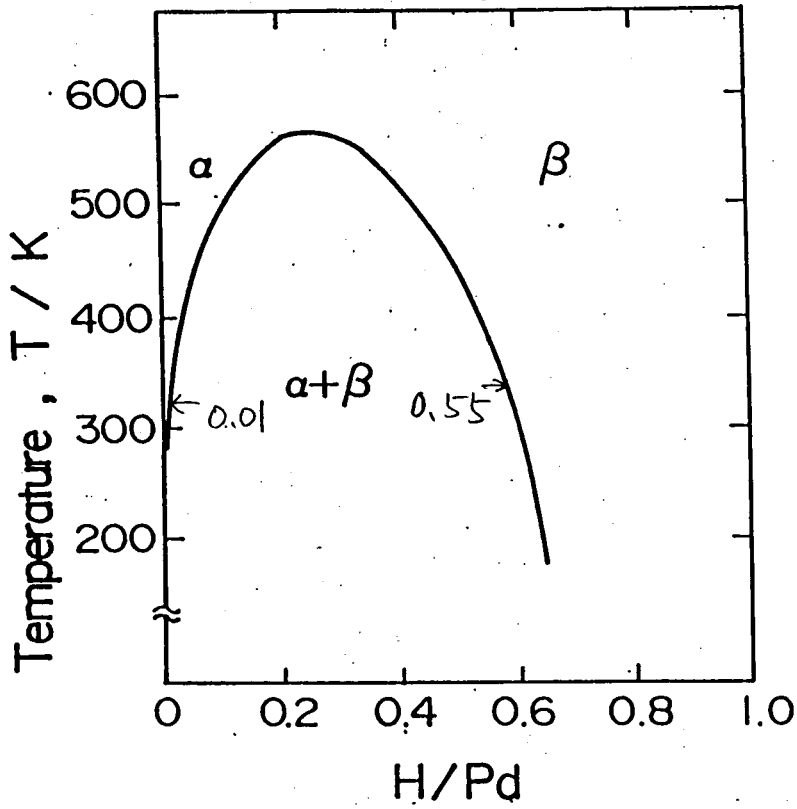
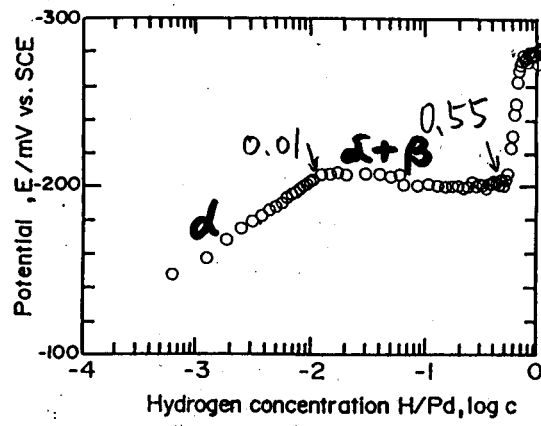
Stepwise measurement of dilation and E_{Pd} after
galvanostatic discharge of constant duration
(100 mC-35 C)



A mode electrolysis



C mode electrolysis



Phase diagram of palladium-Hydrogen system.

α phase: random occupying at 0 site

β phase: ordered phase

金属N原子中に水素がn原子固溶した場合。金属1原子の体積を Ω_H とすれば金属の体積 V_M は、

$$V_M = N \cdot \Omega_M \quad (4)$$

水素の固溶にともなう金属の体積変化 ΔV は、水素1原子の体積を Ω_H として、

$$\Delta V = n \cdot \Omega_H \quad (5)$$

$$\frac{\Delta V}{V_M} = \frac{n \cdot \Omega_H}{N \cdot \Omega_M} \quad (6)$$

水素がランダムに固溶する場合、

$$\frac{V_M}{\Delta V} = 3 \frac{\Delta l}{l_0} + 0 \left(3 \left(\frac{\Delta l}{l_0} \right)^2 \right) + \dots \quad (7)$$

であるから

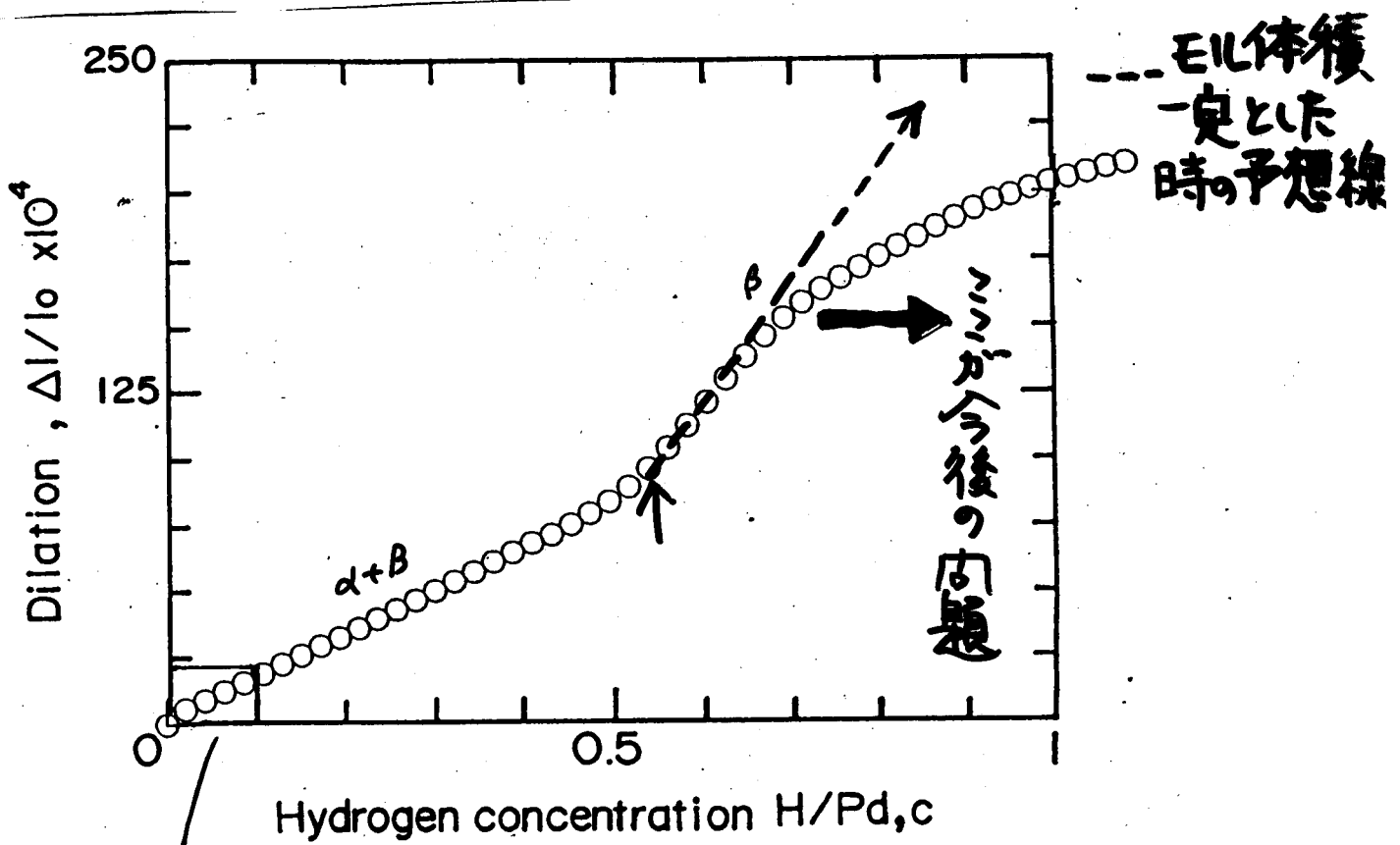
$$\frac{\Delta l}{l_0} = \frac{c \Omega_H}{3 \Omega_M} = \frac{c \bar{V}_H}{3 \bar{V}_M} \quad (8)$$

すなわち

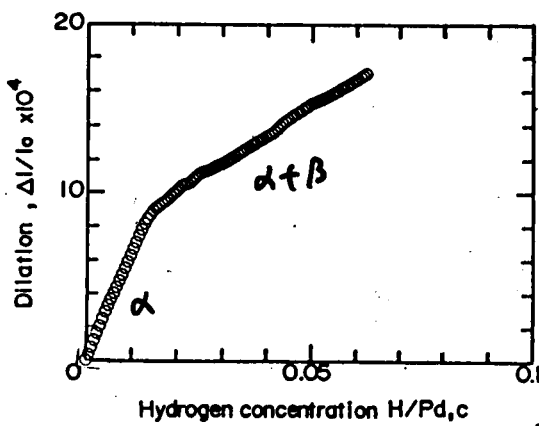
$$\bar{V}_H = 3 \bar{V}_M \frac{d(\Delta l / l_0)}{d c} \quad (9)$$



モル体積



Electrode dilation vs. Hydrogen concentration at 40. °C.



$\bar{V}_H = 1.64 \text{ cm}^3 (\text{mol H})^{-1}$ (α単相), 0.40(α+β)
 \downarrow
 $3.7 \times 10^{23} \text{ H atoms / cm}^3$ (one order higher)
 \uparrow
 $4.2 \times 10^{22} \text{ H atoms / cm}^3$ (liquid H₂)

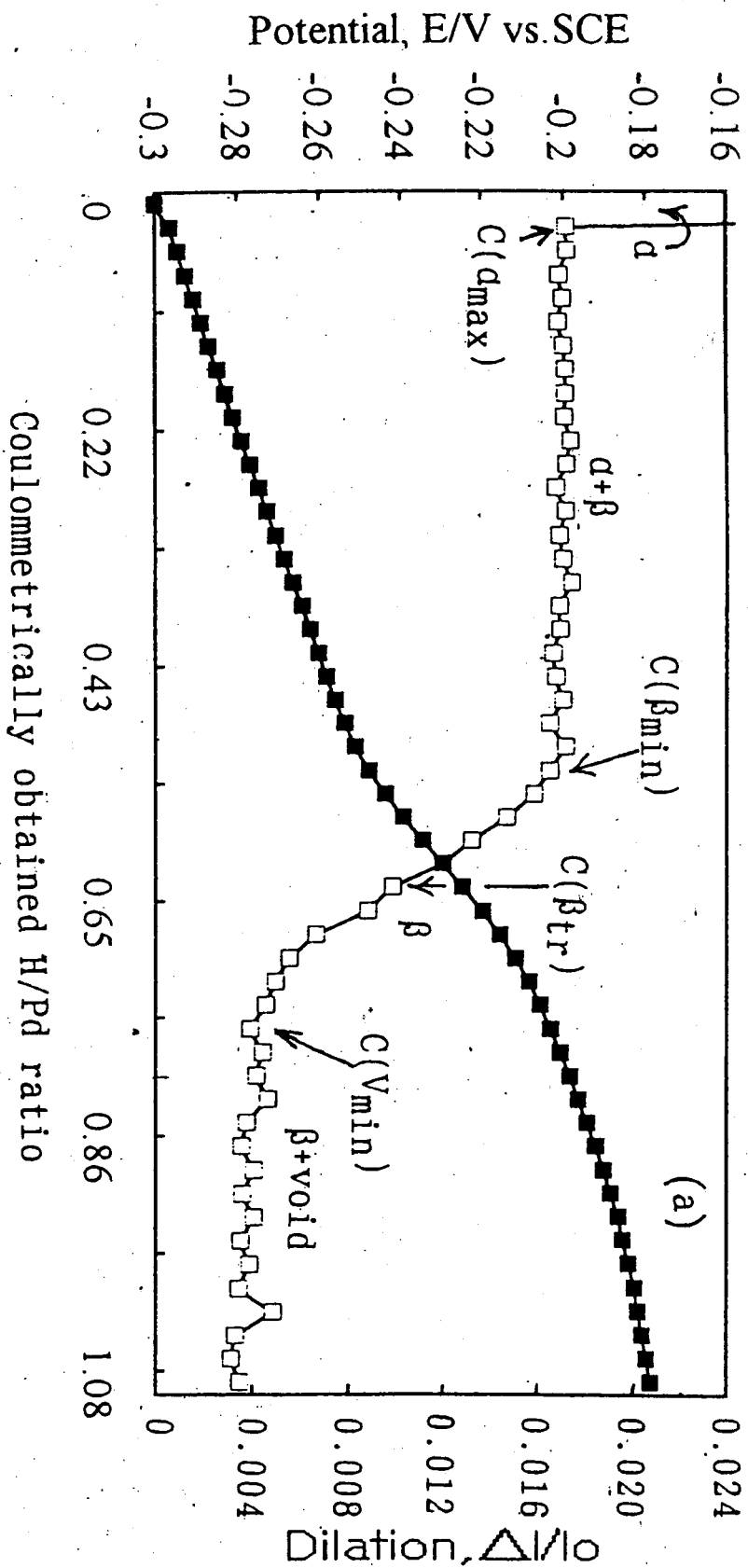
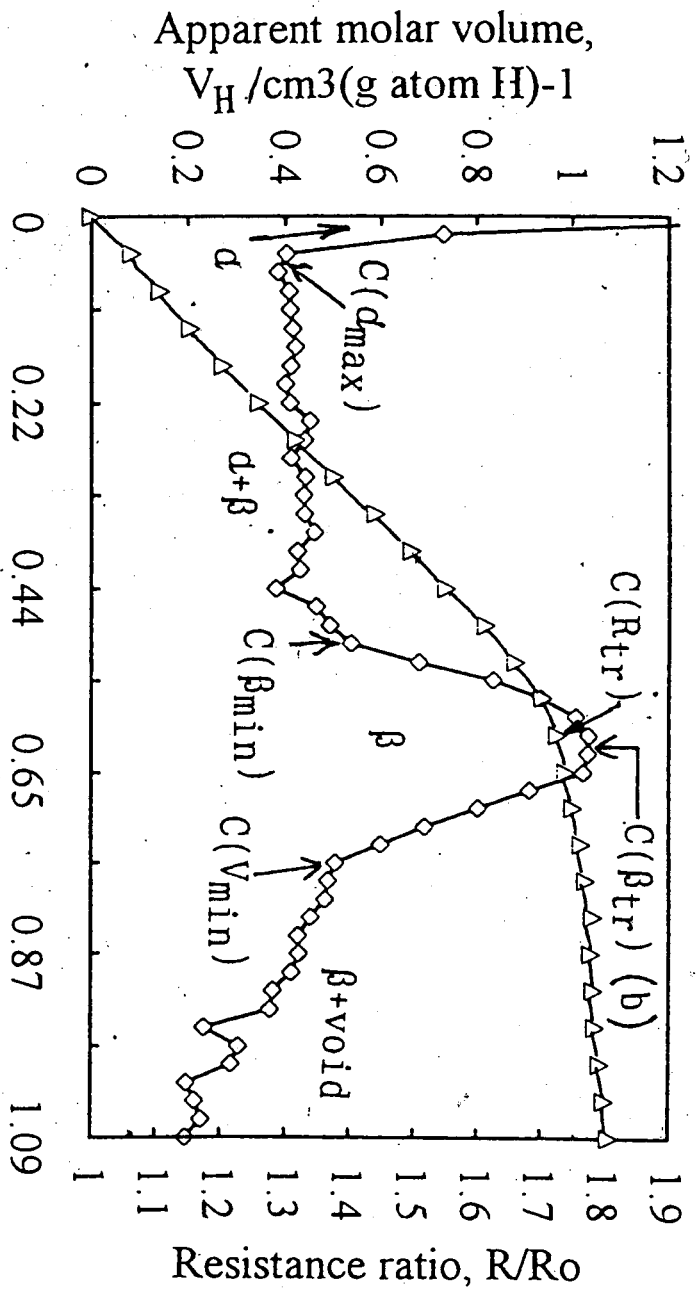


Fig. (a) (b) A mode potential dilation, resistance and apparent molar volume vs. H/Pd ratio of the first absorption at 40°C. Potential (□) and dilation (■) vs. H/Pd ratio: (a), resistance (Δ) and apparent molar volume (◇) vs. H/Pd ratio: (b)

单一毛刺電解

单一电相

Coulometrically obtained H/Pd ratio



Molar volume of hydrogen

- PdH 1.64 cm^3/mol (d phase)
- PdH 0.40 cm^3/mol ($\alpha + \beta$ phase)
- PdH 10.8, PdH 7.25
- PdH 5.15 (cm^3/mol)

PdH n (Theory)

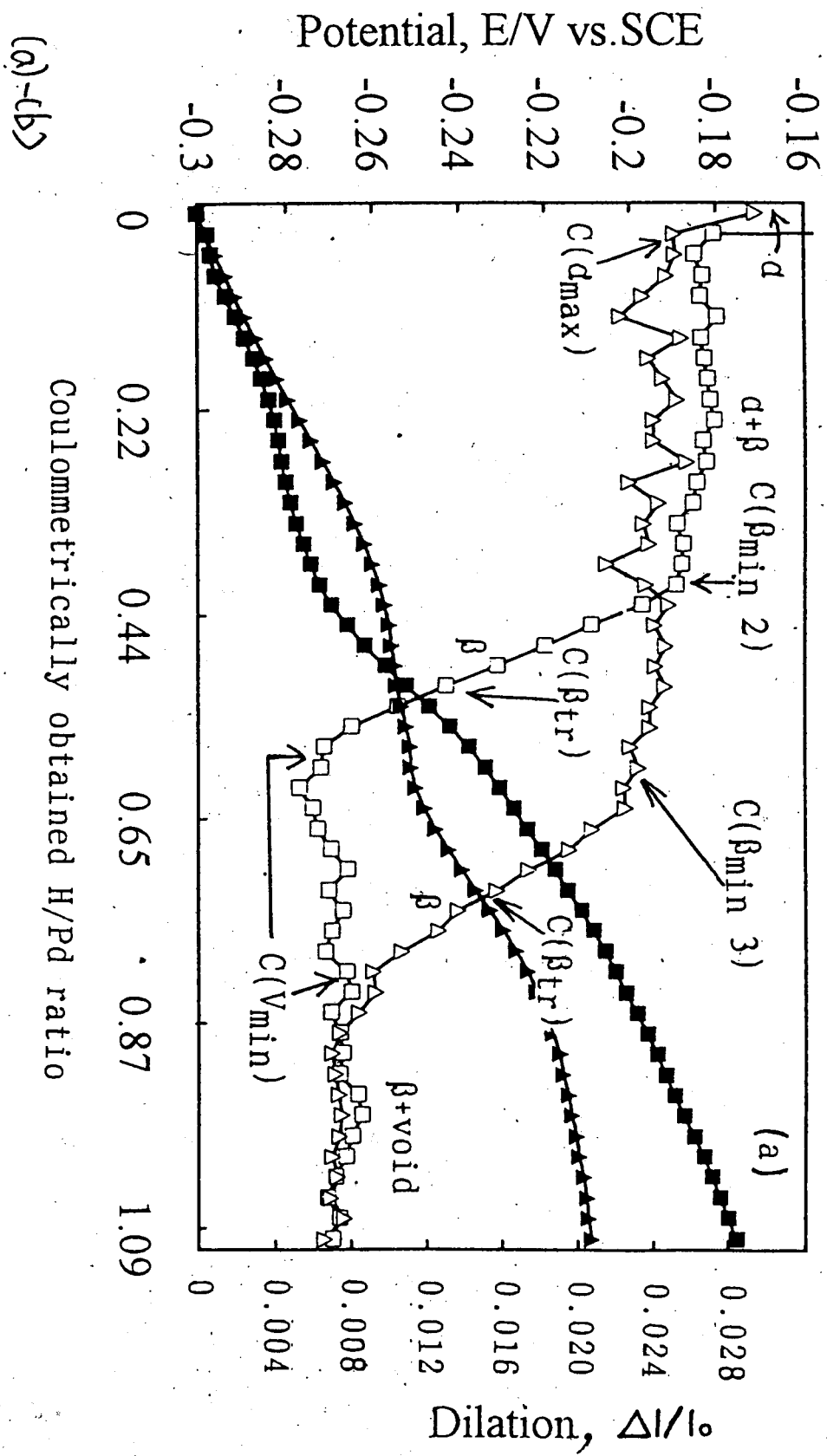


Fig. γ C mode potential, dilation resistance and apparent molar volume vs. H/Pd ratio of the second and third absorption at 40°C.
 Potential, 2nd(-□-) and 3rd(-△-) absorption, dilation of 2nd(-■-) and 3rd(-▲-) absorption: (a), Resistance(-◆-) and apparent molar volume of 3rd(-■-) and first(-□-) absorption: (b)

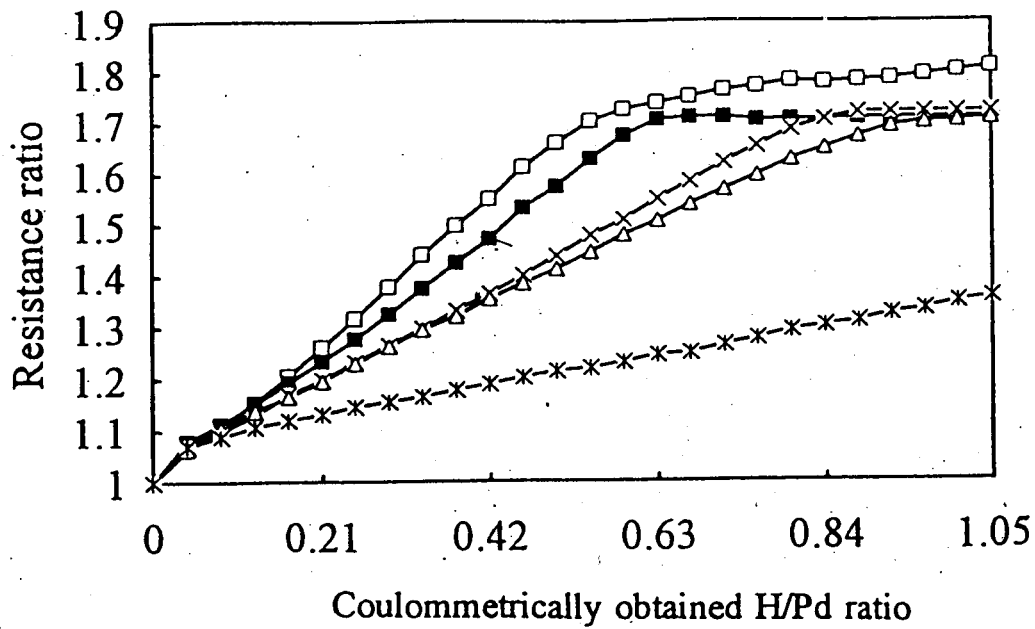
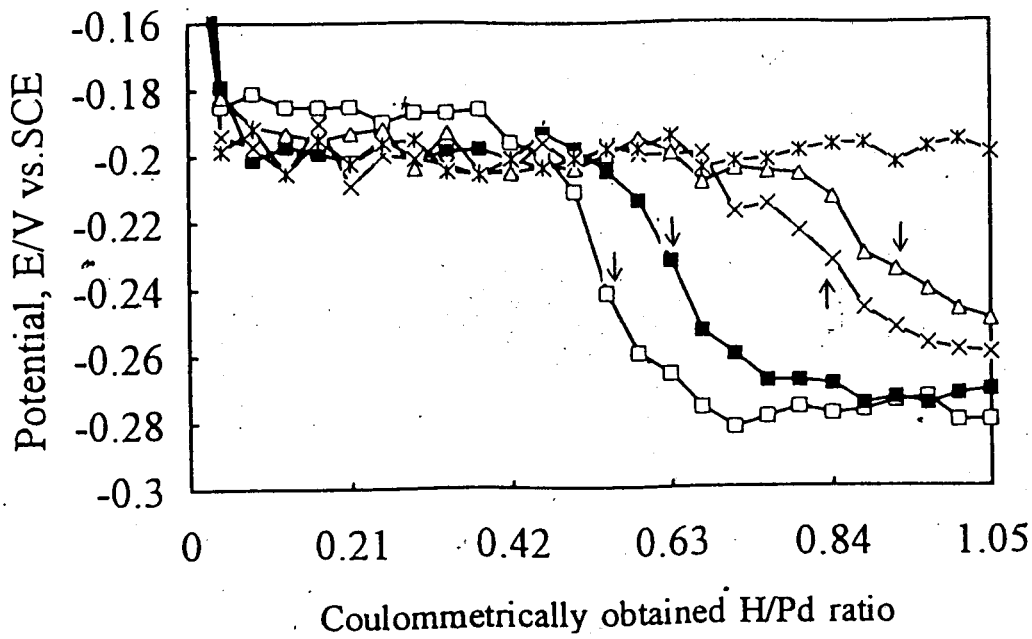


Fig. Effect of repetition number on C mode potential and resistance vs. Pd/H ratio at 40°C.

Potential, 1st(-□-), 2nd(-■-), 3rd(-X-), 4th(-△-), 5th(-*-):(a), resistance, 1st(-□-), 2nd(-■-), 3rd(-X-), 4th(-△-), 5th(-*-):(b)

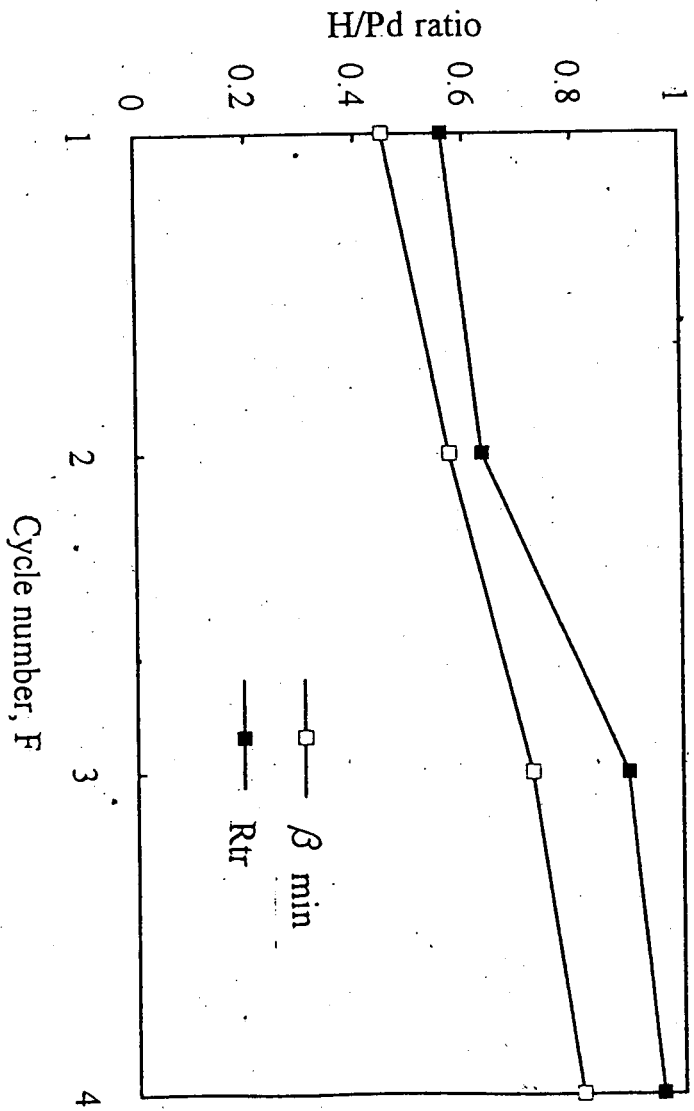


Fig. Effect of repetition number on characteristic values of β_{min} and R_{tr} at 40°C.

結論

1. Cモード繰り返し電解により、 $\alpha + \beta$ 共存組成範囲が増大し、増加分に相当する吸蔵は、ポイド周囲の高欠陥密度層への吸蔵によると考えられる。
2. 電解の電位、抵抗および伸びの同時測定結果を総括的に解析し、Pd棒の水素吸蔵による組織変化を検討した。