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In Situ X-Ray Diffraction Study of Palladium Hydride Electrode during Cathodic Hydrogen Charging or Anodic HCHO Oxidation

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The hydride formation in Pd foils during cathodic hydrogen charging and its reverse process was studied by an in situ X-ray diffraction technique. The α-β phase transformation in the Pd-H system was shown to be accompanied with the formation of PdH_x domain in the electrode. The technique was then applied to demonstrate the occurrence of partial hydride formation during the anodic HCHO oxidation on Pd in alkaline media.

Electrochemical reduction and oxidation reactions are often accompanied with occlusion of the electrolysis products into the electrode, which may cause a phase transformation or appearance of other phases. A typical example is the hydride formation due to hydrogen absorption by some metals or alloys. An X-ray diffraction (XRD) technique may be used to detect such changes, but the measurements should preferably be made in situ, as the new phases formed are sometimes unstable when the electrodes are taken out of the system in which the electrochemical environment has been controlled.

In this letter, we report an in situ XRD technique[1,2] which is used to observe the hydride formation of Pd electrodes (a) during cathodic hydrogen charging and (b) during anodic HCHO oxidation.

A syringe-type electrochemical cell which was a modified form of that used in the in situ IR spectroscopy[3] was used (Fig. 1). This consisted of the working electrode, a Pt net counter electrode, a Ag/AgCl reference electrode, and a window of Kapton foil (polyimid sheet) for X-ray observations. This was mounted on a Rigaku θ-θ scan goniometer: It had a fixed and horizontal sample stage, and rotatable X-ray source and detector. The X-ray radiation used was Mo K_α (λ = 0.70926 Å) monochromatized by a graphite plate.

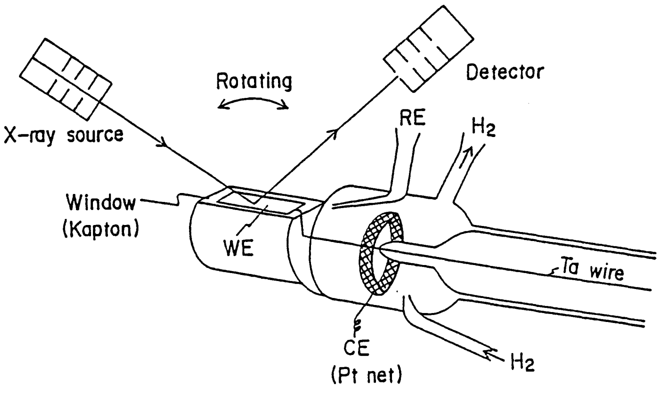

Fig. 1. A syringe type electrochemical cell for the in situ XRD study: WE, working electrode; CE, counter electrode; RE, reference electrode.

The test electrode used was a Pd foil of 10 mm× 10 mm in size and 12.5 μ m in thickness which was spot-welded to a Ta wire sealed into a glass tubing. All the electrochemical measurements were carried out at room temperature (about 293 K) (a) in 0.5 M H_2SO_4 (M = mol dm^{-3}) under H_2 atmosphere and (b) in 1.0 M NaOH + 0.3 M HCHO under Ar atmosphere.

The hydrogen electrode reaction on Pd electrode has been demonstrated to proceed via the Volmer-Tafel reaction scheme.[4] In this mechanism, the equivalent hydrogen pressure during the polarization $\bar{P}_{H_2}$ against its value at equilibrium potential $\bar{P}_{H_2,o}$ is related to the overpotential component η_2' for the Tafel step by the relation[4]

$$-\eta_2' = (RT/2F)\ln(\bar{P}_{H_2}/\bar{P}_{H_2,o}). \qquad (1)$$

Experimentally, this overpotential component is determined on the overpotential decay transient curve as a plateau potential which appears immediately ($\simeq 10^{-3}$ s) after interruption of the polarization current. The overall polarization value was chosen in such a way that it results in η_2' at a desired value: In the hydrogen-charging half-cycle, η_2' was shifted in sequence towards more negative potentials.

The in situ XRD patterns obtained on a Pd foil during cathodic hydrogen charging are shown in Fig. 2. The patterns from the Pd electrode polarized up to $\eta_2' > +50$ mV as well as before the polarization could be assigned to the α phase, viz. a cubic system with the space group of Fm3m. The lattice parameter gradually increased with the negative shift of the polarization potential from ≃ 3.89 to 3.91 Å, which indicated significant amounts of absorption of hydrogen.

At the η_2' value of +49 mV, the potential known to correspond to the α - β coexisting region, the β phase (which takes the same cubic system as the α phase) started to be observed, together with the α phase. The presence of signals of both α and β phase indicated that the transformation took place by the partial formation of PdH_x domain in the Pd bulk. The lattice parameter was 3.92 and 4.40 Å for the α and β phase, respectively. The η_2' value of +49 mV is equivalent to $\bar{P}_{H_2} \simeq 2.1$ kPa according to Eq. 1, which is in agreement with that observed in the process of gaseous hydrogen charging into Pd.[5] The transformation further proceeded

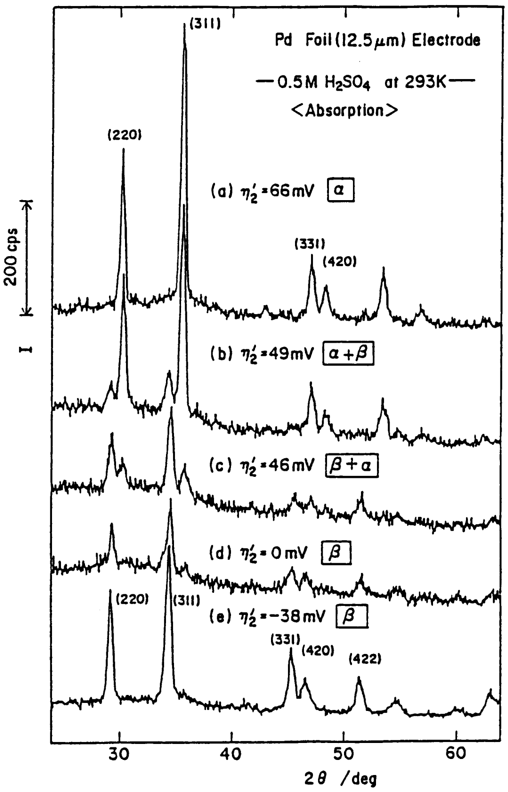

Fig. 2. In situ XRD patterns observed on a Pd foil electrode at various η_2' values. 0.5 M H_2SO_4, 293 K.

under the condition of $\eta_2' < +49$ mV and the completion of a uniform β phase was achieved under the polarizations of $\eta_2' = -38$ mV, along with enlargement of the lattice parameter to ≃ 4.08 Å.

It is well known that the hydrogen pressure vs. hydrogen content relations during the hydrogen charging and discharging half-cycles do not agree with each other and thus there exists a hysteresis.$^{5)}$ Analogously, in the present experiment, the α phase in the hydrogen discharging half-cycle first appeared after the η_2' value attained 66 mV: The extent of the hysteresis was seen to be dependent on the duration of the polarization.

The relationships between η_2' (or the equivalent hydrogen pressure $\bar{P}_{H_2}$) and the lattice parameter of the α and β phases observed of the Pd foil are summarized in Fig. 3. As mentioned above, the α-β phase transformation yielded two branches in the diagram. Also, the hysteresis was clearly seen.

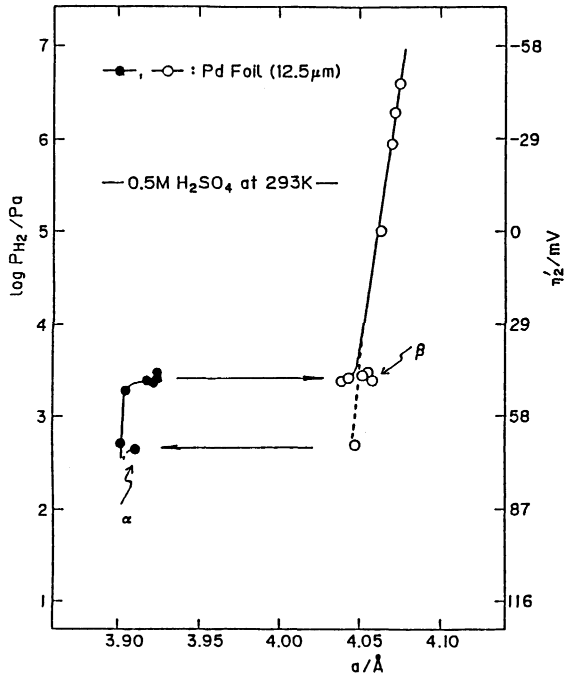

Fig. 3. Relationships between the η_2' (or $\bar{P}_{H_2}$) values and lattice parameters observed for α and β phases on the Pd-H system. 0.5 M H_2SO_4, 293 K.

The XRD technique was then applied to the detection of hydride formation during the anodic HCHO oxidation on Pd. In alkaline media, the reaction is believed to proceed via either of the following two reaction schemes$^{6)}$

$$2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2\uparrow + 2e^- \quad (2)$$

$$HCHO + 3OH^- \longrightarrow HCOO^- + 2H_2O + 2e^- \quad (3)$$

The former scheme proceeds on IB group metal electrodes whereas the latter scheme on Pd, Pt, etc. Mechanistically, it has been concluded$^{7)}$ that the electro-oxidation produces hydrogen adatom H(a) as a reaction intermediate and whether this is evolved as H_2 even at potentials positive to RHE or electro-oxidized further depends on the electrocatalytic activity of the electrode towards the H(a) oxidation. Although no hydrogen gas evolution has been reported on Pd, there may be a possibility that a finite activity of H(a) is realized and thus hydrogen is absorbed by the Pd electrode during the anodic HCHO oxidation. The XRD technique was accordingly applied to this system.

A set of in situ XRD patterns of a Pd electrode before and during the anodic HCHO oxidation at 0.2 V (RHE) for 1 or 15 h are shown in Fig. 4. The patterns obtained after the reaction time of 1 h, as well as the blank one, were to be assigned to the α phase but, after 15 h, weak but definite reflection peaks derived from the β phase were seen admixed with those of the α phase. This indicates that the anodic HCHO oxidation provides the chemical potential of H(a) which is equivalent to $\eta_2' < +50$ mV in RHE scale although the steady-state polarization potential itself is 0.2 V positive to RHE. This substantiates the view[7] that the anodic HCHO oxidation on Pd also involves H(a) formation.

Summarizing the above, the in situ XRD technique could demonstrate the metal-hydride phase formation in the Pd foil electrodes during the cathodic hydrogen charging. The technique can be applied to hydrogen embrittlements of materials, hydrogen storage type secondary cells, etc. This technique was successfully used to reveal the hydrogen entry into the Pd electrode during the anodic HCHO oxidation in alkaline media.

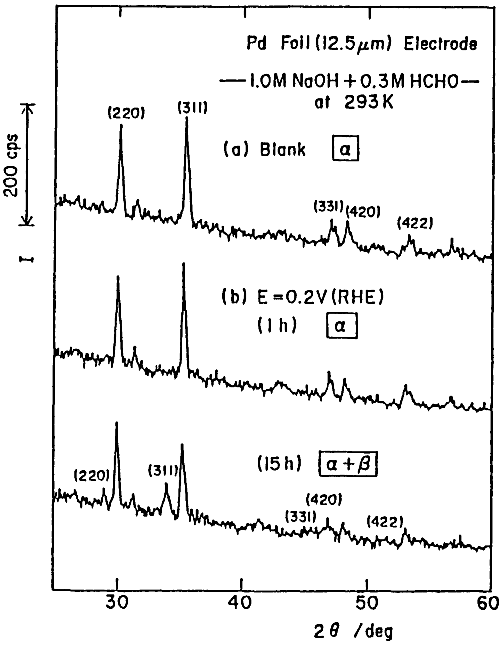

Fig. 4. In situ XRD patterns observed on a Pd foil electrode (a) before and (b) after the anodic HCHO oxidation for 1 and 15 h.

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