

## Reaction Intermediate of Hydrogen Evolution Reaction on a Pt Electrode Studied by Surface-Enhanced Infrared Spectroscopy

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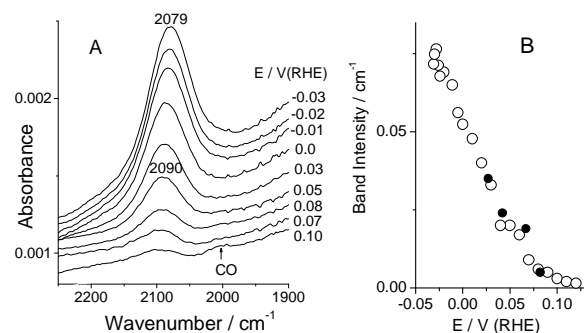
Hydrogen evolution reaction (HER) is the most extensively studied electrochemical reaction. It has been well established that HER proceeds via two successive steps: discharge of proton to give adsorbed H atom (Volmer step) followed by combination of two H atoms (Tafel step) with the latter being rate-determining. Nichols and Bewick<sup>1</sup> proposed H atoms adsorbed at atop sites being the reaction intermediate based on their IRAS studies. Unfortunately, the IRAS measurements were restricted at  $E > 0$  (RHE) since evolved  $H_2$  gas is trapped in the thin-layer and disturbs the spectral measurements and potential control. In the present study, we used surface-enhanced IR spectroscopy (SEIRAS) in the Kretschmann ATR mode<sup>2</sup> to avoid such problems. The measurements could be extended well into  $H_2$  evolution potentials. The spectral data was compared with the kinetics of HER (Tafel plot).

A thin Pt film chemically deposited on a Si ATR prism<sup>3</sup> was used as the working electrode. Potential was measured with respect to RHE. The solution used was 0.5 M  $H_2SO_4$ .

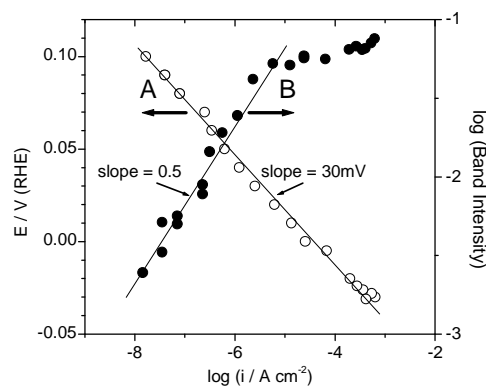
Figure 1A shows a set of SEIRA spectra of H adsorbed on the Pt electrode at potentials denoted. The potentials were corrected for ohmic drop. Consistent with the earlier IRAS study,<sup>1</sup> the band of H adsorbed at atop site is observed around  $2100\text{ cm}^{-1}$ . This band was shifted to around  $1500\text{ cm}^{-1}$  when  $H_2O$  is replaced by  $D_2O$ . As shown in Figure 1B, the band grows in intensity as the potential is made more negative well into the  $H_2$  evolution region.

The open circles in Figure 2 shows the Tafel plot measured simultaneously with the SEIRA spectra in Figure 1. The slope of 30 mV/decade is explained by the Volmer-Tafel mechanism with the Tafel step being rate-determining. The closed circles in the figure are the log-log plot of the intensity of the  $2100\text{ cm}^{-1}$  band versus  $H_2$  evolution current ( $i$ ). The slope of 0.5 indicates that the  $H_2$  evolution current is proportional to the square of the coverage ( $\theta$ ) of adsorbed H, which is consistent with the Volmer-Tafel mechanism. The results strongly argues that the adsorbed H showing the  $2100\text{ cm}^{-1}$  band is the reaction intermediate of HER.

However, the linear relation between  $i$  and  $\theta^2$  does not hold at  $E < 0$  V although the Tafel plot follows the Volmer-Tafel mechanism over the potential range examined. It should be noted that the observed kinetics with the Tafel slope of 30 mV/decade can be explained also by the so-called super saturation effect of  $H_2$  gas evolved in the vicinity of the Pt surface,<sup>4,5</sup> which would bring in diffusion overvoltage and the Tafel step would no longer be rate-determining. The discrepancy between the IR and kinetic measurements at  $E < 0$  V is likely to arise from the growth of diffusion overvoltage.



**Figure 1.** Potential dependence of the SEIRA spectra (A) and integrated band intensity (B, open circle) of the hydrogen adsorbed on a Pt electrode in 0.5 M  $H_2SO_4$ . Closed circle: IRAS data taken from Ref. 1.



**Figure 2.** (A) Tafel plot and (B) log-log plot of the band intensity of the hydrogen intermediate vs. current density on the platinum electrode in 0.5 M  $H_2SO_4$ .

### References

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