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 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 H₂ 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 to avoid such problems. The measurements could be extended well into H₂ 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 was used as the working electrode. Potential was measured with respect to RHE. The solution used was 0.5 M H₂SO₄.

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, the band of H adsorbed at atop site is observed around 2100 cm⁻¹. This band was shifted to around 1500 cm⁻¹ when H₂O is replaced by D₂O. As shown in Figure 1B, the band grows in intensity as the potential is made more negative well into the H₂ 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 cm⁻¹ band versus H₂ evolution current (i). The slope of 0.5 indicates that the H₂ evolution current is proportional to the square of the coverage (θ) of adsorbed H, which is consistent with the Volmer-Tafel mechanism. The results strongly argue that the adsorbed H showing the 2100 cm⁻¹ band is the reaction intermediate of HER.

However, the linear relationship between θ² and i 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 H₂ gas evolved in the vicinity of the Pt surface, 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.

References