

## Characterization of the Platinum/liquid (gas) Catalytic Interface

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Hydrogen Evolution Reaction (HER) taking place at Pt electrodes is among the most studied electrochemical processes regarding its importance for the hydrogen economy and fundamental understanding of the heterogeneous catalysis.<sup>1</sup> Surface sensitive spectroscopy, such as Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy proved to be useful in characterization of the chemical species present at interfaces.<sup>2</sup> Regarding the HER at the Pt electrode, adsorbed hydrogen atom is the primary intermediate and it is known to have vibrational bands (Pt-H) between 2000-2100 cm<sup>-1</sup>.<sup>3</sup> However CO, which poisons Pt surfaces, is also known to have IR bands in the same spectral region.<sup>4</sup> Such overlap makes the unambiguous assignment of the Pt-H band a non-trivial task.

Thin films (< 5nm) of Pt were sputter coated on right-angle prism substrates. The experiments involve either (1) adsorption from gas phase or (2) electrochemical adsorption in solution phase: (1) Gas phase adsorption is induced by admission of high purity H<sub>2</sub> and D<sub>2</sub> gases into the sample cell. Effect of H<sub>2</sub>/D<sub>2</sub> and CO adsorption alone, as well as coadsorption of H<sub>2</sub>/D<sub>2</sub> to CO covered Pt surface were examined. (2) Spectro-electrochemical measurements have been performed both in 0.5 M H<sub>2</sub>SO<sub>4</sub> (in H<sub>2</sub>O) and D<sub>2</sub>SO<sub>4</sub> (in D<sub>2</sub>O) at potentials where HER takes place.

ATR-FTIR results from both set of experiments indicate appearance of bands, which are assigned to adsorbed CO, whose spectroscopic appearance is affected by hydrogen. Previous FTIR experiments have attributed these bands to Pt-H, excluding the possibility of CO formation.<sup>3</sup> 2D ATR IR spectroscopy shows similar lineshapes for all the bands, even though higher anharmonicity is expected from the Pt-H vibration in comparison to that of Pt-CO. Finding the source of CO affected by hydrogen is an important step towards the unambiguous assignment of the Pt-H vibrational band.

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