ELUCIDATION OF H ADSORPTION SITES ON PT/C ELECTRODES IN $HClO_4$ FROM Pt $L_{2,3}$ XAS DATA

M. Teliska, W.E. O'Grady* and D.E. Ramaker*[+]

[+]Chemistry Department, George Washington University, Washington, DC 20052

*Chemistry Division, Naval Research Laboratory, Washington, DC 20375

Hydrogen adsorption on Pt electrodes is often regarded as one of the most important and simple systems in electrochemistry. However, after 25 years of study, it is recognized not to be a simple, clear-cut system. Studies have shown that underpotential deposited (UPD) H exhibits a remarkable dependence on surface-crystallographic orientation and electrolyte. Studies of H adsorption on metal surfaces in the gas phase, supposedly an even simpler system, reveal a variety of phenomena, ranging from localization on a particular binding site with thermally activated hopping or even to delocalization into extended band states, depending on the metal, the face, the coverage, temperature, and other adsorbed species. An extensive review of the literature spanning 30 years [1] reveals considerable progress in our understanding of H adsorption on metals in the gas phase, but a surprising lack of similar information exists for aqueous environments. Thus it is not clear if the adsorption sites in aqueous electrolyte change with coverage similar to those in the gas phase or if they are quite different.

In this work, the adsorption of atomic hydrogen on a platinum electrode in 1 M $HClO_4$ was studied *in situ* with Pt $L_{2,3}$ x-ray absorption (XANES). The Pt XAFS data were collected at room temperature in the transmission mode on beamline X-11A of the National Synchrotron Light Source (NSLS). The Pt electrode was formed of highly dispersed 1.5-3.0 nm particles supported on carbon. A difference procedure utilizing the L_3 spectra at different applied voltages was used to isolate the effects of H adsorption in the XANES spectra. At 0.54 V (vs RHE), the Pt electrode lies in the double layer region where there is no adsorption of the ClO_4^- anion, allowing this potential to be used as a reference. The difference $\Delta\mu(x) = \mu(x) - \mu(0.54)$ then isolates the Pt-H bonding effects at each potential, x.

The $\Delta\mu(x)$ results obtained in this work are compared in Fig. 1 with $\Delta\mu$ results recently reported for strongly and weakly bonded H in the gas phase on supported Pt clusters at high coverage [2]. The good agreement between the gas phase data and our $\Delta\mu$ results at 0.1 and 0.2 V RHE suggest that H adsorption in aqueous electrolyte is in fact quite similar to that in the gas phase.

In contrast to H adsorption in aqueous electrolyte, the adsorption of H in the gas phase has been extensively studied utilizing temperature programmed desorption (TPD), and various vibrational spectroscopies such as IR, He inelastic scattering, and high resolution electron energy loss spectroscopy (HREELS) [1]. Although the interpretation of these results is still open to some question, H definitely adsorbs on Pt(111) in the fcc sites. At low coverage however, the H may undergo thermally activated hopping between the fcc/hcp sites or even delocalize into extended band states. The extent of this delocalization on Pt(111) is not entirely clear. Nevertheless, the H on the flat surface is the "weakly" bonded H in Fig. 1. The Pt-H bonds are stronger near steps or edges on polycrystalline Pt or supported Pt clusters (i.e. the strongly bonded H), but still in the localized or delocalized fcc sites. Finally at still higher coverage, very weakly bonded atop H is visible on polycrystalline Pt, presumably due to H in atop positions on the steps or edges. The agreement between the gas phase and electrochemical data suggests that the usual 0.25 V RHE peak in the CV data is due to fcc adsorption at edge or step sites, and the 0.15 V RHE peak to fcc adsorption on the flat faces.

The experimental results are also compared with $\Delta\mu$ results obtained from real space multiple scattering calculations utilizing the FEFF8 code on model clusters [3]. These calculations reveal that the $\Delta\mu$ is dependent on Pt-H bond length, metallic character of the metal cluster, H coverage, and most important the adsorption site; indeed the shift to higher energy in Fig. 1 with decreasing H coverage is due to decreasing Pt-H bond length. Comparison of calculated results with $\Delta\mu$ (0.0 V RHE) confirms the existence of some atop H below 0.1 V RHE as previously indicated from IR data [4]. Finally at very low coverage, 0.3 V RHE, evidence for the existence of thermal hopping or delocalized fcc/hcp H is found even in the electrolyte. Previously published IR results [5], and EXAFS data [6], suggest that H-bonding with water in the double layer becomes important only after the H becomes fully localized in the fcc sites on the surface below 0.2 V RHE.

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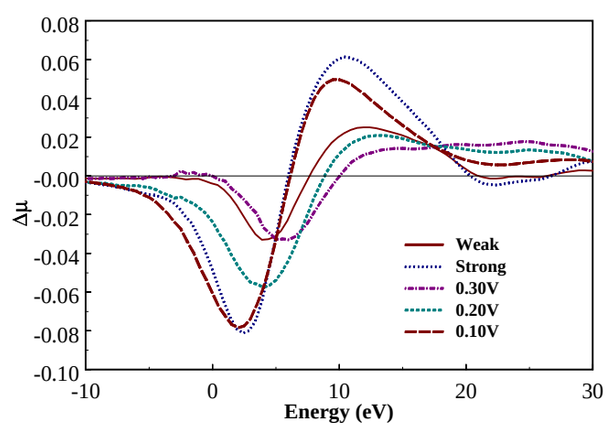

Figure 1 Comparison of $\Delta\mu$ gas phase data [2] and electrochemical cell data at the indicated voltages. $\Delta\mu$(Weak) =μ(H/Pt)-μ(evac. at 323K) and $\Delta\mu$(Stong) = μ(evac at 323K) – μ(evac at 473K) as described in [2]. The amplitude at 0.3 V has been scaled by a factor of 3 and that from [2] have been scaled for best agreement with the electrochemical cell data.