Direct comparison of the electrocatalytic oxidation of hydrogen by an enzyme and a platinum catalyst: Supplementary Information

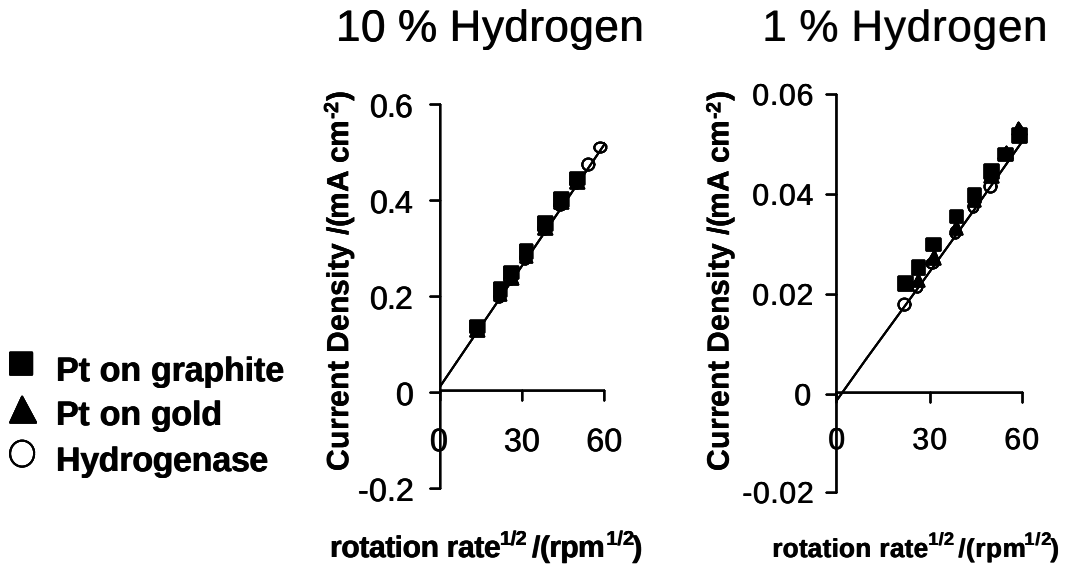

Figure 1: Levich plots for hydrogen oxidation currents from hydrogenase and platinum at +0.242 V vs. SHE, 45 °C and pH 7 under 0.1 atm and 0.01 atm hydrogen.. The lines of best fit are from the hydrogenase data. Platinum currents are from chronoamperometric experiments in which the potential was held at +0.242 V vs. SHE and the rotation rate varied. Hydrogenase currents are from cyclic voltammetry experiments at 0.1 V s^{-1} (0.1 atm hydrogen) and 0.025 V s^{-1} (0.01 atm hydrogen) since maintaining the film at an oxidative potential for prolonged periods of time inactivates the enzyme[11].

Carbon monoxide, a common contaminant (up to 5 %) in industrially produced hydrogen[1], has a higher affinity than hydrogen for platinum. The only mechanism for removal of adsorbed carbon monoxide from platinum catalytic centers involves its oxidation to carbon dioxide at high potentials [2]. Carbon monoxide also binds to and inhibits hydrogenase[3], but in this case it competes with hydrogen. This important distinction from platinum is apparent from the Figure below which compares the effects on the hydrogen oxidation current of a ten-second exposure to carbon monoxide. While the platinum surface is quickly and irreversibly poisoned such that at most 10 % of the initial activity remains (complete removal of the CO layer can only be achieved by applying a potential in excess of 0.6 V vs. SHE, data not shown), the hydrogenase film quickly recovers its initial level of activity simply upon removing the supply of carbon monoxide

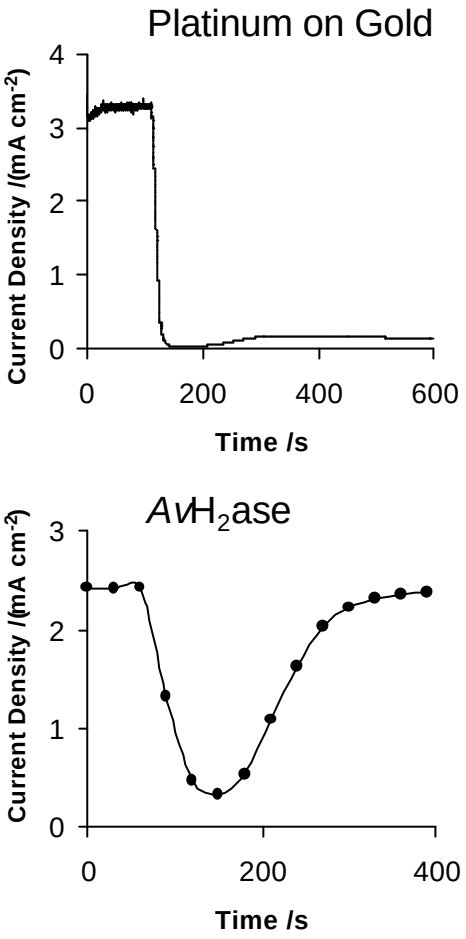

Figure 2: Effect of the introduction of carbon monoxide on hydrogen oxidation currents in 1 atm hydrogen at +0.242 V vs. SHE, pH 7, 45 °C and 2500 rpm. After hydrogen oxidation current stabilized, carbon monoxide was added to the experimental solution for ten seconds by bubbling the gas directly into the electrochemical cell. The platinum data was collected as a chronoamperometric trace. The hydrogenase trace was constructed from currents measured in cyclic voltammograms recorded at 1 V s^{-1} between –0.558 V and +0.242 V vs. SHE with a thirty second delay between each voltammogram (individual points are shown). Hydrogen flow was maintained at the same rate throughout the experiment.

References:
(1)S. Srinivasan, R. Mosdale, P. Stevens and C. Yang *Annu. Rev. Energ. Env.* **1999**, *24*, 281-328.
(2)N. M. Markovic, C. A. Lucas, B. N. Grgur and P. N. Ross *J. Phys. Chem. B* **1999**, *103*, 9616-9623.
(3)J. W. van der Zwaan, S. P. J. Albracht, R. D. Fontijn and Y. B. M. Roelofs *Biochim. Biophys. Acta* **1986**, *872*, 208-215.