Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Depth Probing of the Hydride Formation Process in Thin Pd Films by Combined Electrochemistry and Fiber Optics-Based in situ UV/vis Spectroscopy

Björn Wickman*, Mattias Fredriksson, Ligang Feng, Niklas Lindahl, Johan Hagberg and Christoph Langhammer*

Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

*Corresponding author, e-mail: bjorn.wickman@chalmers.se, clangham@chalmers.se

Wavelength dependence of the response

Figure S1 shows the extinction and reflectance signals measured at five different wavelengths between 500 and 900 nm. Qualitatively, the curves look similar, with the difference that for the 700, 800, and 900 nm signals the measured relative change in reflectance and extinction is larger.

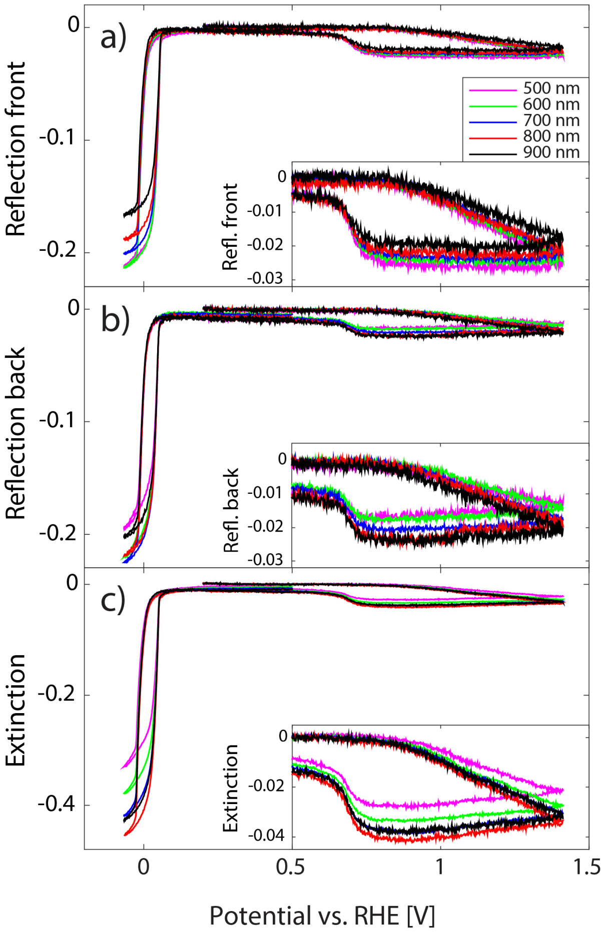

Figure S1. Reflection from front (a), back (b,) and extinction (c), optical signals during cyclic voltammetry in 0.5 M H_2SO_4 with a scan rate of 5 mV s^{-1} on a 20 nm Pd film.

Quantifying the H/Pd ratio

It is straight forward to quantify the amount of hydride formed as long as hydride formation is the only electrochemical reaction taking place. Since we in this work scan the potential down to and below 0 V vs. RHE, we can expect the hydrogen evolution reaction (HER) to occur at some extent. In addition, there will also be a layer of adsorbed H on the surface, which can make a considerable contribution to the current for very thin samples. Birry et al. [1] suggested that the amount of hydride can be determined from the complete oxidation charge following a slow scan and hold of the potential. But, as pointed out by the authors, it is essential that the electrolyte close to the electrode is free from dissolved H_2 in order to not overestimate the amount of hydride formed. With the setup used in this work, it is not possible to rotate the sample or effectively flush the sample surface with H_2-free electrolyte. However, we propose another option for estimating the contribution of HER to the total current, namely to perform potentiostatic current measurements in the potential regime around 0 V vs. RHE and below. The result of such a measurement on a 20 nm Pd film is shown in figure s2. Each point represents the mean value and the error bar corresponds to the standard deviation of 5 repeated measurements. It is clear that the onset of HER occurs just below 0 V, and at potentials more anodic there are no Faradaic reactions taking place. At -28 mV (the point colored blue and highlighted with a blue arrow), the HER current is 10.6 μA, which corresponds to 1.6 % of the total current during the cyclic measurements presented in fig 3 in the main article. This value is low enough to argue that the total current at potentials anodic of -28 mV originates solely from hydrogen adsorption and absorption (except for the double layer charging). At -38 mV (the point colored red and highlighted with a red arrow), the HER current is 22.3 μA, which corresponds to 3.6 % of the total current. Thus, cathodic of -38 mV, the HER is a substantial fraction of the total current. This means that one cannot simply integrate the current to obtain the total amount of hydrogen adsorbed and absorbed below this limit. In the inset of fig S2, these limit potentials (blue and red points) are indicated on the CV data from fig 3, and it is clear that there is an overlap between the processes of hydride formation and HER.

To estimate the amount of hydride formed during one cycle (figure 3) we simply subtract the measured HER contribution. It should be stressed that the absolute currents obtained in the potentiostatic case, especially at large HER currents, might differ from the potentiodynamic case e.g. due to mass transport and local pH effects. Thus, the HER contribution might be slightly underestimated in this approach. The amount of adsorbed H was obtained from the charge associated with the hydride formation, after the double layer charge and the charge estimated to originate from HER was subtracted. The total amount of Pd was calculated from the thickness of the Pd film and the molar volume of Pd (8.56 cm^3). This resulted in a H/Pd ratio of 0.51 at -28 mV (blue point), 0.57 at -38 mV (red point), and 0.80 at -67.7 mV (end point) for the 20 nm Pd film. Due to the uncertainties in this simple HER correction, it is likely that the H/Pd ratio at -67.7 mV is overestimated (HER is underestimated). The true H/Pd ratio is probably closer to 0.7 at 67.7 mV. However, at potentials anodic of the red point in figure S2, the H/Pd ratio derived above should be accurate. Thus the maximum H/Pd ratio formed in this experiment is between 0.6-0.8.

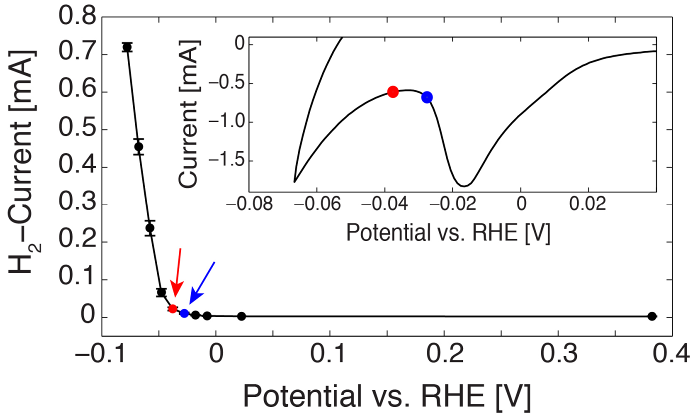

Figure S2. Steady state HER current obtained by potentiostatic hold on a 20 nm Pd film. The error bars represent standard deviation of 5 repeated measurements. The blue and red points (highlighted with arrows) at -28 and -38 mV, respectively, indicate where HER is large enough to contribute significantly to the total current measured. The inset shows where on the CV curve (from figure 3) these two points are located.

1. L. Birry and A. Lasia, *Electrochimica Acta*, 2006, 51, 3356-3364.