

QUARTZ CRYSTAL MICROBALANCE STUDY OF  
PALLADIUM/HYDROGEN INTERACTIONS

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ABSTRACT

Thin palladium films deposited on quartz have been loaded with hydrogen (deuterium) by electrochemical reduction of 0.1 M LiOH (LiOD) in H<sub>2</sub>O (D<sub>2</sub>O). Coulometric measurements during both the hydrogen deposition and subsequent removal steps have shown that H:Pd ratios of 0.7 are reached under these conditions, in accord with accepted values for bulk samples. The frequency decrease observed at AT-cut crystals during hydrogen (deuterium) loading is larger than that expected for the mass of hydrogen deposited into the film. Considering that palladium undergoes a substantial increase in volume upon hydrogen uptake, the role of the resulting film stress in influencing the observed frequency must be addressed. It has been found that such film stresses at an AT-cut crystal produce frequency decreases and that these effects can be accounted for using techniques which are well established in the frequency control field. Measurements at BT-cut crystals, the stress/frequency response of which is opposite to that of AT-cut crystals, have confirmed that stress plays a major role in the present work and have allowed the determination of a quantitative value for this stress. Investigations of mixtures of H<sub>2</sub>O and D<sub>2</sub>O have also been carried out and shed some light on the effect of small amounts of H<sub>2</sub>O in determining the H/D content in the palladium.

INTRODUCTION

It has become apparent that the extent of deuterium loading in palladium is important in producing excess heat and other phenomena as discovered by Fleischmann, Pons, and Hawkins [1]. Another interesting effect which is dependent upon loading is superconductivity in palladium/hydrogen systems [2]. With these considerations in mind, we decided to investigate the uptake of hydrogen into palladium by using the electrochemical quartz crystal microbalance. This device

has been used in a number of studies to more clearly define mass changes accompanying various electrochemical processes [3,4]. In the present case, we were particularly interested in determining relative extents of H and D loading from mixtures of H<sub>2</sub>O and D<sub>2</sub>O.

EXPERIMENTAL

Palladium film electrodes were vapor-deposited onto quartz crystals (Valpey-Fisher) as 8.0 mm diameter discs, with thicknesses ranging from 400 nm to 500 nm.

A 5 nm underlayer of chromium was deposited directly onto the quartz to promote good adhesion of the palladium. Both AT-cut and BT-cut 5.00 MHz crystals were used in this work. These quartz discs were clamped between two O-rings into an electrochemical cell (Figure 1). This cell features a Luggin probe for the reference electrode. Electrochemical experiments were carried out in H<sub>2</sub>O (0.1 M LiOH) and D<sub>2</sub>O (0.1 M LiOD) solutions. Instrumentation consisted of a Wenking Model PCA 72M potentiostat and a PARC Model 175 Universal Programmer for producing voltammograms, and a Philips Model 6674 Universal Frequency Counter for frequency measurements. Keithley 197 multimeters were used for current/potential measurements. A Lotus Measure data acquisition package was used in the IEEE488 mode for obtaining and processing information from these instruments.

#### RESULTS AND DISCUSSION

Initial studies were directed toward an understanding of the processes occurring upon loading of palladium with hydrogen. This loading was carried out by electrochemical reduction of H<sub>2</sub>O at the palladium cathode under potentiostatic conditions. The potential was scanned toward more negative potentials until the current density reached approximately 0.3 mA/cm<sup>2</sup>, at which point the potential was held constant. As the loading process began, a decrease in frequency was observed. The current density typically reached a value of 50 μA/cm<sup>2</sup> at the end of

the loading process, which was apparent when the frequency no longer decreased. A subsequent positive-going sweep resulted in the anodic removal of the hydrogen, with a corresponding frequency increase to the initial value. This behavior is illustrated in Figure 2. In this figure, a frequency decrease of 370 Hz was found; however, scaling the results to a film thickness of 400 nm gives a value of 351 Hz. From the Sauerbrey equation [5], one can obtain the sensitivity of the microbalance as 9 ng/Hz. Assuming that the entire frequency shift is due to hydrogen uptake, this approach leads to a H:Pd ratio of approximately 1.4, whereas coulometric measurements on the anodic hydrogen removal indicate a ratio of only 0.7. This latter result is in accord with values obtained at bulk palladium samples [6]. It is evident that an effect other than simple mass loading is at work in the hydrogen uptake process. Considering that palladium undergoes an 11% volume expansion upon loading with hydrogen [7], it is expected that the film, and therefore the underlying crystal, would be subjected to considerable strain as loading occurs. From other work in thin films, this strain involves compressive forces in the film itself, giving rise to tension in the quartz crystal and a resulting frequency decrease for an AT-cut crystal [8]. Using the coulometry data to obtain the mass of deposited hydrogen, the frequency shift due to mass loading can be calculated using the Sauerbrey equation and gives a value of -185 Hz. The remaining 166 Hz decrease is due, then, to the strain effect.

A very important aspect of this work involves the use of BT-cut crystals in assessing the role of film stresses during the loading process. It is known that tension in a BT-cut crystal produces a frequency increase as hydrogen is introduced into the palladium film [8], so that measurements carried out at such crystals can be used to confirm that film stress is an important factor in this process. From the results given above, it is apparent that the mass loading and film stress effects are approximately of the same magnitude, so that one would expect a virtual cancellation in the corresponding frequency shifts at a BT-cut crystal. This is indeed found to be the case, and an overall frequency decrease of 20 Hz is measured for H uptake (400 nm film). The mass loading effect can again be calculated for this case, although the mass sensitivity for the 5.00 MHz BT-cut crystal is lower than that of the 5.00 MHz AT-cut crystal by a factor of 0.654 due to the different shear moduli for the AT and BT cuts [4,9]. The various frequency shifts for H loading into palladium on both AT and BT crystals are summarized in Figure 3.

The amount of stress in the film can be calculated according to a method, developed in the frequency control field, known as the "double resonator" technique [10,11]. This technique involves measurements at both AT and BT-cut crystals, and the interested reader is referred to the original work [10,11] and more recent investigations by the present authors [4] for details of the calculations. Using this approach, an integrated stress value

of  $-3.9 \times 10^5$  dyne/cm has been found for H loading into palladium.

Analogous measurements for deuterium loading into palladium have been carried out and are summarized in Figure 4. As with the H system, it is apparent that stress is also very important in determining the frequency response in the D system. The greater mass of deuterium is responsible for the greater decreases in frequency observed for the D case. The integrated stress value for D loading into palladium was calculated to be  $-2.6 \times 10^5$  dyne/cm. It is interesting that this finding is in accord with the fact that the Pd-D force constant for interstitial binding is less than that for the Pd-H force constant [12].

As seen from the frequency shifts reported above, the cases of H and D loading are very readily distinguishable from one another, so that in a "competitive" situation of a solution containing both H<sub>2</sub>O and D<sub>2</sub>O one can easily determine the relative amounts of H and D loading into palladium. In this manner, it is possible to find the extent to which the presence of H<sub>2</sub>O as an impurity in D<sub>2</sub>O affects the loading of D. Such an experiment has been carried out at an AT-cut crystal in a solution initially containing D<sub>2</sub>O/0.10 M LiOD. As expected, the frequency decrease observed upon D loading is 442 Hz (400 nm film). As H<sub>2</sub>O is added, the frequency decrease becomes progressively lower, reaching the value seen for pure H<sub>2</sub>O (-351 Hz) at 10 volume percent H<sub>2</sub>O. This result indicates that a

significant separation factor is involved, favoring H reduction, as has been observed by other methods [13]. Even at low (1 %) levels of H<sub>2</sub>O, the effect is noticeable (approximately 10% of the ultimate effect) by the present technique, indicating the importance of maintaining the purity of D<sub>2</sub>O solutions in "cold fusion" investigations.

#### CONCLUSIONS

By carrying out measurements at both AT- and BT-cut crystals, the roles of mass loading and film stress have been defined for H and D loading into palladium films. A method has been developed for determining the effect of H<sub>2</sub>O impurities on deuterium loading by cathodic reduction of D<sub>2</sub>O solutions.

#### ACKNOWLEDGEMENT

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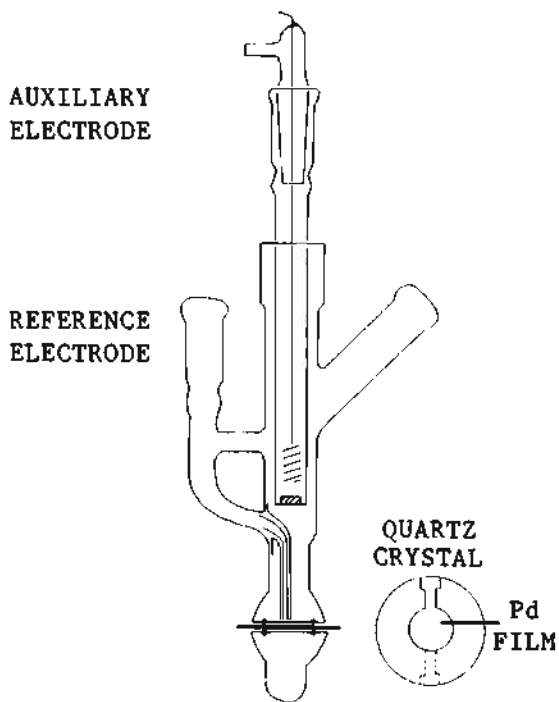


Figure 1. Electrochemical cell used in this work.

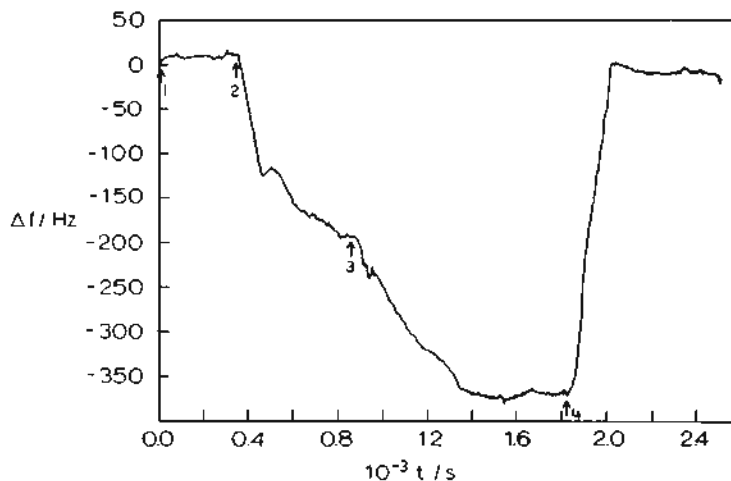


Figure 2. Frequency shift (Hz) vs time (s) for a 367 nm Pd film on an AT-cut crystal (0.10 M LiOH/H<sub>2</sub>O solution). The applied potential is indicated by the numbered arrows: (1) 0.00 V; E scanned and held successively at (2) -1.14 V (3) -1.27 V (4) 0.00 V.

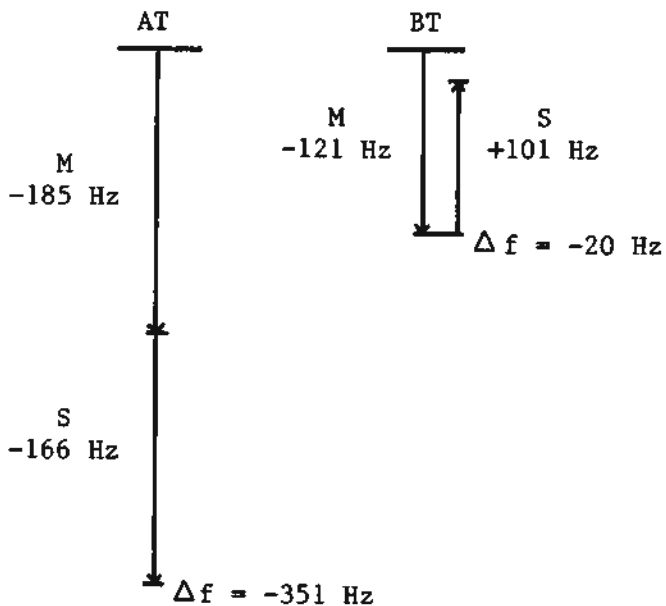


Figure 3. Frequency shifts at 5.00 MHz quartz crystals in 0.10 M LiOH/H<sub>2</sub>O solution. Shifts due to stress (S) and mass (M) are indicated on the figure.

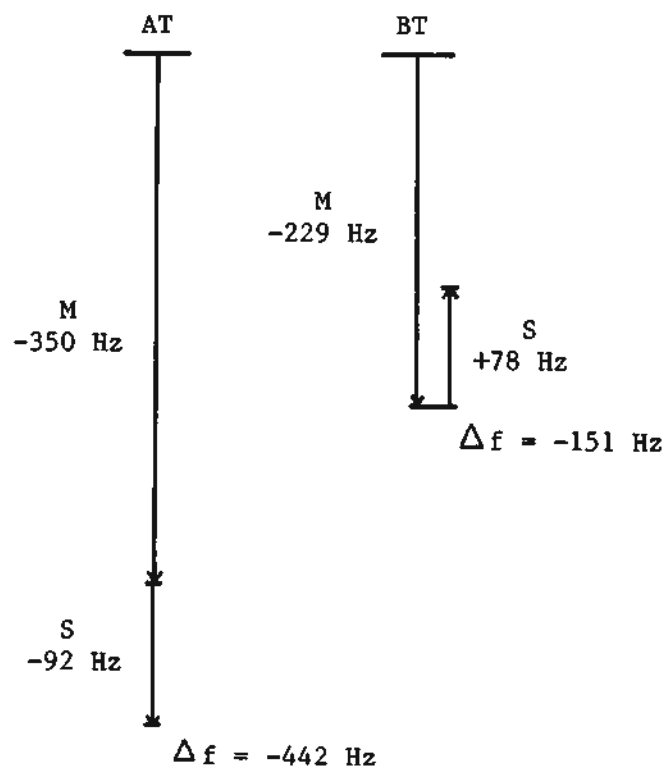


Figure 4. Frequency shifts at 5.00 MHz quartz crystals in 0.10 M LiOD/D<sub>2</sub>O solution. Shifts due to stress (S) and mass (M) are indicated on the figure.