V.D.16 A Surface Stress Paradigm for Studying and Developing Catalyst and Storage Materials Relevant to the Hydrogen Economy

C. Friesen
School of Materials
Arizona State University
PO Box 878706
Tempe, AZ 85287-8706
Phone: (480) 965-3954
Fax: (480) 965-1384
E-mail: cfriesen@asu.edu

DOE Program Officer: Raul Miranda
Phone: (301) 903-8014
E-mail: Miranda@science.doe.gov

Objectives

The overarching scientific objective of this program is to enhance the understanding of hydrogen-economy critical phenomena through a surface stress paradigm. This BES program is the *first* time that surface stress measurements have been used to look at critical phenomena such as oxygen reduction, catalyst poisoning, and H-storage. In this context, surface stress measurements have proven to be a powerful spectroscopic tool for studying catalysts and hydrogen storage materials in both vacuum and electrochemical environments. In each of these cases we have been able to determine thermodynamic, kinetic, and structural aspects of the phenomena under study.

Technical Barriers

One could reasonably argue that of all the technical barriers to the hydrogen economy, the overpotential required for the turn-on of oxygen reduction on Pt and the stable-high density storage of hydrogen are two of the most critical. We have been using high-sensitivity surface stress measurements (the most sensitive known to exist) to examine oxygen reduction on Pt electrodes. We have found that the water structure at the catalyst interface plays a critical role in the overpotential required for oxygen reduction, a big step in understanding the origins of this technical barrier. We have also been examining H-loading into storage materials to directly inspect thermodynamic parameters (e.g. molar volume, etc.), kinetics and cycling fatigue. Developing a fundamental understanding of what leads to and how to prevent cycling fatigue in H-storage will be critical to implementation.

Abstract

Pt Electrocapillarity: Interphase Structure, Oxygen Reduction, and Poisoning

Our BES program focuses on the use of surface thermodynamic principles and high-resolution surface stress measurements to study surface phenomena relevant to the hydrogen economy. The work involves surface stress measurements in vacuum and electrochemical environments. In vacuum, the focus has been on examining surface stress changes with adsorption, where the data correlates to adsorption energies and e.g. transition states in reactions. In electrochemical environments our focus has been on looking at oxygen reduction and poisoning on Pt catalysts and the evolution of stress with H-loading into Pd.

Here we present the electrocapillarity behavior (*in situ* surface stress evolution) of Pt{111} as a function of potential. All experiments were carried out in non-specifically adsorbing electrolytes saturated with O_2, N_2, H_2, or CO. In the inert case (N_2 saturation), we are able to convincingly relate the magnitude and anodic/cathodic hysteresis of the stress-potential behavior to potential dependent water orientation at the electrode/electrolyte interface. We show that our results are strongly correlated to previously published infrared spectroscopy data on the potential dependence of interphase structure. The degree of hysteresis provides a measure of the coercivity and remanence of water polarization at the electrode surface (small for Au and large for Pt). The O_2 saturated system was used for direct comparison between features in the surface stress behavior and the ‘turn-on’ potential for oxygen reduction. Interestingly, it was found that oxygen reduction only occurs once the potential was cathodic enough to begin depleting the interface of oxygen-down oriented water, an effect associated with both a potential drop across the inner Helmholtz plane and O_2 access to the catalyst. We have also been examining the effect of CO adsorption on surface stress, allowing for a direct, real-time measurement of this phenomenon. The long term intention is to begin using surface stress as a real-time spectroscopy for the study of poison-tolerant catalysts.

Progress Report

Synopsis

We have made great progress in the first year and a half of this program across all measurable facets. The equipment modifications and calibration that had to occur to perform this work are finished. New devices were designed and have now been calibrated, enabling us to perform electrochemical experiments at previously unachievable sensitivity and time resolution. We have one publication in print, one submitted, and two publications in preparation that acknowledge this DOE grant; this program had an incubation period and over the next year we expect to submit about a half dozen more publications. The program is now supporting multiple excellent students who are now nearly fully trained. The experimental data that we've been collecting and our computational results are demonstrating that the surface stress paradigm is a *powerful* way of examining catalysts. And we have received newspaper, internet, radio, and television press on our ground breaking work.

Equipment

As pointed out in the proposal for this program, the most important capability that our group has with respect to this project is our ability to monitor surface stress *in situ*, in real-time, and with very high sensitivity. The stress state at the surface of the samples is determined by monitoring changes in curvature of the cantilevered substrates and established through the Stoney relation. The device used for this measurement, developed by the PI, works by monitoring curvature induced changes in the gap between the sample and a detector. Curvature measurements are carried out at a rate of 10 kHz and the device has a cantilever tip displacement resolution of less than 1 nm (a surface stress resolution of order 1×10^{-3} N/m or ~1/1000 of the typical metallic surface free energy). The combination of both high data acquisition rates and high sensitivity enables the extraction of real-time kinetic information and experiments at low adsorbate coverages to be resolved. The monolithic design eliminates sample placement errors, reduces drift, and minimizes parasitic capacitance issues and is a dramatic improvement over commercially available devices. We have created the next generation of this device, which has been optimized for this program, pictured in Figure 1a.

In addition to the analytical techniques described in the proposal, we have added capabilities to our UHV system. We have optimized our dosing setup with a manifold of three sapphire seal leak valves, shown in Figure 1b. This allows us to expose the catalyst surfaces to up to three gases simultaneously with the highest achievable control (leak rates as low as 10^{-10} Torr-liter/s).

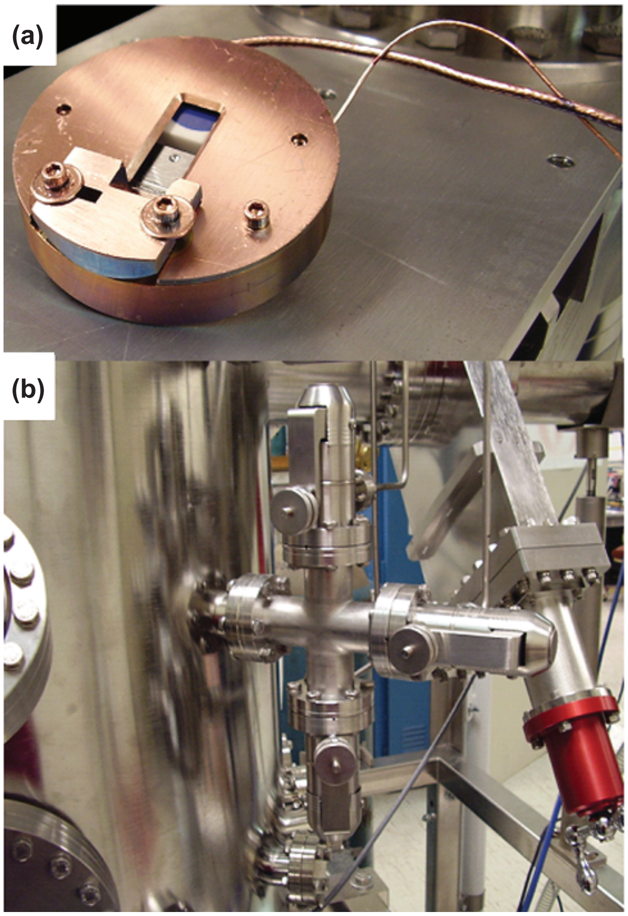

FIGURE 1. (a) The new high-sensitivity stress monitor, optimized for this program. (b) The new sapphire leak valve manifold shown attached to the chamber.

In Section *B.2.3 Electrochemical Environment* of the proposal we described performing surface stress measurements under fuel cell-like conditions. At the time the proposal was written, the intention was to use the laser-based stress monitor described in section *B.2 Experimental and Computational Competencies*. That device is quite capable and at the time probably the best electrochemical stress monitor available. We decided to develop a capacitance based stress monitor similar to our vacuum device. Doing this allowed us to optimize the design for this program and markedly improve the reproducibility of our results. The data shown in the Selected Results section below was taken with this new capacitance based electrochemical stress monitor, shown in Figure 2. To our knowledge, this is by far the most sensitive electrochemical surface stress monitor in existence.

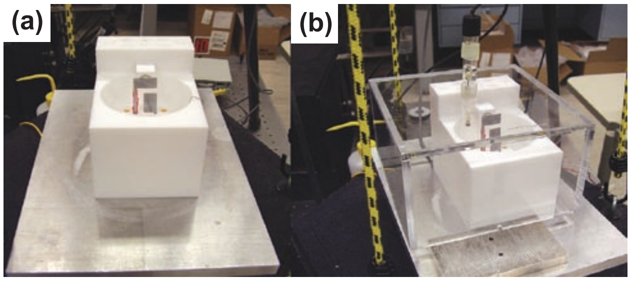

FIGURE 2. (a) The new high-sensitivity electrochemical stress monitor, optimized for this program. (b) The device shown within its environmental shroud and hanging from the vibration isolation cords.

Selected Results

In Figure 3, the surface stress change with applied potential (known as the electrocapillarity curve) is displayed. Note the significant hysteresis, which in our recent *J. Phys. Chem.* submission we demonstrated was due to the strong water dipole interaction with Pt surfaces. In that context, we were able to show how this hysteresis was akin to the coercivity (ΔV) and retentivity (Δ*f*) of the dipole-dipole interaction at the interphase (pre-print available upon request). Interestingly, we discovered a new method for measuring the potential of zero charge (pzc), an important and fundamental electrochemical parameter, and our results are compared to published values in the figure. Also in Figure 3 is displayed IR spectroscopy data from Habib and Bockris [1] showing the orientation of water dipoles at the interface. It is observed that as the potential is swept positive the interface becomes saturated with oxygen-down oriented water dipoles. Associated with this saturation, we observed a saturation in compressive stress at the anodic end of the potential sweep.

Figure 4 shows possibly our most interesting result to date. The electrocapillarity curve in this figure was taken in an oxygen saturated electrolyte. Overlayed on our data is water orientation data from two other sources. The sum of this work is that the potential dependent water dipole orientation appears to have a large effect on the electrocapillarity behavior of solid electrodes. The magnitude of the surface stress positive of the pzc and the previously reported work function changes demonstrate that oxygen-down oriented water interacts strongly with metal surfaces. The question that arose during this work was: can an interface saturated with potential induced oxygen-down water dipoles block oxygen reduction? And, is the origin of the overpotential for oxygen reduction related to this blocking? In Figure 4 it is shown that in oxygen saturated electrolytes, oxygen reduction on Pt{111} does not occur until the surface stress begins to decrease in magnitude (become less compressive) and the dipole saturation decreases. The observed turn-on potential of ~910 mV is approximately 300 mV negative of the reversible potential for oxygen reduction. If an oxygen-down saturated interface is playing a significant role, the 0.4 eV potential drop across the oriented interphase is large enough to account for the required overpotential. Additionally, the saturation of an electrified interface with oriented water molecules tends to 'pack' the first layer of water into a high density phase[4]. This packing

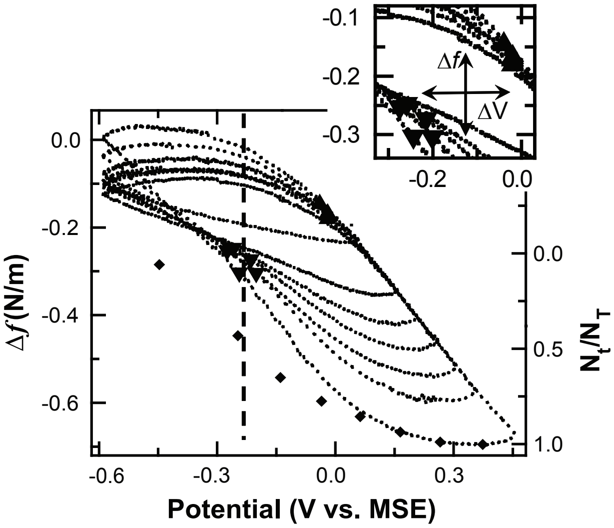

FIGURE 3. Surface stress change versus potential for Pt{111} in 0.1 M NaF. Lower scan limit was -590 mV vs. MSE. The upper scan limits are -40, 60, 160, 210, 260, 310, 360 and 460 mV. Scan rate 20 mV/s. Diamonds represent the Habib and Bockris[1] water orientation data. The vertical dashed line indicates a previously reported value of the pzc[2].

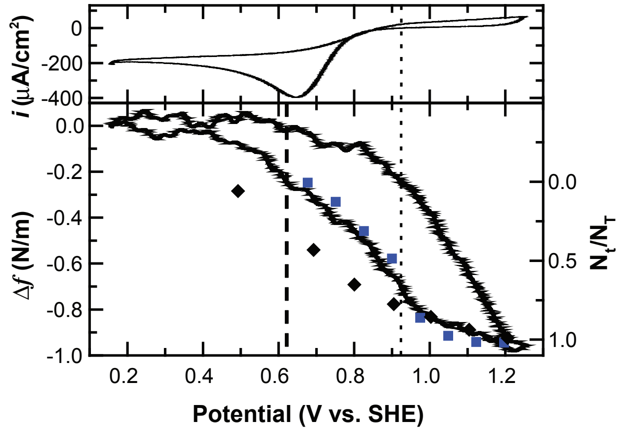

FIGURE 4. Plot of cyclic voltammetry and surface stress behavior for Pt{111} in oxygen saturated 0.1 M $HClO_4$ system. Lower scan limit was -500 mV v. MSE. Scan rate 20 mV/s. Square markers are water orientation data from Ataka, *et al.* (Au in 0.5 M $HClO_4$)[3] and diamonds represent water orientation data reproduced from Habib and Bockris with a +300 mV shift to account for pH difference (Pt in 0.1 M NaF)[1]. The thick dashed line indicates a previously reported value of the pzc[2] and the dotted line is the oxygen reduction turn-on potential.

could physically block molecular oxygen from reaching the electrode surface.

Oxygen electroreduction on Pt has been studied by many groups over a long period of time[5,6]. Much of that work has focused on the need to understand the origins of the large overpotential for this reaction. The typical outcome of these works is the suggestion of a reaction pathway and/or a rate limiting step in the reaction. However, the PI has not found any prior work suggesting that the saturation and subsequent packing of the interface with oriented water molecules could create both a deleterious potential drop and physically block oxygen from reaching the interface.

Because of space limitations, the vacuum and hydrogen storage results are not displayed in this progress report, but will be discussed in the presentation at the contractor's meeting.

Future Directions

We are continuing to explore the origins of the oxygen reduction overpotential. The next set of planned experiments is to show that the dipole saturation and oxygen reduction turn-on potential vary the same with pH.

A set of experiments examining the surface stress changes with CO adsorption are currently under way. These experiments will allow for the direct, real time inspection of various alloying components on CO poisoning.

We have developed a protocol for the electrochemical loading of Pd films with H, using both stress and gravimetric real-time analysis. Next on the docket is to use a Pd film as a catalyst and protective layer for the electrochemical cycling of B, Mg, Al and Li based H-storage systems.

References

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Publications (Including Patents) Acknowledging the Grant or Contract

1. T. Heaton and C. Friesen, "Pt{111} and Au{111} Electrocapillarity: Interphase Structure, the pzc, and Oxygen Reduction", Submitted to *J. Phys. Chem.*

2. T. Heaton, R. Zeller, E. Engstrom, J.R. Hayes, C. Friesen, "Hydrogen UPD and Uptake in Pd{111}: a Gravimetric and Stress Evolution Study", In Preparation.

3. C. Friesen, "Thermodynamic Separability of Ultra-Thin Film Surfaces and Interfaces" *Surf. Sci.* **600**, 1012 (2006).