Coupled Chemo-Mechanics of Heterogeneous Catalysis (sponsored by ARO MURI)

Background and scope: The need to control the rates of chemical reactions is ubiquitous across many technologies, including chemical synthesis via catalysis, chemical sensing via adsorption and reaction, chemical embrittlement in structural materials, and microstructure and precipitate evolution in structural materials. It is commonly thought that mechanical energies cannot compete with chemical energies, so that "Chemistry" and "Mechanics" have little overlap. Roughly, chemical energies are on the order of an eV while the mechanical (e.g. elastic) energies are on the order of meV. However, mechanical energy can be harvested from a large volume by relaxing elastic strains or, equivalently, be concentrated near a defect such as a crack tip or dislocation, generating stresses approaching the theoretical material strengths (a few GPa) and thus provide large enough energies that can alter chemical reactions. More subtly but of equal importance is the fact that mechanical energy can tip the energy landscape to drive reactions or diffusive processes preferentially in one "direction". The role of stress in influencing reactions appears across a broad range of materials applications such as strained-layer superlattice, self-organization of quantum dot structures in Si-Ge, dynamic strain aging in Al-Mg alloys, and stress corrosion cracking.

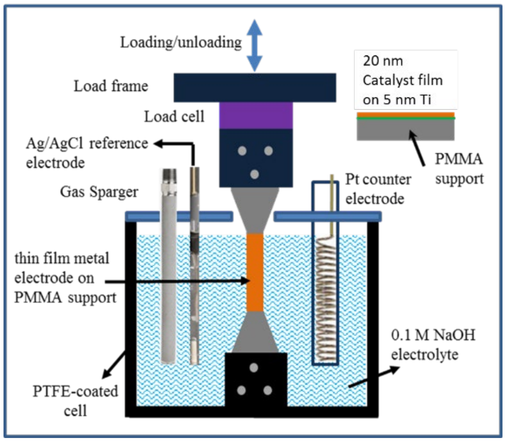

Figure 1. Schematic illustration of the experimental setup to study the influence of externally applied stress (i.e., elastic strain) on the catalytic activity of metal thin films.

Here, we aim to extend the mechanics of materials framework to address the following questions: can elastic strains be used to modify the rates of chemical reactions and thus the efficiency of heterogeneous catalysts? If yes, what is the magnitude of the strain effect and what are the underlying principles that govern the coupling between mechanical strain and the catalytic chemistry? We demonstrate the scientific underpinnings of stress controlled catalysis in carefully designed experiments for select electrochemical/chemical reactions of scientific and technological interest (e.g. oxygen reduction reaction (ORR), hydrogen evolution reaction (HER), methanation of carbon monoxide). An illustrative example of our work is summarized below in the context of HER.

Electro-catalytic Hydrogen Evolution Reaction (HER), which is one of the reactions in a hydrogen fuel cell, is chosen as a model reaction to study the influence of externally applied strain on catalytic efficiency. We developed an experimental setup (Figure 1) in which thin film catalyst specimens participate in HER while they are subjected to controlled elastic straining in cycles of tension and compression while the reaction rates are monitored. We carried out what is perhaps the most definitive and direct demonstration of the role of elastic strain on HER, which is shown in Fig. 2 [1].

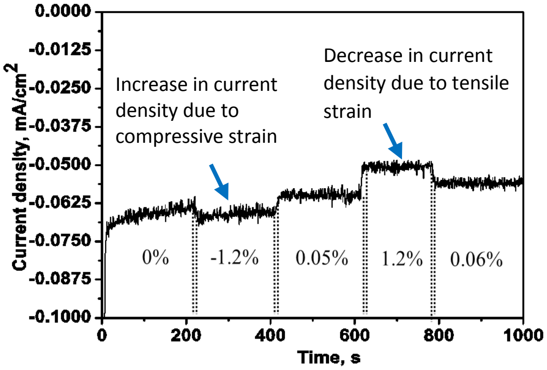

Figure 2. The influence of elastic strain (i.e. stress) on the current density in HER on the surface of tungsten carbide catalyst. Note the distinct change in the current density with applied strain; tensile and compressive strains have the opposite effect.

The electrochemical cell in Fig. 1 is kept at a constant potential while the current was monitored for a tungsten carbide (WC) catalyst film. After reaching a steady current, the specimen is subjected to a compressive strain, followed by a tensile strain. Fig. 2 shows that the applied strains result in a significant increase and decrease, respectively, in the cell current. In other words, compressive stress improves the performance of the WC catalyst and tensile stress has the opposite effect. Moreover, the stress coupling on catalytic activity is non-trivial, which implies that mechanical strain can be employed as a design variable in arriving at optimal catalysts in addition to the traditional compositional design variables.

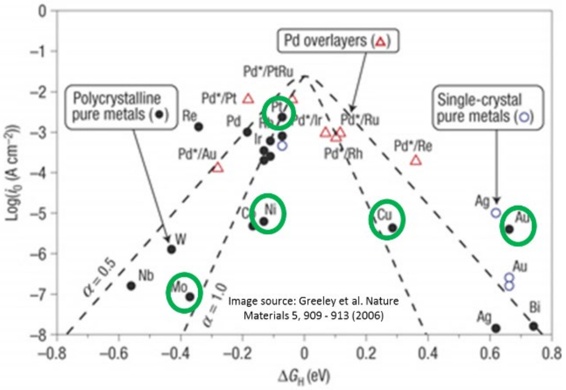

Image source: Greeley et al. Nature Materials 5, 909 - 913 (2006)

Figure 3. The “volcano” plot for HER, which shows the relative performance of HER catalysts as a function of the adsorption energy of the H atom on the catalyst surface.

To explore the phenomenon more systematically, we considered the effect of stress on the so called “volcano” plot for HER [2]. In the catalysis literature, volcano plots are used to represent the relative performance of catalysts for a specific reaction in the coordinate space of the parameters that control the performance of the catalyst for that reaction. The volcano plot for HER is particularly simple with only one controlling parameter, which is the adsorption energy of a hydrogen atom on the catalyst surface (Fig. 3). Adsorption energy is shown on the x-axis; more negative adsorption energy implies stronger binding and more positive adsorption energy implies weaker binding. HER proceeds in two steps: (i) a proton in the electrolyte reacts with an electron in the electrode at a vacant site, resulting in an adsorbed H atom on the electrode surface. (ii) Next, the adsorbed H atom reaction with a proton in the electrolyte and an electron from the electrode to form a H_2 molecule, which then desorbs from the surface. Stronger binding of the H atom on the electrode surface favors the first step, but retards the second one. Similarly, weaker binding retards the first and promotes the second. The volcano plot shows that optimal performance is achieved at an intermediate adsorption energy, which represents the optimality condition for maximizing the overall reaction rate across the multiple intermediate steps. Fig. 3 shows that Pt is near the volcano peak, hence it is among the best catalysts for HER. Metals like Ni and Mo are to the left of the volcano peak because H binds strongly with them; and metals like Cu and Au are to the right of the peak since H binding is too weak.

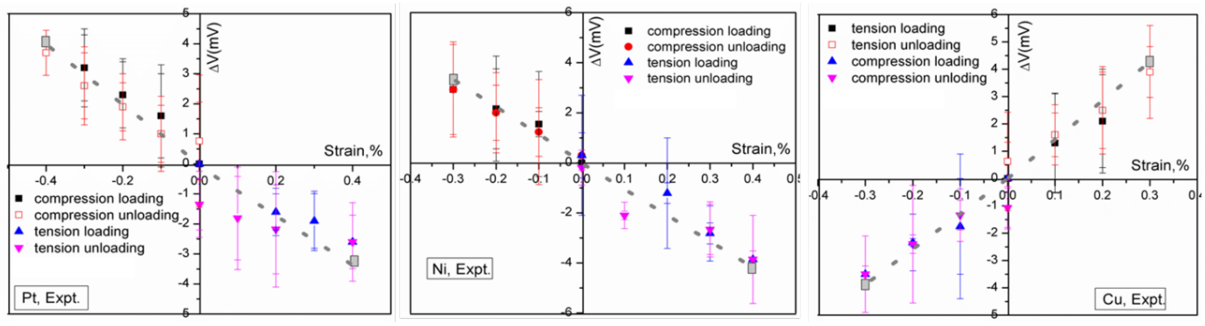

Figure 4. Effect of elastic strain on catalytic activity, as measured by the shift in the cyclic-voltammogram. Results are shown for Pt, Ni and Cu. Pt and Ni are to the left of the volcano peak and Cu is to the right. Note the difference in the slope of the relation between Pt & Ni and Cu, which clearly demonstrates the systematic and predictable effect of strain on the catalytic activity for HER.

To study the effect of stress on the volcano plot, we carried out a systematic investigation on three metals: Pt, Ni and Cu, which are chosen to span the volcano plot [2]. Pt is near the volcano peak, but slightly to the left; Ni is to the left of the peak and Cu is to the right of the peak. We measured the shift in their cyclic-voltammograms as a function of externally applied elastic strain, which are shown in Fig. 4. Here, the shift in the cyclic voltagram is a direct measure of the change in the catalytic activity. One can immediately notice the difference in the slope of the data; for Pt & Ni, which are to the left of the volcano peak, compressive stress makes them a better catalyst. For Cu, which is to the right of the volcano peak, the effect of the strain is the opposite. In other words, applied elastic strain systematically shifts all catalysts to the right or left with respect to the volcano plot! This is a significant discovery with implications for HER catalyst design with strain as a design variable, not just for known catalysts like Pt, but also for improving the performance of the other inexpensive catalysts near the volcano peak (i.e., a judicious choice of strain can move them towards the volcano peak).

In order to gain insights into the experimental observations, Guduru's collaborator A.Peterson carried out density functional theory calculations to compute the influence of strain on adsorption energy of H and the corresponding shift in the cyclic voltammograms. The predictions from Peterson's calculations are also shown in Fig. 4, which agree with the experimental results very well [2]. These studies were extended to other technologically important reactions (oxygen reduction reaction [3] and methanation of carbon monoxide [4]) and catalyst materials.

Taken together, the main conclusion from these studies is that mechanics and catalytic chemistry are inherently coupled through the dependence of adsorption energy of molecules on the elastic strain field of the catalyst surface. The discoveries of this study reveal the strain-activity coupling through well-controlled experiments and computations and offer a pathway to use externally applied or internally induced strain as a variable in optimal design of catalysts.

Relevant Publications:

1. Yan, K., Kim, S.K., Khorshidi, A., Guduru, P.R., Peterson, A.A., High elastic strain directly tunes the hydreogen evolution reaction on tungsten carbide. *Journal of Physical Chemistry C* 121: 6177- 6183. 2017.
2. Yan,K., Maark, T.A. Khorshidi, A., Sethuraman, V.A., Peterson, A., Guduru. P.R. The influence of elastic strain on catalytic activity towards the hydrogen evolution reaction. *Angewandte Chemie* 55:6175-6181, 2016.
3. Sethuraman, V.A., Vairavapandian, D., Lafouresse, M.C., Maark, T.A., Karan, N., Sun, S.H., Bertocci, U., Peterson, A.A., Stafford, G.R., Guduru, P.R. Role of Elastic Strain on Electrocatalysis of Oxygen Reduction Reaction on Pt. Journal of Physical Chemistry C. 119: 19042-19052, 2015.
4. Johnson, B., Guduru, P.R., Peterson, A.A., Strain-induced changes to the methanation reaction on thin-film nickel catalysts. *Catalysis Science & Technology*. Accepted for publication, 2019.