## PD MONOLAYER - TRANSFORMATIVE CONCEPT FOR EFFICIENT ELECTROLYTIC H - ISOTOPE SEPARATION

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## Abstract

Platinum and Palladium are considered as very attractive catalysts for electrolytic hydrogen isotope separation. The high cost of Pt and Pd makes it necessary to minimize the amount of the catalyst, if any practical application is considered. The solution to reduce the cost of the Pd and Pt catalyst and increase their activity is two-dimensional (2D) monolayer (ML) morphology where every catalyst atom is on the surface. The issue is that deposition of noble metals as 2D ML at room temperature is quite challenging. To overcome this challenge, an underpotential deposition (UPD) phenomenon was studied as critical step for successful 2D catalyst monolayer synthesis and design. The Pd monolayer was deposited on Au (111) and Ru (0001) single crystal substrates with the help of conventional electrochemical techniques and investigated by in-situ scanning tunneling microscopy (STM). The epitaxial strain as a result of lattice mismatch with substrate was induced within the catalyst monolayer. Analysis of the strain effects in monolayer catalysts (Pd<sub>ML</sub>/Au (111) and Pd<sub>ML</sub>/Ru (0001)) on the energy of hydrogen and deuterium adsorption bond was investigated by subtractively normalized interfacial FTIR spectroscopy (SNIFTIRS). The results suggest that tensile strain in bimetallic monolayer catalyst (Pd<sub>ML</sub>/Au (111)) increases the bond strength of atop adsorbed hydrogen and deuterium, compared to bimetallic monolayer catalyst with compressive strain (Pd<sub>ML</sub>/Ru (0001)) and bulk Pd catalyst. Results from SNIFTIR studies used as input for theoretical calculations to predict the isotope separation factor between Pd<sub>ML</sub>/Au (111), Pd<sub>ML</sub>Ru (0001) and bulk palladium. Data showed that tensile strain in Pd monolayer deposited on Au increases the value of hydrogen isotope separation factor by 20%, whereas for Pd monolayer on Ru this value is less. Mass spectrometry measurements with pre-determined ratio of H<sub>2</sub>O/D<sub>2</sub>O

solution mixture was also performed on HER products for monolayer catalysts and bulk Pd. The experimental data confirms that when the Pd surface is stretched, activity of the surface is increased, resulting in higher H isotope separation efficiency. Kinetic measurements for hydrogen evolution reaction (HER) and deuterium evolution reaction (DER) was performed on Pd<sub>MI</sub>/Au (111) and Pd<sub>MI</sub>/Ru (0001), and used for hydrogen separation efficiency analysis. Results suggest that surface strain affects the recombination of atoms on the surface, at small overpotential regions where the recombination of H/D atom is the rate determining step. Agreement between theoretical calculations and experimental data confirms that 2D monolayer catalyst under tensile strain (Pd monolayer deposited on Au substrate) can improve hydrogen isotope separation efficiency.

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## 1. Introduction

The progress in nanostructured materials with enhanced properties and improved functionality has gained much of the scientists' attention in past few decades. There is only one major problem left, which is overcoming the challenging part of scaling down the dimensions and keeping the devices indestructible, vigorous and consistently fabricated. There is a need for reliable and low-cost methods that can produce nanostructured materials with better characteristics compared to conventional methods <sup>[1]</sup>. Electrochemical deposition can be considered as one of the methods that can be used for producing nanostructured materials with superior qualities. This method of deposition is very popular in the semiconductor industry, catalyst design for fuel cells and magnetic materials deposition.

The fact that using electrochemical techniques for producing nanomaterials is very cost effective and enable the deposition of any materials of any shapes and sizes with precise thickness control, has made it advantageous compared to other methods. The electrodeposition process is based on the deposition of metal cations on a conductive substrate with the help of an electrical current <sup>[2,3]</sup>.

Electrodeposition is being used widely as it enables the uniform deposition and continuous metal film growth with good adhesion and controlled physical properties. The development of the electrochemical techniques and instruments makes electrodeposition process a useful method in catalyst design. The deposition of a foreign metal adlayer on another metal substrate alters its physical, chemical and catalytic properties of the electrode surface from both the substrate and the deposited metal <sup>[4,5]</sup>.

The underpotential deposition (UPD) of metals on another metal substrate provides an interesting approach for thin film deposition. In this process the metal monolayer deposits at potentials more positive than the potential required for reversible deposition. The fact that the chemical potential of the deposited adatoms ( $\mu_{ads}$ ) is different from chemical potential of the bulk metal ( $\mu_{bulk}$ ), causes a strong binding of adatoms to the surface of the foreign substrate <sup>[6,7]</sup>. The differences in the chemical potentials can be expressed as

$$\mu(\theta)_{ads} - \mu_{bulk} = -\text{Ze}[E(\theta)_{ads} - E_r] = -\text{Ze}\Delta E_p, \tag{1}$$

where the bulk metal reversible electrode potential is  $E_r$  and  $E(\theta)_{ads}$  is the reversible electrode potential at coverage  $\theta$  for underpotential deposition layer. As a result,  $E(\theta)_{ads} - E_r$  expresses the value of the binding energy of the UPD layer to substrate of the foreign metal <sup>[8]</sup>.

Understanding the process of heterogeneous catalysis that accelerates a chemical reaction with the help of the solid surface is of a great importance. Improving catalysts properties of deposited metals is possible by studying the concept of chemical bonding of atoms to transition metal surfaces. The best transition metal catalyst for a given reaction is determined by the ability of the substrate to bond with reaction intermediates in a way that favorably accelerates formation of preferred products. The energy of the adsorbate-surface bonds has significant impact on the catalytic process. The overall properties of the catalytic process depends on the interaction between the metal surface and adsorbed molecules <sup>[9]</sup>. It's very important to understand how the chemical reaction starts and proceeds in order to better design the catalyst.

Transition state theory (TST), enables investigation of the reaction rates for elementary chemical reactions and how chemical reactions take place. Based on the transition state theory, there is a quasi-equilibrium between reactants and transition state, and studying the activated complexes at transition state can determine rates of the reaction. Kinetic theory is also used to calculate the rate in which activated complexes convert to products. Understanding the activated complexes helps to gain information on how to overcome potential barriers and form products <sup>[10]</sup>. This mechanism is of great importance in catalyst design. By knowing the activated complex structure, the rate constant of any reaction can be calculated.

By determining the rate constants, the transition state theory enables us to calculate the Gibbs free energy, standard enthalpy and entropy of activation for a particular reaction. Figure 1 shows the reaction coordinate diagram vs. Gibbs free energy. The reactants should pass the energy barrier to form products.



Figure 1 - Schematics of reaction coordinate diagram vs. Gibbs free energy

Eyring equation explains the changing in the rate of chemical reactions with temperature:

$$K = \frac{\kappa K_B T}{h} e^{-\frac{\Delta G^+}{RT}}.$$
 (2)

In equation 2,  $\kappa$  is the transmission coefficient (which is considered to be 1 when species at the transition state proceed to products and not the reactants), K<sub>B</sub> expresses the Boltzmann's constant, T and h are the absolute temperature and Plank's constant respectively, and  $\Delta G^+$  is the free energy of the activated complex. Equation 2 can be simplified as

$$K = \frac{\kappa K_B T}{h} e^{\frac{\Delta S^+}{RT}} e^{-\frac{\Delta H^+}{RT}}$$
(3)

and

$$\ln\left(\frac{K}{T}\right) = -\frac{\Delta H^{+}}{RT} \cdot \frac{1}{T} + \ln\frac{\kappa K_{B}}{h} + \frac{\Delta S^{+}}{R} \,. \tag{4}$$

Equation 4 explains that a chemical reaction is taking place at various temperatures <sup>[10,11]</sup>. In the case of heterogenous catalysts, where catalysts are in a different phase than reactant molecules, the first step is adsorption of reactants on the highly reactive catalyst surface. Interaction and binding of reactant molecules with the catalyst surface lowers the activation energy and increases the probability of a successful collision. Arrhenius equation can be used to study the relation between the rate constant (K) and the frequency of collision:

$$k = A e^{\frac{-E_a}{RT}},$$
(5)

where, k is the rate constant, A is the frequency factor,  $E_a$  is the activation energy and T is the temperature. Based on equation 5, the rate constant is proportional to frequency factor and inversely proportional to activation energy <sup>[12,13]</sup>.

Transition state theory can explain how catalysts can accelerate a chemical reaction and ease the reaction on surfaces by lowering activation barriers for activated complexes. In catalytic reactions, heat of adsorption affects activation energies. Subtracting the heat of adsorption from activation energy, lowers the activation energy from true activation energy value. As a result, the value of activation energy for the catalytic reaction gets lower and frequency of a successful collision is increased. The increase in the probability of successful collisions (increase in the frequency factor) affects the overall rate of the reaction <sup>[12,14,15]</sup>.

Hydrogen evolution reaction (HER) and hydrogen adsorption are important electrochemical concepts that rely on catalytic reactions. In the early 1970's, Ultra High Vacuum (UHV) surface science tools were being used to analyze the hydrogen adsorption on catalysts, such as platinum single crystal surfaces <sup>[16,17]</sup>. Although the results from those studies were in disagreement with energies of H adsorption on the Pt (111) surface, it is now clear that the differences between the reported heat of adsorption data are in correlation with adsorption of hydrogen on defect sites. Although it was previously accepted that H atoms occupy three-fold hollow sites, due to H atom tendency to occupy highly coordinates sites, the density functional theory (DFT) calculations with the generalized gradient approximation (GGA) shows that H atoms prefer to occupy top sites. By increasing the H coverage ( $\theta_{\rm H}$ ) on platinum (111) single crystal surface, the adsorption energy decreases and when hydrogen coverage reaches a definite point, H-H repulsion comes to play, causing differences in the heat of adsorption <sup>[18]</sup>. Studying hydrogen chemisorption energy on noble and transition metal surfaces, confirms that Pt is an efficient electrocatalyst for HER. Exchanging current density data helps to understand the activity

of different metals to catalyze the HER, as different metals show different rates for hydrogen evolution. Volcano curves are used to show the trends for exchanging currents for hydrogen evolution reaction. Figure 2 shows the volcano curve in which the hydrogen adsorption energy ( $\Delta E_H$ ) and free energy ( $\Delta G_{H^*}$ ) on different metals are plotted vs exchange current densities <sup>[19]</sup>.



Figure 2 - Exchange current density values on different metal surfaces for hydrogen evolution reaction vs. hydrogen chemisorption energy ( $\Delta E_H$ ) and hydrogen adsorption free energy ( $\Delta G_{H^*}$ ) taken from ref<sup>[19]</sup>.

Thermochemistry of the reactions reveals that platinum group metals are the most efficient metals for hydrogen evolution. In Figure 2, all reactive metals are on the left leg of the curve and on the right side the unreactive metals are placed. The Gibbs free energy for H adsorption on catalytic platinum metal is almost zero. The free energy for hydrogen adsorption ( $\Delta G_{H^*}$ ) based on the kinetic model is expressed as

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H, \tag{6}$$

where  $\Delta E_{H}$  is the hydrogen chemisorption energy,  $\Delta E_{ZPE}$  is the zero-point energy difference between the adsorbed and gas phase and  $\Delta S_{H}$  is the entropy of adsorption. Equation 6 can be simplified as

$$\Delta G_{\mathrm{H}^*} = \Delta E_{\mathrm{H}} + 0.24 \text{ eV} . \tag{7}$$

Decreasing the value of  $\Delta E_{\rm H}$ , decreases the value of the exchange current density. As a result, on the left side of the volcano curves, hydrogen atoms bonds more strongly to metal surfaces. Also, increasing in the value of  $\Delta E_{\rm H}$ , results in a decrease in the rate of reaction, due to the hydrogen atoms becoming unstable on metal surfaces <sup>[19,20]</sup>.

By knowing the heat of adsorption  $\Delta H_{ad}$ , the absolute value of the Pt-H bond energy can be easily calculated on the Pt surfaces by

$$2E_{Pt-H} = |\Delta H_{ad}| + E_{diss}, \qquad (8)$$

where the dissociation energy of H<sub>2</sub> is E<sub>diss</sub>, which is 432 KJ/mol. Based on the factors such as specific adsorption site and coverage, the Pt-H bond energy value can vary from 240 to 270 KJ/mol. This value shows that Pt-H bond is a weak chemical bond and makes H<sub>ad</sub> a reactive intermediate on the Pt surface. Pt has been known as the best and most efficient metal for studying HER, as it has a large current density for HER and small Tafel slope (30 mV/decades). However, due to the high price of platinum, there is a need for other new efficient electrocatalysts with well-defined surfaces as an alternative active catalyst for studying HER <sup>[16,17]</sup>. Bimetallic systems can be used as new and effective electrocatalysts to substitute platinum. Bimetallic systems improve the catalytic behavior of the surface. These systems help to achieve unique surface composition and structures by placing a catalytically active material on a conductive electrode <sup>[21]</sup>. There are different methods for preparing bimetallic catalysts, including electrodeposition of second metal on pure metallic surface or bulk alloys. The reactivity of bimetallic surfaces is affected by two factors: one is the direct electronic interaction between substrate and the over-layer, and the second is the lattice mismatch between the over-layer and substrate, resulting in the geometric strain effect. When the substrate has week electronic effect, the important factor affecting the energy level of the d band is lattice mismatch between substrate and the over-layer <sup>[18,22]</sup>.

One of the ideal examples of bimetallic over-layer is the palladium over-layer on a gold single crystal surface. In this system, palladium (transition metal) is deposited on Au (an inert noble metal electrode). The layer thickness of the deposited metal affects the electro-catalytic activity of the bimetallic system with respect to hydrogen adsorption <sup>[23]</sup>.

M. Kolb et al. studied hydrogen adsorption behavior on different single crystal electrodes (Au (111), Pt (111), Rh (111), Ru (0001), Ir (111), Re (0001) and PtRu (111)) with pseudomorphic palladium monolayers deposited on top. They observed a variation in the electrochemical properties of the palladium overlayer for hydrogen adsorption energy and high overpotential values for absorption of hydrogen. Positive voltammetric sweeps for all the substrates reveals the hydrogen adsorption strength based on the peak potentials. The potential for hydrogen desorption on various Pd surfaces is shown in Figure 3 versus changes in the d-band.



**Figure 3** - d-band center shifts vs. potentials for hydrogen desorption for palladium overlayers taken from ref<sup>[24]</sup>.

Based on the Figure 3, the electronic properties of the Pd overlayers is affected by two factors, geometric effect (differences in the lattice parameters of the overlayer Pd and substrate) and ligand effect (electronic interaction of the substrate and Pd overlayer). Both of these effects can change the position of the d-band center and improve the catalytic activity of the surface. For example, the positive strain in  $Pd_{ML}/Au(111)$  results in upshift in the value of the d-band center and increases the hydrogen adsorption bond, compare to Pd(111), whereas for  $Pd_{ML}/Ru(0001)$  the negative strain in the Pd layer on Ru(0001) decreases the hydrogen adsorption bond strength <sup>[24]</sup>.

The goal of this research project is to develop an electrocatalyst system that can effectively separate hydrogen isotopes with the help of 2D monolayer catalysts. Techniques such as in situ infrared spectroscopy (studying the adsorption bond strength of the atoms adsorbed on the surface of the electrocatalyst), scanning tunneling microscopy and mass spectrometry (studying the separation factor ratio for Pd monolayers) are used in our study. In first step, with help of conventional electrochemical techniques and in-situ STM, we design effective electrocatalysts (Pd<sub>ML</sub>/Au (111) and Pd<sub>ML</sub>/Ru (0001)) that are stable during an electrochemical reaction and show selectivity for adsorption of desired atoms. The strain effect in the Pd monolayer on Au (111) and Ru (0001) is studied for electrolytic hydrogen isotope separation. The positive or negative strain in palladium overlayer affects the strength of adsorbed hydrogen bonds compared to bulk Pd and Pt and change the probability for recombination of the hydrogen isotopes. The results from FTIR used as input for theoretical calculations and were compared to experimental data from mass spectrometry and kinetic measurements to calculate the hydrogen isotope separation efficiency.

## 1.1. Study of Hydrogen Adsorption on Metal Surfaces

The chemisorption of hydrogen on transition metals has been studied by UHV and electrochemical systems. The first study to characterize adsorbed hydrogen species by in-situ infrared spectroscopy was reported by Bewick and R.J. Nichols <sup>[25]</sup>. The adsorbed hydrogen was studied in acid solutions on polycrystalline Pt, Rh, Ir and single crystal Pt (111) electrodes. The results for polycrystalline Pt showed that the hydrogen atom was coordinated on top of the surface metal atom, with adsorption band around 2090 cm<sup>-1</sup>. The intensity of the band depends on the potential and the rate of hydrogen formation.

They concluded that in the hydrogen evolution reaction (HER), hydrogen atom is intermediate. The  $H_2SO_4$  electrolyte was then substituted with  $D_2O+H_2SO_4$  to confirm that the observed band is hydrogen. By using  $D_2O+H_2SO_4$  instead of  $H_2SO_4$ , the band shifted from 2090 cm<sup>-1</sup> to 1500 cm<sup>-1</sup>, with a factor of 1.39 for isotope effect as expected. They also saw a band at 1450 cm<sup>-1</sup>, related to HDO, produced in the 1M  $D_2O+H_2SO_4$  electrolyte.

M. Osawa et al. <sup>[26]</sup> investigated the hydrogen adsorption on polycrystalline Pt electrodes by surface-enhanced infrared spectroscopy in acid solutions. They observed Pt-H spectral adsorption band around 2100 cm<sup>-1</sup> which was due to the coordination of the hydrogen atom on top of the Pt surface atom in the H<sub>2</sub> evolution potential range (E < 0.1 Vvs. RHE). They concluded that the reaction intermediate is the adsorbed hydrogen atom and the rate-determining step is defined by the combination of the two adsorbed hydrogen atoms. There is still uncertainty regarding the H adsorption process (H<sub>UPD</sub>). However, it is known for sure that the adsorbed hydrogen atom does not play any role in the hydrogen evolution reaction process. This means that different metallic sites than H<sub>UPD</sub> are used for producing H adsorption for formation of H<sub>2</sub> gas <sup>[27]</sup>. Hydrogen adsorption on Pt (100), Pt (110), Pt (111) and Pt (1111) electrodes was investigated by in situ infrared reflection absorption spectroscopy. The Pt-H band was seen at 1990-2080 cm<sup>-1</sup> for Pt (100), Pt (110) and Pt (1111). However, for Pt (111), no Pt-H bands were observed under same circumstances, as the adsorption of terminal hydrogen is sensitive to the crystallographic orientation of the surface <sup>[28]</sup>. A. Bewick and J.W. Russell <sup>[29]</sup>, measured adsorbed hydrogen bands on polycrystalline rhodium with the help of IR reflectance spectroscopy. They observed that in sulfuric acid, the hydrogen adsorption band appears at 2090 cm<sup>-1</sup> and by changing the solution to  $H_2SO_4+D_2SO_4$ , the deuterium adsorption band appears around

1500 cm<sup>-1</sup>. Infrared spectroscopy techniques can be used to study reversibility of hydrogen adsorption on metal surfaces. The reversibility of hydrogen adsorption on alumina-supported platinum was investigated by infrared spectroscopy and strong adsorption bands near 2040 cm<sup>-1</sup> were observed <sup>[30]</sup>.

Platinum and palladium over-layer systems are being used extensively in studying hydrogen adsorption energy. The hydrogen-metal binding energy affects the mobility of the hydrogen, adsorbed at the over-layer surface. Both ligand and strain effects change the electronic structure of Pd and Pt over-layers. For instance, the adsorption of H on Pd<sub>ML</sub>/Pt (111) surface is more favored in comparison to clean Pt (111) surface. This will decrease the mobility of the adsorbed hydrogen on  $Pd_{ML}/Pt$  (111). As a result of this change, the strongly adsorbed species (H<sub>UPD</sub>), are placed in deeper potential wells (hallow sites) and ease the formation of weakly bound adsorbed species (H<sub>opd</sub>) which are the intermediate in HER at top sites <sup>[31,32]</sup>.

## **1.2.** Hydrogen Evolution Reaction (HER)

One of the most important topics in electrochemistry is hydrogen adsorption and hydrogen evolution reaction (HER). HER is very important in the electrocatalytic reaction. The HER in acid solutions involves the following steps <sup>[27]</sup>. Step one, discharge of protons and production of adsorbed hydrogen atoms, which is expressed by Volmer step,

$$H_3O^+ + e^- \leftrightarrow H(a) + H_2O. \tag{9}$$

At this step, the bonding of hydrogen adsorbed to the catalyst occurs.

The next step can be either recombination of the two adsorbed hydrogen atoms (Tafel step), which is shown in the following equation:

$$2\mathrm{H}(\mathrm{a}) \to \mathrm{H}_2,\tag{10}$$

or it can be the electrochemical desorption step of adsorbed H with  $H_3O^+$  (Heyrovsky step), which can be seen in the following equation:

$$H(a) + H_3 0^+ + e^- \rightarrow H_2 + H_2 0.$$
 (11)

The hydrogen evolution reaction mechanism depends on the composition of the solution, the crystallographic orientation of the electrode surface and the cathode metal under consideration. The crystallographic orientation of the electrode surface affects the kinetics of the HER, so it may happen by Volmer-Tafel or Volmer-Heyrovsky mechanisms <sup>[33]</sup>. Figure 4 shows two mechanisms for HER in acid solutions.



Figure 4 - Two different mechanisms for HER in acid solutions

The rate determining step (rds) in each of the reaction sets is the slower reaction. The catalyst surface and the  $H_{ad}$  binding energy should be adequate in order for

decomposition to happen. However, this binding should not be too strong to block the active site of the surface and become the rate determining step. When the electrode surface is covered by under potential deposition hydrogen ( $H_{upd}$ ), at less positive potential, the hydrogen evolution reaction happens. Indeed,  $H_{opd}$  is the adsorbed intermediate and not the  $H_{upd}$ .

Bulter-Volmer equation is used to describe the kinetics of the hydrogen evolution reaction. This equation gives information about the relation between electrical current of the electrode and the potential of the electrode <sup>[34]</sup>. By assuming that the same electrode is used for cathodic and anodic reaction, the Bulter-Volmer equation can be expressed by <sup>[35]</sup>

$$i_{K} = i_{0} \left[ e^{\left(\frac{\alpha n F}{RT}\right)\eta} - e^{\left(\left[-\frac{(1-\alpha)n F}{RT}\right]\right)\eta} \right],$$
(12)

where  $i_K$  is the HER kinetic current density,  $i_0$  is HER exchange current density (current at equilibrium), n is the number of electrons transferred, T is absolute temperature, R is universal gas constant,  $\alpha$  is charge-transfer coefficient (symmetry factor) and  $\eta$  is the applied overpotential. Overpotential is the potential value of the reaction beyond the potential at equilibrium,

$$\eta = E - E_{\text{equilibrium}}.$$
(13)

When the system is at equilibrium, both terms in the Bulter-Volmer equation are equally important. However, when the system is not at equilibrium, one of the terms gets dominated and equation 12 can be expressed by the Tafel equation which connects the rate of electrochemical reaction and overpotential, shown in equations

$$i_a = i_0 \exp\left(\frac{\eta}{b}\right) \tag{14}$$

and

$$i_C = -i_0 \exp\left(-\frac{\eta}{b}\right),\tag{15}$$

where b is the Tafel slope that includes all constants. The Tafel slope gives information about the rate of the reaction and the activity of the catalyst. The plot of the current vs overpotential can be seen in Figure 5.



Figure 5 - Current potential curves

At high anodic and cathodic overpotential, the Tafel equations can be expressed as

$$\eta = -2.303 \left(\frac{RT}{(1-\alpha)nF}\right) \log j_0 + 2.303 \left(\frac{RT}{(1-\alpha)nF}\right) \log j_a , \qquad (16)$$

and is simplified as

$$\eta = a + b \log j \quad . \tag{17}$$

In equation 17, a and b are constants, and a is the intercept which can gives information about exchange current density, while b is the Tafel slope. The value of the Tafel slope (b) is positive for anodic reaction, and negative for cathodic reaction. The Tafel slope value is of great importance in studying electrochemical kinetics such as for elementary reactions, in which it enables us to calculate the value of the symmetry factor and helps to determine the mechanism of a reaction and reveals the rate determining step.

The Tafel slope value also helps to calculate the amount of overpotential that is needed to increase the rate of reaction based on the change of the activation energy. When the value of the Tafel slope is small, it means that the electrochemical reaction will occur more easily. It can be concluded that the best catalyst for HER should have small Tafel slopes. For example, platinum metals have a Tafel slope around -30 mV in acid solutions <sup>[8,36,37]</sup>. The work on hydrogen evolution reaction, and studying potential-current curves leads to better understanding of the kinetics of electrode reactions <sup>[8]</sup>. Various values for Tafel slopes for HER based on the theory is predictable as seen in Table 1.

		Tafel slope, b/mV dec <sup>-1</sup>		Temkin
		Langmuir adsorption condition		adsorption
Mechanism	Rate-determining step	$\boldsymbol{\theta}_H \rightarrow 0$	${oldsymbol{ heta}}_H  o {f 1}$	conditions
	Volmer	-120	-40	-60
	Heyrovsky	-40	-120	-60
ИΤ	Volmer	-120	-120	-120
v - 1	Tafel	-30	8	-60
V-T	Volmer-Tafel	-120	$\infty$	-180
V-H	Volmer- Heyrovsky	-120	-120	-120

 Table 1 - Tafel slopes for hydrogen evolution reaction, calculated from theoretical values at room temperature. Taken from reference [8].

When the Tafel slope value is -60 and -30 mV, Volmer and Heyrovsky steps are rate determining steps (RDS) respectively for metals like Au and Ag. For HER, one step is considered as a rate determining step with mostly one reaction intermediates. Studying intermediates heat of adsorption helps to plot volcano curves. Figure 6 shows volcano curve of hydrogen evolution on metal electrodes.



Figure 6 - Volcano curve for hydrogen evolution on metal electrodes. taken from ref<sup>[38]</sup>.

It is clear from Figure 6 that the most active catalysts for HER are platinum group metals. Studying the heat of adsorption of intermediates helps to design better catalysts. for instance, a combination of two metals from the two sides of the volcano curve are expected to show better activity for HER.

## **1.3.** Hydrogen Isotopes

Hydrogen is considered as one of the most abundant elements in the universe (~70 %) with three isotopes that are naturally occurring, including  ${}_{1}^{1}H$  that is called protium,  ${}_{1}^{2}H$ which is called deuterium and  ${}_{1}^{3}H$  that is called tritium. The hydrogen and deuterium are stable while tritium has half-life of 12.32 years and undergoes a radioactive decay to  ${}_{2}^{3}He$ . Among all these three H isotopes, protium is the most stable one due to the proton stability. Deuterium with one proton and one neutron is also considered as a stable isotope for hydrogen and is mostly found in the ocean water in the form of D<sub>2</sub>O and HDO molecules. Deuterium is a nonradioactive isotope which is used widely in chemical laboratory and industrial enterprise. Tritium is the radioactive isotope and only traces of it can be found on earth surface. Due to its radioactive property it is used as tracer in medical research <sup>[39,40]</sup>. The need to use other isotopes of hydrogen makes it important to separate hydrogen isotopes with low cost methods. The current techniques for separating hydrogen isotopes are relying on different hydrogen isotopes effects. In these techniques chemical isotope exchange is used with electrolysis. The newest approach in separating hydrogen isotopes, that can lower the cost for this process, is the combination of the hydrogen fuel cell with electrolysis <sup>[41]</sup>.

#### **1.4.** Separation Factor

Hydrogen/deuterium isotope effects help us to better understand HER kinetics. There are two types of quantity that can be studied. Identification of the respective rates of both hydrogen (H) and deuterium (D) production, in aqueous solutions with low D content, is possible by separation factor (S),

$$S_{k} = \frac{\left[\frac{C_{H}}{C_{D}}\right]_{gas}}{\left[\frac{C_{H}}{C_{D}}\right]_{Soln}} .$$
(18)

In equation 18, C<sub>H</sub> and C<sub>D</sub> are the relative concentrations of H and D respectively. The  $\left[\frac{C_{H}}{C_{D}}\right]_{gas}$  is the ratio after separation and  $\left[\frac{C_{H}}{C_{D}}\right]_{soln}$  is the ratio before the separation takes place. The products of electrolysis are mostly H<sub>2</sub>, HD and D<sub>2</sub> in the gas phase and H<sub>3</sub>O<sup>+</sup>, H<sub>2</sub>DO<sup>+</sup> and  $D_3O^+$  in acid solutions. In the electrolysis process of the solution, taking the hydrogen away from the water molecules assists the hydrogen isotope separation <sup>[42]</sup>. The separation factor is affected by temperature, electrode materials, current density, nature of the electrolyte and the electrode potential at the cathode. It has been shown by G.P. Lewis and P. Ruetschi that electrode potential has influence on the cathodic hydrogen-deuterium separation factor <sup>[43]</sup>. They observed that by going toward more negative potentials, values of the separation factor will increase due to the faster discharge of hydrogen than deuterium. As a result of this, the amount of deuterium in the gas phase gets lower. The results on different electrodes show that the potential at which the discharge starts is different in value, depends on the electrode materials, and is defined by the overvoltage characteristics. When the potential of the electrode reaches a specific point, adsorbed protons and deuterons cover the surface sufficiently and push the ions to discharge at less desired surface sites. Increasing the adsorbate coverage on the cathode surface, decreases the adsorption sites and affects isotope discharge in high negative potential regions. As a result of this, the discharge of the hydrogen will not be favored over deuterium and the separation factor value will decrease from its maximum value, compared to uncovered electrode surface <sup>[42,43]</sup>.

The separation value at the transition metal, where the desorption is the rate determining step, is between 6-8, and this value can be greater if the H evolution reaction is being facilitated. The bimetallic overlayers can increase the separation factor efficiency due to the strain effect. For instance, a positive strain in the bimetallic overlayer can cause isotopes with smaller mass to recombine more easily, by increasing the diffusion barrier for adsorbate hydrogen atoms.

The second effect that can be studied from pure hydrogen (H<sub>2</sub>O) and deuterium (D<sub>2</sub>O) containing solutions, is the ratio (R) of current densities (rates) for hydrogen evolution reaction (HER) and deuterium evolution reaction (DER). R and S present different quantities. By knowing an appropriate partition function, a theoretical relation between R and S can be calculated <sup>[42,43]</sup>. The separation factor in solutions with high concentration of H<sup>+</sup> and low concentration of D<sup>+</sup> can be defined as

$$S_k = 2 \, \left(\frac{R_{H_2}}{R_{HD}}\right),\tag{19}$$

where  $\frac{R_{H_2}}{R_{HD}}$  is the ratio of the production rates of H<sub>2</sub> and HD. Whereas in solution with about the same order of magnitude between H<sup>+</sup> and D<sup>+</sup> concentration, separation factor is expressed as

$$S_k = 1 + 2 \left(\frac{R_{H_2}}{R_{HD}}\right).$$
 (20)

The rate determining step is the recombination of the adsorbed H or D atoms (Tafel step), and in ordinary water solution HD, is the product for combination of  $H_{ads}$  and  $D_{ads}$ . When the surface coverage is high, the differences of the zero-point energy determine activation energy differences and is considered as vibrational frequency of the MH and MD. The ratio of the rate of evolution of H<sub>2</sub> to HD in which the partition function ratio is  $\frac{4}{3}$  can be shown as

$$\frac{R_{H_2}}{R_{HD}} = \frac{4}{3} \exp\left(\left[\frac{1}{2}h\nu_{MH} - \frac{1}{2}h\nu_{MD}\right]/K_bT\right).$$
(21)

The 4/3 ratio is a result of the partition functions ratio,  $\frac{f^*}{f_R}$ , for activated complexes (Pd-H----D-Pd) and adsorbed H and D as reactants. In more elaborate form it can be represented as

$$\frac{f^*}{f_R} = \frac{4}{3} = \frac{2m_H^*}{(m_H)^2} / \frac{m_H^* + m_D^*}{m_H m_D}.$$
(22)

In equation 21, K<sub>b</sub> is the Boltzmann's constant, h is the Plank's constant and T is absolute temperature. The  $\frac{R_{H_2}}{R_{HD}}$  represents the ratio between H<sub>2</sub> and HD production rate which is indeed a consolidated ratio between partition function of adsorbed H and D and activated complexes multiplying the exponential term related to their bonding energies.  $m_H^*$  and  $m_D^*$ represent masses of hydrogen adsorption in an activated complex form, while  $m_H$  and  $m_D$ represent the adsorbed state. The frequencies of the fundamental vibration mode ( $v_{0,H}$  and  $v_{0,D}$ ) for H<sub>adsOPT</sub> and D<sub>adsOPT</sub> atoms on the crystal surface can be measured with vibrational spectroscopy techniques such as infrared spectroscopy (IRS). The partition functions of the adsorbed hydrogen atoms contain vibrational energies <sup>[44]</sup>. The more elaborated form of the separation factor, S<sub>K</sub> can be defined as

$$S_k = 1 + 2\frac{R_{H_2}}{R_{HD}} = 1 + 2 \times \frac{2m_H^*}{(m_H)^2} / \frac{m_H^* + m_D^*}{m_H m_D} \cdot \exp\left(\frac{0.5hC(v_{0,H} - v_{0,D})}{k_D T}\right).$$
 (23)

#### 1.5. Volcano Curves

Electrocatalysis enables us to study the rate of electrochemical reactions, which depends on the properties of the electrode surface. The electrode surface transfers electrons like other redox reactions and at the same time has influence on the reaction rates. In these heterogeneous reactions, the electrode which is the catalysts, remains unchanged <sup>[8]</sup>. The electrode surface has a direct effect on the rate of the reaction. For example, the exchange current density in the case of hydrogen evolution differs in magnitude by 11 orders <sup>[45]</sup>.

The combination of the kinetics for hydrogen evolution reaction and the electrode materials results in plots known as volcano plots. These plots are based on the relation between exchange current density and standard free energy for hydrogen adsorption <sup>[46,47]</sup>. Exchange current density helps to measure the ability of the metal to catalyze HER. When the reaction is at equilibrium, exchange current density is considered as the rate of HER per surface area at the electrode potential. The value of exchange current density is different for different metals.

Volcano plots express that a good catalyst has an adequate interaction with adsorbates. These interactions should not be too weak, nor to strong. As for weak interaction, the binding between the catalyst and the adsorbate fails and there will be no reaction. On the other hand, for strong interaction between the catalyst and the adsorbate, strong binding of the adsorbates blocks the surface of the catalyst. For designing catalysts, it is important to know the volcano correlations. For an electrocatalytic reaction, B formation is the rate determining step as

$$A + e \to B^- \to C. \tag{24}$$

Adsorption of the B on electrode surface happens with lower activation Gibbs free energy, compared to the case in which there is no adsorption. The rate expression can be explained as

$$I = const C_A (1 - \theta_B) \exp(1 - \frac{\Delta G}{RT} - \alpha \Delta G_B \frac{\alpha E}{RT}).$$
(25)

At constant values of potential when there is no adsorption due to the weak hydrogen bonding to the surface ( $\theta_B = 0$ ), equation 25 is expressed as  $\ln i \sim -\Delta G_B$ , and in cases where the surface is too reactive and binds strongly to hydrogen,  $\theta_B = 1$ , will be  $\ln i \sim \Delta G_B$ . It can be concluded that HER will happen fast on the surface, when H binds to the surface not too strong nor too weak.

Volcano curves help to understand the kinetics of catalytic reactions. Figure 7 explains the volcano curves, where free energy based on the kinetic model is plotted <sup>[8,19]</sup>.



Figure 7 - Volcano curve. taken form ref<sup>[8]</sup>
On the left leg of the volcano curves, all reactive metals are placed. On the surfaces of metals like Ni and Pd , hydride is formed. By going toward more negative values, the rate of the reaction will decrease, due to the strong hydrogen bonding, that lessens the available sites for recombination of hydrogen atoms at the surface. On the other hand, for noble metals at the right side of the volcano curve, weak hydrogen bonding makes proton transfer difficult and can make hydrogen unstable on the surface, and going toward positive values, will decrease the rate. At equilibrium, platinum is near the apex of the graph and is considered as the best electrocatalyst for studying hydrogen evolution reaction <sup>[48]</sup>.

### **1.6. Bimetallic Electrocatalysis**

Electrocatalytic reactions are based on the heterogenous reactions. These reactions occur at the interface where catalysts and electrolytes are available. At the catalyst surface, all the adsorption, desorption, recombination of the adsorbed species on the surface, and product desorption happen. All these reactions depend on the surface of the catalyst and how the atoms are distributed at the surface of the catalyst. Surface atoms are very important in solid catalysts, as they can affect the kinetics of the reaction. Changing the activity of the surface atoms is possible by alloying metals to form bimetallic or multimetallic catalysts <sup>[49,50]</sup>. The bimetallic catalyst can be prepared by electrodeposition of second metal on the surface of a pure metallic surface. Adzic et al. demonstrated a method for preparing platinum monolayer electrocatalyst by having only one atomic layer of platinum on Ru surfaces for hydrogen gas oxidation and higher CO tolerance. Monolayer electrocatalysts for reactions with slow kinetics by reducing the content of the needed electrocatalyst. Another advantage of using monolayer catalysts is improving their

catalytic performance <sup>[51,52]</sup>. Due to the high importance of electrocatalysts design, it is of great importance to understand the electronic factors that affect the bimetallic surface reactivity. Electrochemistry techniques and methods can offer a useful and unique information for designing electrocatalysts <sup>[53]</sup>.

Bimetallic catalysts can be prepared by electrodeposition in a way that only one monolayer or sub-monolayer is deposited on the surface. These bimetallic catalysts have some important qualities. For instance, all the atoms on the surface can be involved in the catalytic reaction. The ligand effect which is also called the electronic effect can change the properties of the catalyst. The Ligand effect is due to the transfer of electronic charge from the substrate metal to the monolayer metal on top or the other way. This phenomenon can change the binding energy of the reactants. Another important effect of bimetallic catalysts is called the strain effect, which is caused by the lattice mismatch between the substrate metal atoms and the deposited metal <sup>[54]</sup>.

Brankovic et.al studied the size effect of the Pt sub-monolayer clusters on Au (111) and observed that different sizes of the Pt<sub>subML</sub> are under tensile or compressive strain from the substrate metal. These tensile or compressive strains change the d-band center <sup>[55]</sup>. Norskov et al. used a series of bimetallic systems and measured their catalytic activity with the help of DFT calculations. With pseudomorphic Pd monolayer at the surface of the transition metals substrate, HER exchange-current density was measured. As demonstrated in Figure 8, the exchange current density differs in magnitude even though all the experiments were done on the Pd surface layer. They concluded that the adsorption features of the transition metal surface settled by the average energy of local d band center. As a

result, stronger bonds between surface and adsorbed hydrogen atoms are formed when the d states are higher in energy <sup>[45]</sup>.



Figure 8 - Exchange current density measurements for hydrogen evolution on bimetallic systems, taken from <sup>[45]</sup>.

A. Roudgar and A. Grob investigated atomic CO and hydrogen adsorption on Pd/Au bimetallic surfaces and found that stronger adsorbate bonding can be achieved by expansion of the Pd overlayer by 5% and can lead to relative weak coupling of the d-bands between Pd and Au. They noticed an upshift of the d band in Pd as a result of a positive strain that increases the catalytic activity. They observed that the electronic effect is efficient up to the first two Pd overlayers <sup>[18]</sup>.

The improved catalytic activity can be achieved by combination of ligand and strain effects. The electronic charge transfer from substrate metal to the overlayer can refine the

binding energy of the reactants. These hetero-metallic bonding interactions (ligand effect) affect the chemical properties of the surface. The difference between the average bond length of the substrate metal and the deposited monolayer metal results in strain, which in turn can change the average energy of the d-band. Constant d band filling can be retained by broadening or narrowing the d band and changing the d band average energy along with its width. For instance, the average energy of the d band is reduced, when the d band gets broadened. The d-band model, explains the variation in adsorption energies <sup>[56]</sup>. The d-band model is explained in the following section.

### 1.7. The d-Band Model

During last few decades, there were successful improvements in the theoretical methods to study the surface reactivity of the electrocatalysts. Due to these developments, it is now possible to predict the catalytic activity of these surfaces. Hammer and Norskov, developed the d-band theory of metal surfaces. Based on the d-band theory, the reactivity of the metal surface depends on the electronic states in the valence band <sup>[57]</sup>. The contribution from sp states is different and depends on the metal. For example, in the case of transition and noble metals, sp states contribution is relatively steady and ruling. What causes the differences in the interaction energy of different metals is the coupling of the d-states of the metal and the adsorbate. The d-band theory suggests that the binding energy of the adsorbates relies on the position of the d-band center <sup>[58]</sup>.

Understanding the solids electronic structure is important to explain the d-band model. Based on the theory of the molecular orbits, when homonuclear molecules are brought together, the wave function is divided into two states. One is the low energy level which is called the bonding state and the other has high energy and is called anti-bonding. The two energy states are

$$\varepsilon_{\pm} = \varepsilon_{\text{Atom}} \pm \beta - S\beta \,. \tag{26}$$

In equation 26,  $\varepsilon_{Atom}$  is the energy level of the non-interacting atom, the coupling matrix is  $\beta$  and the overlap matrix element is expressed as *S*. Whenever there is a big overlap between the two atoms, the value of  $\beta$  (coupling matrix) will increase and the split between the bonding and anti-bonding states also increases. <sup>[59]</sup>.

In case of solids with well-defined structures, when the energy states split, there will be continuous bands and not split orbitals. If transition metals are considered, large overlapping of the electronic states forms a broad band for s and p. This results in the splitting of orbitals. However, d electrons in transition metals are very localized and overlapping is small. As a result, d-bands are continuous and narrow. the adsorbate-surface bond energy is expressed as

$$\Delta E = \Delta E_0 + \Delta E_d, \tag{27}$$

where  $\Delta E_0$  represents the coupling of adsorbate states to s-states, and  $\Delta E_d$  is the result of extra interaction with d-states of the metal. For transition metals, s-bands are half filled and broad. So,  $\Delta E_0$  is assumed to be independent of the metal and  $\Delta E_d$  determines the total bonding energy. S and P electrons would form broad bands (huge overlap of the electronic states) and have split orbitals, whereas d electrons are localized (small overlap) with a continuous narrow d-band <sup>[9,58]</sup>. Transition metals density of states (DOS) can be seen in Figure 9.



Figure 9 - Schematic of the chemical bond formation from adsorbate state and the transition metal surface, taken from <sup>[9]</sup>.

In the beginning, the adsorbate states and s states couple together and broaden the adsorbate state, followed by d states interaction. The center of the d-band can help understanding the bonding energy strength.



Figure 10 - d-band center and Fermi energy level

In Figure 10, W is width of the d-band,  $E_d$  is the d-band center energy, and  $E_f$  is Fermi level energy. If the width of the d-band (W) is decreased (for example as a result of tensile strain), less electrons are needed to fill the band up to Fermi level. However, since for a given metal, the number of d-electrons are constant, the system has to shift up the energy of d-states <sup>[24]</sup>. Figure 11 shows the d-band center shifts for a fixed number of delectrons.



**Figure 11** - schematic of coupling with fixed number of d-electrons between bandwidth and d-band center, taken from <sup>[24]</sup>.

The width of the d-Band is related to the bonding interactions between d orbitals of an atom and its nearest neighbor. When a monolayer is deposited on the substrate metal, the monolayer metal matches its lattice constant with the substrate metal. This leads to combination of strain and ligand effects which can change the d-band center. In the case where the lattice is expanded parallel with the surface, a decrease in the overlap between d electrons of the neighboring metal atoms occur, and this causes a decrease in the bandwidth. As a result, the d-bands center will change due to change in the d-band width. For systems with d-bands that are more than half filled, in order to keep the fixed d occupancy, the energy of d-states has to shift up and gives stronger interaction with adsorbates, whereas for systems with d-bands less than half filled, a downshift of d-band center will happen to retain the same d-band filling <sup>[60,61]</sup>. The d- band model helps to gain knowledge about how to change the reactivity of metals by depositing them on other metals. Metals with higher d-band center, enhance the catalyst activity by making stronger chemisorption bonding <sup>[9]</sup>.

### **1.8.** Density Functional Theory Calculations in Electrocatalysis

Density functional theory (DFT) is based on the computational modeling method. In DFT, the electronic structure of atoms and molecules are investigated and are based on the fact that the system properties can be predicted. In the case of electrocatalysis, due to the high precision of standard generalized gradient approximation (GGA) functions, they are very popular. Moreover, for using DFT calculations, it's crucial to use a surface model that is aligned with the experimental findings <sup>[62]</sup>. Surface reactivity of a catalyst can be predicted by d-band theory and DFT calculations. For transitions and noble metals, coupling of the d-states of the metal and adsorbate causes differences in the interaction energy for different metals. The important parameters of the d-bands are the coupling matrix element, filling of the d-band, and the energy weighted center. The interesting information that can be gained from this theory is that the position of the d-band center affects the binding energy of the adsorbates. DFT calculations shows a shift of the energy weighted center toward higher values, when there is tensile strain and downward shifts to lower values, in the presence of compressive strain. The position of the d-band center is affected by the strain effect and electronic effect between the monolayer and substrate <sup>[58]</sup>. A. Roudgar et al. used density functional theory calculations to study adsorption of atomic hydrogen and CO on Pd/Au bimetallic surfaces. They observed an upshift in the d-band, due to the weak coupling between d-bands of Pd and Au, and the expansion of the Pd overlayer on Au. This d-band upshift results in stronger adsorbate bonding <sup>[63]</sup>.

This PhD dissertation consists of 8 Chapters. Chapter 1 introduces the general idea for electrocatalyst design and characterization and gives some information obtained from literature about the previous studies in the field and some backgrounds. Chapter 2 covers the basics of metal deposition, thin film growth, and electrochemical techniques that were used. Chapters 3, 4 and 5 discusses the most important techniques and equipment that were used in our study. Chapter 6, introduces the conditions in which experiments were performed and the experiment procedures that were used. Chapter 7, explains results and discussion which is followed by a conclusion and future works in chapter 8 and 9.

## 2. Metal Deposition

One of the primary topics in electrochemistry is investigating the structure and kinetics of deposition of metal adsorbates on metal surfaces. The properties and structure of the deposited metal is dominated by the early steps of adsorption/deposition, as well as the growth mechanism. When metal M is in contact with the electrolyte containing its ions  $(M^{Z+})$ , some atoms from metal M lose electrons and dissolve into the electrolyte, while some metal ions  $(M^{Z+})$  gain electrons and get deposited on the metal surface. At the beginning, when the metal M becomes in contact with the electrolyte that contains its metal ions  $(M^{Z+})$ , either deposition or dissolution will happen faster compared to the other, but eventually there will be a dynamic equilibrium state and both reactions will be, happening at the same rate. The overall reaction of the formation and dissolution of metal  $(M/M^{Z+})$  electrode is expressed by

$$M^{Z+} + Ze^{-} \leftrightarrows M_{bulk} , \qquad (28)$$

where Z is the number of electrons in the reaction. As a result of the deposition and dissolution of metal M on the surface and from the surface, a charge interface will form between the metal surface and the electrolyte. The difference in the potential of the metal surface ( $\emptyset_M$ ) and the electrolyte ( $\emptyset_S$ ) leads to a driving force for charge interphase and is expressed as

$$\Delta \phi (\mathbf{M}, \mathbf{S}) = \phi_{\mathbf{M}} - \phi_{\mathbf{S}}. \tag{29}$$

The value of the potential difference can be measured by connecting a reference electrode and forming an electrochemical cell. Reference electrodes are used widely and saturation hydrogen electrodes (SHE) are one of the most traditionally accepted and used

reference electrodes. The potential value for SHE is considered to be zero. The Nernst equation is used to calculate the equilibrium potential:

$$E_{M^{Z^{+}}/M} = E^{0} + \frac{RT}{nF} \ln(a_{M^{Z^{+}}}) .$$
(30)

In equation 30,  $E_{M^{Z+}/M}$  is Nernst equilibrium potential, E<sup>0</sup> is the standard electrode potential, R is the universal gas constant, F and T represent Faraday's constant and absolute temperature respectively and  $a_{M^{Z+}}$  is the activity of the metal ions in the electrolyte. For electrolytes with low metal ions concentration, the activity can be replaced by concentration <sup>[64]</sup>.

If more negative potential than the  $E_{M^{Z+}/M}$  is applied to the electrode, it is at the overpotential state ( $\eta = \Delta E = E - E_{\frac{M^{Z+}}{M}} < 0$ ) and the deposition reaction takes place at the electrode:

$$M^{2+} + Ze^- \to M_{bulk}.$$
 (31)

If the value of the applied potential is more positive than the  $E_{M^{Z+}/M}$ , the electrode is at underpotential conditions ( $\eta = \Delta E = E - E_{\frac{M^{Z+}}{M}} > 0$ ) and dissolution reaction is expected:

$$M \to M^{Z+} + Ze^- . \tag{32}$$

In some cases where a metal electrode is in contact with an electrolyte that contains different metal ions, at underpotential conditions, deposition could happen <sup>[65,66]</sup>. This phenomenon is called underpotential deposition (UPD) and will be discussed in the following chapters.

### 2.1. Cyclic Voltammetry and Linear Sweep Voltammetry

Cyclic voltammetry (CV) is one of the most popular electrochemical techniques used widely to study reduction/oxidation processes of molecular species, adsorbed molecules on the surface, and electron transfer. CV gives information about catalysts behavior in electrochemical systems and the activity of the catalyst <sup>[67]</sup>. Figure 12 shows cyclic voltammogram for Pt (100) electrode in acid solution. The x-axis shows the values of the applied potential to the working electrode (E) and the y-axis shows the current values (I). The potential variation with the scan speed is expressed as the scan rate. During the forward scan which is called the cathodic scan, the potential is swept negatively from the start point toward the switching potential, and then during an anodic scan, the scan direction is reversed and the potential is swept toward the initial potential value.



Figure 12 - Cyclic voltammogram for Pt (100) in 0.5 M H<sub>2</sub>SO<sub>4</sub> with scan rate 20 mV/s.

linear sweep voltammetry (LSV), is another useful electrochemical technique that is used to identify unknown species and it helps to calculate the cathodic charge of monolayers. The potential is swept linearly between the working and reference electrode and the values of the current is measured. Wherever species oxidized or reduced, a peak will appear. For both CV and LSV a three-electrode setup are used.

### **2.2.** Underpotential Deposition (UPD)

Advances in surface electrochemistry and methodologies has brought attention to the underpotential deposition of metals on foreign metal substrates. In the underpotential deposition process, a monolayer of metal is placed on a foreign substrate at potentials positive of the potential for reversible Nernst deposition. A monolayer of atoms is deposited on the substrate as a result of the strong interaction between the metal ions and the substrate. The UPD process leads to formation of an atomic layer with control surface coverage <sup>[68]</sup>. As expressed earlier by equation 1, the chemical potential of the monolayer deposited in the UPD layer ( $\mu_{ads}$ ) is different from the bulk metal chemical potential ( $\mu_{bulk}$ ). Based on this difference, the atoms at the monolayer are bound strongly to the surface of the foreign substrate, compared to the surface of a substrate of their own species. The differences in the value of the potentials is the binding energy value of the UPD layer and the substrate [<sup>69</sup>].

Polycrystalline electrode surfaces were used for early studies of UPD phenomenon, due to the drawbacks of preparing single crystal electrodes. Ultra-high vacuum systems were used for studying UPD on polycrystalline systems. However, since those studies were ex-situ, the nature of the surface under study was unclear. This field was altered dramatically by the arrival of procedures for developing single crystal surfaces <sup>[68]</sup>. Major advances in understanding the details of the underpotential deposition (UPD) process happened by development of in situ scanning probes and surface x-ray scattering techniques. The first studies of the UPD phenomenon were in the early 1940's, where an Ag was deposited on Au and Pt <sup>[70]</sup>. Using single crystal surfaces, made the structural studies for the UPD process clarified, and enabled atomic level studies by the help of scanning probe microscopes <sup>[71]</sup>. Since then, several aspects of the UPD process have been investigated widely, including structure of the substrate metal, growth mechanism and thermodynamic and kinetics properties. Figure 13 shows the schematics of the UPD process for underpotential deposition of a metal on to a foreign substrate. During the UPD process, the potential starts to sweep from the more positive potentials (right end of the potential axis) toward more negative potentials and then a reverse scan to the initial potential value.



Figure 13 - Schematics of underpotential deposition process

Before the Nernst equilibrium potential, we can see the first cathodic peak which shows the formation of a UPD of metal on the foreign substrate. The deposition of the UPD metal ions on substrates continues as the potential is more positive than the Bulk deposition. When the potential gets more negative than the Nernst equilibrium potential, bulk deposition starts at overpotential conditions (OPD). At the reverse anodic sweep, as the potential goes from more negative values to more positive ones, first the bulk materials are removed, followed by removal of the monolayer of the deposited foreign metal. In ideal cases, the stripping peaks (anodic sweep) and deposition peaks (cathodic sweep) should be symmetrical. However, due to the effects of the other reactions on UPD processes, such as oxygen reduction and alloying, the reversibility of the system may be compromised. In some systems, more than one UPD peak may appear due to the additional formation of UPD layer or adsorbates <sup>[72,73]</sup>.

### 2.3. Thermodynamics of UPD

During the UPD, the discharge of the metal ion  $(M^{Z+})$  in contact with the substrate metal (S) can occur. This process is as follows:

$$M^{Z+} + \gamma_{UPD} e(S) \leftrightarrows M^{(n-\gamma_{UPD})^+}(S) .$$
(33)

In equation 33,  $\gamma_{UPD}$  is the electrodeposition valence. Based on this equation, the underpotential- coverage dependence can be calculated as

$$\Delta E = \Delta E^{\to 0} + \frac{RT}{F} \left( \frac{1}{\gamma_{\text{UPD}}} - \frac{1}{n} \right) \ln[a_{\text{M}}^{\text{Z}+}] - \frac{RT}{\gamma_{\text{UPD}}^{\text{F}}} \left[ \ln\left(\frac{\theta}{1-\theta} + f\theta + g\theta^{\frac{3}{2}}\right) \right], \quad (34)$$

where  $\theta$ , *f* and *g* are coverage of the monolayer, Temkin and Frumkin parameters respectively. For UPD layer-substrate interactions, the Temkin parameter (*f*) and for lateral adatom interactions, Frumkin parameter (g) are used. Equation 34 can be simplified to the Langmuir adsorption model if the value of f and g equal to zero <sup>[74]</sup>:

$$\Delta E = \Delta E^{\to 0} + \frac{RT}{F} \left( \frac{1}{\gamma_{UPD}} - \frac{1}{n} \right) ln[a_M z_+] - \frac{RT}{\gamma_{UPD} F} ln\left( \frac{\theta}{1 - \theta} \right).$$
(35)

The relationship between the underpotential shift  $(\Delta E_p)$  and work function difference  $(\Delta \emptyset)$  of the substrate and adatoms is explained by

$$\Delta E_{\rm p} = 0.5 \Delta \phi \quad . \tag{36}$$

In equation 36,  $\Delta E_p$  is the difference between the value of the potential at the most positive desorption peak and the Nernst equilibrium value. Equation 36 is useful for polycrystalline systems and suggests that work function of the substrate must be larger than deposited metal <sup>[75]</sup>. However, this model fails for single crystals due to the effects of the crystallographic orientation. In the next two sections, the underpotential deposition of Pd on Au (111), Au (100) and Ru (0001) will be discussed.

#### **2.4.** Underpotential Deposition of Pd on Au (hkl)

Pd monolayers can be considered as good electrocatalysts as they show selectivity, stability and high reactivity. The only important factor will be to have stable Pd electrocatalysts in electrolytes with different PH values <sup>[8]</sup>. The important parameter that affects the growth behavior and the morphology of the deposited monolayer is defined by the early stages of deposition <sup>[66]</sup>.

D.M. Kolb et al. <sup>[76]</sup> studied the electrochemical Pd deposition onto Au(111) in UPD regime with the help of cyclic voltammetry and scanning tunnel microscopy (STM). They observed that Pd underpotential deposition on Au (111) was irreversible in chloride free

solutions, and so they only studied the UPD of Pd on Au (111) in chloride solutions which is a reversible process. By using stepped Au (111), the effect of the surface defects during the nucleation process and deposition can be studied <sup>[77]</sup>. Figure 14 shows cyclic voltammetry (CV) for Au (111) in solution containing H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>PdCl<sub>4</sub>. Pd deposition on Au (111) starts at potentials below 0.6 V (vs. SCE) <sup>[78]</sup>. At potentials more positive than the bulk deposition (bulk deposition starts at potentials negative than 0.49 V (vs. SCE)), there are two underpotential cathodic peaks around 0.53 V and 0.5 V, and two anodic peaks around 0.58 V and 0.63 V, respectively. Peaks 0.53 V and 0.58 V are due to the deposition and stripping at steps, while peaks 0.5 V and 0.6 V correspond to deposition and stripping at terraces. These suggest that Pd deposition starts at steps, and by going to higher potentials, the deposition at the terrace can occur.



**Figure 14** - Cyclic voltammetry for Au (111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 0.1 mM H<sub>2</sub>PdCl<sub>4</sub> with scan rate 1 mV/s. taken from ref <sup>[76]</sup>.

The UPD process makes it possible to form exactly one monolayer of Pd on Au (111). Calculation of the cathodic charge related to the CV shows that a charge of about 450  $\mu$ C.cm<sup>-2</sup> is gained which is equal to one monolayer of Pd layer. The deposition of Pd on Au (111) starts at the underpotential regions with a pseudomorphic layer of Pd formed on the gold substrate and by going to the overpotential region, the second layer is formed on top of the first layer. The mechanism for the first two Pd layers' growth is layer-by-layer and when the first layer has been completed, deposition of the second layer will start.

In another study, D.M. Kolb et al. investigated the Pd deposition on island-free and island Au (100) in 0.1 M  $H_2SO_4 + 0.1$  mM  $H_2PdCl_4$ . Cyclic voltammetry for Pd underpotential deposition on Au (100) island free is presented in Figure 15.



Figure 15 - Cyclic voltammetry for Au (100) in 0.1 M  $H_2SO_4 + 0.1$  mM  $H_2PdCl_4$  with scan rate 1mV/s. Taken from ref <sup>[79]</sup>.

Cyclic voltammetry data for Pd UPD on Au (100) shows one cathodic peak in which Pd starts to nucleates at steps and grow toward terraces to form a full monolayer. In

the case of Pd UPD on Au (100), growth mechanism is very similar to Pd UPD on Au (111) with cathodic peak at 540 mV vs. SCE. STM images of Pd underpotential deposition on Au (100) shows that at potential equal to 520 mV vs. SCE, nucleation of Pd at monoatomic high steps starts and continue to cover terraces. STM images reveals that by going to more negative values of the potential (around 0.47 V vs. SCE), second layer will form on top of the steps on the first layer. The deposition of Pd on Au (100) is layer by layer up to the third layer and forth layer starts to form when third layer is not completed yet. Figure 16 shows STM images for this process.



Figure 16 - STM images of Pd deposition on Au (100)- island free in 0.1 M  $H_2SO_4 + 0.1$  mM  $H_2PdCl_4$  taken from ref<sup>[79]</sup>.

At overpotential regions, an epitaxial growth of Pd films was observed that behaved as the massive Pd (100) single crystal. An interesting difference between Pd deposition on Au (111) and Au (100) is the alloy formation in the underpotential regions for Au (100), which affects the coverages of sub-monolayers <sup>[79]</sup>.

### 2.5. Pd Deposition on Ru (0001)

Ruthenium has specific catalytic properties and by being part of Pt- Ru catalysts for methanol in fuel cells, has gained a lot of attention. The fact that Ru can function as an active oxygen provider, makes it possible for CO to oxidize more easily on the Ru surface and clear the surface from CO at lower potentials, compared to platinum. This property of the Ru can make it an ideal Ru-based electrocatalyst <sup>[80,81]</sup>.

In a study by Brankovic et al., in situ scanning tunnel microscopy technique was used to investigate spontaneous Pd deposition on Ru (0001)- single crystal surface. Ru (0001) was prepared with ultrahigh vacuum and was immersed in solution containing palladium ions. Surface oxidation voltammetry curves for Ru (0001) in sulfuric acid shows two cathodic peaks for reduction and one anodic peak. This process involves one electron per atom exchange. Figure 17 shows CV for Ru (0001) surface oxidation process. It was shown that without applying any external potential, they were able to deposit an epitaxial and textured multilayer Pd on Ru (0001) crystal surface. By controlling the amount of ion in the solution, the deposition process was controlled. They conclude that Pd starts to form a monolayer on Ru (0001) initially and then forms three-dimensional Pd <sup>[82]</sup>.



Figure 17 - Surface oxidation of Ru (0001) in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Taken from ref<sup>[80]</sup>.

Kolb et.al <sup>[24]</sup> studied the effect of the surface structure on catalytic activity by deposition of palladium on single crystal substrates with different lattice constants, which results in a surface strain. Deposition of the metal onto the metal substrate helps to tune the catalytic activity of the surfaces. Single crystal substrates that used were Au (111), Pt (111), Rh (111), Ru (0001), Ir (111), Re (0001) and PtRu (111). The observed behavior for palladium monolayer on single crystals were different from bulk palladium and showed high overpotential for hydrogen absorption. The anodic scan for palladium monolayer on the single crystal substrates is shown at Figure 18.



Figure 18 - Positive potential scans for palladium monolayers on single crystal electrodes in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Taken from ref <sup>[24]</sup>.

The peak potentials demonstrate the strength for hydrogen adsorption on single crystal electrodes and explain that the palladium deposition on the surface of the single crystals can change their catalytic properties and affect the binding energies. Palladium monolayer on Ru (0001) is affected by the lattice parameter of the deposited palladium that is different from ruthenium substrate and also the electronic interaction between palladium overlayer and ruthenium. The combination of these two effects modifies the properties of  $Pd_{ML}/Ru$  (0001).

Pd deposition on Ru (0001), makes it possible to design Pd-Ru electrocatalysts with properties of interest and low Pd content. One of the important factors during the deposition

of Pd on Ru (0001) is to make sure the Ru crystal surface is free from oxidation. The activity of the Pd monolayer on Ru (0001), depends on the d-band center. The DFT calculations can help to understand and compare the d-band center for Pd monolayer on metal substrates, such as Au (hkl) and Ru (hkil). The binding energy of the adsorbate and d-band center of the top metal layer determines the electrocatalytic activity of the catalyst. In the case of Pd monolayer on top of Ru (0001), the position of the d-band center (with respect to Fermi level) controls the reactivity of the surface<sup>[57,83]</sup>. Negative strains in Pd monolayer on Ru (0001) cause a compression in the Pd atoms on the surface and lower the binding energy.

# 3. Scanning Tunneling Microscope (STM)

In the early 1980s, Gred Binning and Heinrich Rohrer developed a surface characterization technique at IBM research laboratory with high resolution that can give information about surface structure at atomic level. This technique is called scanning tunneling microscopy (STM), and is used widely at the nanoscale level for imaging <sup>[84,85]</sup>.

STM stands on the fact that the electron tunneling effect can happen. By applying a bias voltage across two metals which are very close together (1 nm), the quantum mechanical tunneling current flows across the two metals

$$I_{t} = V_{b} e^{-cd\sqrt{\phi}} . \tag{37}$$

In equation 37,  $I_t$  stands for tunneling current,  $V_b$  is the potential bias, the distance between the two metals is d,  $\emptyset$  is the work function and c is the constant, which is

$$C = 4\pi \sqrt{\frac{2m}{h}} = 10.25 \text{eV}^{-\frac{1}{2}} \text{nm}^{-1}, \qquad (38)$$

where m is the mass of electron and h is planks constant.

Based on equation 37, keeping adequate distance between the two metals is important, as by increasing the distance between the two metals (d), the value for tunneling current (I<sub>t</sub>) will decrease exponentially. Another way to make sure the tunneling effect is improved, is by using a sharp tip (needle), which will scan across the second metal surface. Measuring the fluctuations in the tunneling current gives information at the atomic scale about measuring the distance in Z direction and enables us to investigate the atomic arrangements of the metal surface <sup>[85]</sup>. Figure 19 shows the working principle for STM. A small metal needle (tip) is brought very close to the surface (around several atomic layers). This metal probe is from W wire or etched Pt-Ir, and ideally should have only one atom at its tip, as the radius of the tip curvature determines the STM resolution. The tunneling current (usually less than 1 nA) is measured with digital signal processing (DSP) and is converted to a discretized image. One of the factors that affects the quality of the STM images is the quality of the tip, which should be sharp at the end (only one atom) with a wide body to withstand the noise <sup>[86]</sup>. Double imaging happens when tips do not have good shape and causes tunneling from more than one tip point and produce low quality images.



Figure 19 - Schematic view of STM- An ideal tip has only one atom at the very end.

STM can scan the surface in two modes (Figure 20), Constant current or constant height. In the constant current mode, the height of the piezo stages change, and the tip heights change is recorded while the current is being kept constant. For scanning at constant height, the tip scans the surface in a straight line (constant height) and the changes in the tunneling current is recorded.



# **Constant Current Mode**

# **Constant height Mode**

Figure 20 - Operation modes of STM

The tip is not colliding with the surface due to feedback electronics, constantly changing the distance of the tip and substrate. The substrate is positioned on a piezoelectric material, so it can move in 3D.

### **3.1. Electrochemical Scanning Tunneling Microscope**

STM can be used for studying electrochemical reactions and the deposition process. The electrochemical STM is called EC-STM and enables the in-site measurements using STM. For this purpose, STM systems run electrochemically, where a reference electrode and a counter electrode are used. The reference electrode helps to control the potential of the tip and the substrate. For controlling the potential of the working electrode and the tip, a potentiostat is used. The EC-STM schematic can be seen in Figure 21. During the in situ STM, the tip acts as an electrode in the STM electrochemical cell and this exposure of the tip can affect the tunneling current and the shape of the tip. In order to eliminate the effect of the tip exposure in the electrochemical process, the STM tip gets coated with some hydrophobic material to reduce the exposed area and only very end of the tip remains uncoated <sup>[87,88]</sup>.



Figure 21 - Schematic of in-situ STM with coated tip

# 4. Subtractively Normalized Interfacial Fourier Transform Infrared Spectroscopy (SNIFTIRS)

Infrared spectroscopy is one of the useful analytical techniques to study any sample in almost any state. Invention of the Fourier-transform spectrometers improved this field, and using Fourier-Transform infrared (FTIR) spectroscopy enhanced the quality of infrared spectra. Vibrations of the atoms in molecules are the foundation of infrared spectroscopy. Infrared spectrum is acquired by passing infrared radiation along a sample and calculating the part of the incident radiation that is absorbed at a specific energy. Frequency of a vibration of a sample molecule determines the energy of the peak in the absorption spectrum <sup>[89]</sup>. FTIR is used as an important analytical technique that gives information about interfaces at molecular level with high accuracy and sensitivity. The adsorbates bonding geometry and interaction can be investigated with this technique, as it is possible to study the in situ surface reactions <sup>[89,90]</sup>.

### 4.1. Fundamental Vibrations

Infrared spectroscopy covers the infrared region of the electromagnetic spectrum (oscillating electrical field and magnetic field that are perpendicular to each other) with wave numbers from 13000 cm<sup>-1</sup> to 10 cm<sup>-1</sup>. Electromagnetic spectrum covers three regions in the infrared spectrum, near, mid and far infrared. Mid-Infrared gives information about the fundamental vibrations of the molecules. Only materials that have small energy differences in vibrational and rotational states absorb infrared due to the change in the dipole moment of the molecule. Absorption will take place only when the frequency of the radiation matches the frequency of the molecule <sup>[91,92]</sup>.

The electric dipole moments (D.M) of the molecule, that shows infrared absorption, should change during the vibration. The larger the D.M changes, the higher the intensity of the absorption band. There are several types of fundamental vibrations of the bonds like symmetrical and asymmetrical stretching vibrations or in-plane and out-of-plane bending modes that contribute to infrared spectra. The metal surface selection rule predicts that infrared absorption bands with the oscillating dipole moment parallel to the surface are absent from the spectra of molecules adsorbed on metal particles and only p-polarized light interacts with the adsorbed particles. Both polarizations interact with solution species. In stretching vibration, the bond length changes while in bending vibrations, bond angle changes <sup>[93]</sup>. Figure 22 explains some of the fundamental vibrations. In symmetrical



Figure 22 - Stretching and bending vibration modes

stretching vibration, bonds move away and toward the common atom at same time, but in the asymmetrical vibrations, one or more bonds move in opposite directions of the others. Bending vibrations include scissoring (atoms remain in the same plane while the valence angle is changing), Rocking (atoms remain in the same plane while bonds are swinging right and left at the same time), twisting (out-of-plane twisting of bonds) and wagging (bonds swinging out-of-plane back and forth at the same time).

In general, stretching takes more energy than bending, and as a result, stretching vibrations usually happen at higher frequencies. The number of fundamental vibrations for a linear molecule is 3N-5 (N is the number of atoms in the molecule) and for non-linear molecules this value is 3N-6.

### 4.2. Surface Selection Rule

Based on the metal-surface selection rule, the infrared absorption bands for molecule vibrations that has an oscillating dipole moment parallel to the surface are absent from the spectra of molecules, and only vibrations with oscillating dipole moment perpendicular to the metal surface are infrared active <sup>[94]</sup>. Surface selection rule, is based on the fact that infrared electromagnetic waves produce an oscillating field that can only excite a vibration in an adsorbed molecule, when that molecule has a dipole moment in the direction of the field, which is perpendicular to the metal surface <sup>[95]</sup>.

### 4.3. Hook's Equation

Hook's equation helps to estimate the stretching vibrations of the bonds from the force constant, and is expressed as

$$N = \frac{1}{2\pi c} \sqrt{(K/(\frac{m_1 m_2}{(m_1 + m_2)6.02 \times 10^{23}}))}, \qquad (39)$$

where v, is frequency (cm<sup>-1</sup>), c is the velocity of light (cm/Sec), K is the force constant (dyne/cm),  $m_1+m_2$  is sum of the atomic masses of the atoms connecting the bond and  $\frac{m_1m_2}{(m_1+m_2)}$  is the reduced mass ( $\mu$ ). Equation 39 can be simplified as <sup>[89,96]</sup>

$$\nu (cm^{-1}) = 4.12 \sqrt{\frac{\kappa}{\mu}}$$
 (40)

#### 4.4. Infrared Methods for Electrochemistry

In conventional IR spectroscopy, the light transmitted from the sample is measured, whereas in reflection IR spectroscopy, the IR spectroscopy is combined with reflection theories. In-situ infrared techniques can be used for investigating surface reactions, such as adsorbate bonding geometry and the interaction between adsorbates. One of the examples of in-situ methods for identifying the catalysts' surface is reflection absorption infrared spectroscopy (RAIRS) which is based on the fact that single metal crystal surfaces have high reflectivity and this helps to detect monolayer adsorbates. In this technique, IR radiation is passing the solution and being reflected at the interface, and it is very important that a thin layer of solution is formed between the infrared window and electrode. However, this method is not practical for electrochemical systems and is only useful in UHV environments, due to the strong absorption of infrared radiation with electrochemical solvent. One way to solve the effect of the absorption of the light by solvent is to use surface enhanced infrared absorption spectroscopy (SEIRAS). SEIRAS is an infrared spectroscopy surface-sensitive method that is used widely, as it can improve the vibrational bands of an adlayer molecule by using the electromagnetic properties of the metal films. The sensitivity of SEIRAS is 10-50 times higher than RAIRS which makes it a perfect method for investigating reactions at both surfaces and interfaces. Enhancement in the local electric fields due to excitation of the localized plasmon of metal particles leads to the infrared absorption enhancement. The enhanced electric field can excite the molecules that are adsorbed on the surface. The localized surface plasmon resonance (LSPR) is considered as an optical incident caused by the interaction of light and conductive nanoparticles which are smaller than the incident wavelength. The electric field of the incident light, can excite the electrons of a conduction band <sup>[97]</sup>. The SEIRAS method is very popular for studying electrochemical reactions, as it provides information about the interface and species on the surface which makes it possible to investigate the electrode and electrolyte interfaces with high sensitivity <sup>[98,99]</sup>. Other configurations are also used for in-situ study of the interfaces and adsorbates; one of them is the Kretschmann configuration <sup>[100]</sup>, in which the infrared optical window is the working electrode with a thin film (tens of nanometers) deposited on it. This method reduces the penetration of the incident light to a relatively low amount of electrolyte <sup>[101]</sup>. Figure 23 shows the detail of this configuration. The internal reflection enhances the intensity of the absorption spectrum and the mass transport which makes it



Figure 23 - Schematics of the Kretschmann setup

useful for electrochemical kinetics studies. However, the stability of the working electrode makes this method imperfect <sup>[98,99,102]</sup>.

Besides the internal reflection method for in-situ FT-IR studies, external reflection methods are also used for characterization of electrodes in electrochemical systems. In this method, in order to decrease the amount of electrolyte in the external reflection experiment, the working electrode is pushed tightly against the optical window (materials with low reflectivity index, like Ge, Si, ...) so that a thin a layer of electrolyte is formed. This method is called Otto configuration <sup>[103]</sup>. Otto configuration reduces the mass transport and does not allow the kinetics measurements. Any flat polycrystalline, single crystal electrode, or any other flat surfaces with catalyst layer deposited on it can be used in Otto configuration. Figure 24 shows configuration of the external reflection method. The electrolyte between the electrode and optical window can cause background noise that is larger in magnitude



Figure 24 - Schematics of Otto setup

than the signal from the interface, which can provide misleading information about the adsorbates and make it necessary to delete the effect of the electrolyte layer <sup>[102]</sup>.

Subtractively normalized interfacial FT-IR spectroscopy (SNIFTIRS) is another external reflection technique, used widely as it can remove the solution background by coadding a set of interferograms. All sample spectra are acquired with respect to the reference spectrum. Two potentials are used to gain spectra which are denoted  $E_1$  and  $E_2$ . At potential equal to  $E_1$ , the sample spectrum is recorded. In this potential, the adsorption species or intermediates are at the electrode surface, whereas at potential  $E_2$ , the reference spectrum, there are no adsorbates on the electrode surface as the reaction is completed <sup>[104]</sup>. The final spectrum is calculated by subtracting the reference spectrum from sample spectrum, which removes the background information and is then normalized by dividing by the reference spectrum

$$\frac{\Delta R}{R} = \frac{R(E_1) - R(E_2)}{R(E_2)} \,. \tag{41}$$

The potential- difference technique improves the signal to noise ratio (S/N) and eliminates spectral background. However, to further enhance the S/N ratio, attenuated total reflection (ATR) is used at the phase boundary between the prism and the electrolyte interface. ATR is based on the total internal reflection and the evanescent wave. Total internal reflection happens when the IR radiation enters materials with high refractive indices and the incident angle at the interface is greater than the critical angle (which depends on the refractive indices of the two surfaces). The critical angle can be calculated with Snell's law:

$$\theta_c = \sin^{-1}\left(\frac{n_2}{n_1}\right),\tag{42}$$

where  $n_2$  is the medium with lower refractive index (electrolyte) and  $n_1$  is the medium with higher refractive index (prism).

According to quantum mechanics, the electromagnetic wave can't be discontinuous at the reflection interface, which helps to get the evanescent wave when total reflection happens. The evanescent wave spreads with respect to the phase boundary and penetrates into the sample structure (medium with lower refractive index). So, only regions close to the prism/medium interface will be recorded, as the evanescent wave declines exponentially with the increasing distance from electrolyte. The attenuated wave is then reflected back to the IR prism. The intensity of the evanescent is maximum at the point where it is generated and decreases exponentially by increasing the distance from the interface. If the electrode is placed within the range that the evanescent wave penetrates, the reflected IR radiation can provide information regarding the adsorbates on the electrode surface. The beam penetrates a fraction of a wavelength beyond the reflecting surface and adsorbates absorb the light at the interface. The depth of penetration (d) is expressed by

$$d = \frac{\frac{\lambda}{n_1}}{\left\{2\pi \left[\sin^2\theta - \left(\frac{n_2}{n_1}\right)^2\right]^{\frac{1}{2}}\right\}},$$
(43)

where  $\lambda$  is the wavelength of the infrared light,  $\theta$  is the incident angle of the radiation (few angles larger than the critical angle). Equation 43 shows that by changing the incident wavelength, depth of penetration will also change <sup>[92]</sup>.

### 5. Mass Spectrometry

One of the analytical techniques that is used widely is mass spectrometry (MS). This technique can give information about unknown compounds in a sample by quantifying known materials. In the early days of mass spectrometry, it was used for giving information about an element's atomic mass, which revealed that some elements showed several masses. This phenomenon led to isotope discovery. This discovery leads to using of this technique for determining the isotopes of elements. Mass spectrometry can measure the mass to charge ratio (m/z) of ions and gives a plot of the mass to charge ratio versus the intensity. This plot is called mass spectrum, and it provides information about the masses of both particles and molecules as well as information about their isotopes. The sample for mass spectrometry should be ionized with the help of electron ionization and then separated based on their mass to charge ratio. The separation can proceed with the help of electric or magnetic fields, after which the ions are detected based on their abundance.

A mass spectrometer has three main parts which are an ion source, a mass analyzer and detector system. The ion source ionizes the sample into ions which are then moved toward the mass analyzer and the detector. The ion source produces electrons that moves toward the sample gas. The mass analyzer separates the ions based on their mass to charge ratio and the detector measures the value of each ion for their m/z ratio. The computer is used to convert and provide the data. Figure 25 shows basic concepts of mass spectrometry analysis <sup>[105,106]</sup>.


Gas Phase sample molecules

Fragmentation

Figure 25 - Schematic of mass spectrometry basic concepts

The mass to charge ratio versus intensity is displayed on the computer and is called mass spectrum. This mass spectrum can provide the information about hydrogen to deuterium ratio by integrating the area below each peak. In the mass spectrum, mass 2 presents the H<sub>2</sub> and mass 3 stands for HD. The  $\frac{H}{D}$  ratio can be calculated as

$$\frac{H}{D} = \frac{H_2 + \frac{1}{2}HD}{\frac{1}{2}HD}$$
 (44)

The hydrogen atom has two common isotopes, hydrogen with nominal relative mass of one and deuterium with nominal relative mass of two. In the mass spectrum, distribution of the hydrogen isotopes altered the appearance of peaks. For direct mass spectroscopy measurements of H/D ratio in the gas product, an electrochemical cell (Hoffman cell) was used. H/D ratio in the gas products was calculated from electrolysis of acidic water with pre-determined H<sub>2</sub>O and D<sub>2</sub>O ratio. This cell can store the gas for mass spectrometry measurements. The Hoffman cell has two limbs that are connected together with a reservoir tube and a funnel shaped bulb at the top. This system is used to run in situ water electrolysis with pre-determined H/D ratio in conjunction with gas phase mass spectrometry.

# 6. Experimental Procedure

# 6.1. Single Crystal Electrodes

The surface structure of an electrode plays an important role in reaction kinetics of the electrocatalytic reactions. Single-crystal electrodes are used widely for studying electrocatalytic reactions as they can provide information about surface crystallography on reaction kinetics, sites that are active on the surface, and information about the substrate-adsorbate interaction <sup>[107]</sup>.

Most metals from the platinum group crystalize in a face-canter cubic (fcc) lattice. Only Ru and Os have hexagonal close-packed (hcp) lattices. Fcc and hexagonal closepacked crystal lattices are described with Miller indices as (hkl) and (hkil), respectively. On fcc metals with miller indices (111) surfaces, the adsorption sites are the top, bridge, and threefold sites. The coordination number of atoms in steps and terraces are different, such that atoms in steps have lower coordination numbers. This makes atoms at steps more active, compared to atoms at terraces, with some exception.

# 6.2. Well-Ordered Single-Crystal Electrodes Preparation and Pre-Treatment

It is very important to prepare well-ordered single crystal electrodes. Au (111) single crystal, Ru (0001) single crystal, Pt (111) single crystal, and Pd (111) single crystals are used for thin film deposition in the experiments. Single crystals are mechanically polished with diamond suspension of 9  $\mu$ m, 3  $\mu$ m, 1 $\mu$ m, and 0.25  $\mu$ m, then sonicated and washed thoroughly with DI water (>18.2 MΩ, Millipore Direct Q-UV with Barnstead A 1007 pre-distillation unit). Before each experiment, single crystals are annealed and

prepared for the next step. Au (111) single crystal with diameter of 10 mm and thickness of 2 mm is polished both mechanically and electrochemically. After polishing the Au (111) mechanically with diamond suspension, it is also polished electrochemically in a solution containing ethylene glycol, hydrochloric acid, and ethanol (2.5:1.5:1) with around 1.4 A/cm<sup>2</sup> current density, applied to oxidize the Au surface. In this electrochemical polishing process nickel sheet is used as a cathode with approximately the same surface area as Au (111). After the electrochemical polishing, the crystal is rinsed thoroughly with DI water, and annealed for 15 minutes with hydrogen flame until white hot, and then naturally cooled down in air. The Au (111) surface after the polishing and annealing process can be seen in Figure 26.



Figure 26 - Freshly annealed Au (111) surface taken with STM

For Ru (0001) single crystal, the surface is reactive with air and oxygen, so it should be kept away from oxygen contamination during the annealing and cooling process. As a result, after the mechanical polishing, an induction heating is used for the annealing process. The configuration of this process can be seen in Figure 27.



Figure 27 - Induction annealing setup for Ru (0001)

The Ru (0001) single crystal is placed on a ceramic base and sealed in quartz cell. The crystal is heated up for one hour up to 1400  $^{0}$ C inductively in the Ar and H<sub>2</sub> (96:4) atmosphere. The inlet and outlet of the cooling gas can be seen in Figure 27. A PID controller is used for controlling temperature and an infrared sensor is used for monitoring. After the annealing process is finished, the same gas is used to cool down the Ru crystal to room temperature. In order to cover the Ru crystal surface during the cool down process, a CO saturated solution is dropped on the Ru (0001) surface, and finally the Ru (0001) crystal is transferred to an electrochemical cell for next steps.

Pt (111) and Pd (111) single crystals with diameter of 10 mm and thickness of 2 mm are also used as working electrodes. After the same mechanical polishing is applied, the single crystals are ready for the annealing process. Pt (111) single crystal can get oxidized while cooling in the air. So, after annealing with propane flame for 15 minutes to red hot, it is transferred immediately to the quartz tube which is purged with Argon gas to eliminate the influence of the oxygen contamination <sup>[108]</sup>. Pd (111) single crystal is also treated with same manner as Pt (111) single crystal. Pd (111) single crystal surface is more sensitive to oxygen contamination and can adsorb hydrogen from the air and form palladium hydride. So, the Argon gas is purged into the quartz tube even during the annealing process. Figure 28 shows the cooling system for Pd (111) and Pt (111) crystals after annealing. Cooling gas is purged from the inlet to the quartz tube, and for monitoring the gas flow the outlet hose is covered with DI water. After the annealing process, single crystals are transferred to an electrochemical cell for the experiment.



Figure 28 - Flame annealing cooling system

# 6.3. In-situ STM

Nanoscope Multimode V scanning Probe Microscope (Digital Instrument Corp.) was used for studying electrochemical in-situ STM. One important part of the electrochemical in-situ STM is tip preparation. For this purpose, a 2 cm long Pt/Ir wire (90%:10%) was etched in a saturated CaCl<sub>2</sub> solution. In order to have only one atom on the very end of the tip to create a sharp end, approximately 2 mm of the Pt/Ir wire is submerged in the saturated CaCL<sub>2</sub> solution and an AC potential around 30 V is applied for some time. When the wire starts to form a neck, the Ac potential reduces to 8 V until the submerged part of the Pt/Ir wire breaks from the rest. For this tip etching process, nickel foil is used

as a cathode. The next step is to wax the tip to decrease the exposure area and only the very end of the tip remains uncoated for electrochemical in-situ STM.

Electrochemical in-situ STM is performed by Nanoscope Multimode V scanning Probe Microscope in a glove box which was purged with high purity Nitrogen gas. A custom-made Teflon cell is used to perform the in-site STM. The substrate (single crystal electrode) was placed on the cell as shown in Figure 29, an Ag/AgCl electrode was used for the reference electrode and Pt wire as a counter electrode. To avoid contamination in the cell from Pt wire, before the experiment it was annealed with hydrogen flame.



Figure 29 - Electrochemical in-situ STM setup

#### 6.4. Experimental Routines

All the glassware, STM, and FTIR Teflon cells are cleaned by keeping them in piranha solution overnight and then rinsed thoroughly with DI water. Electrochemical studies are conducted by a BASi Epsilon system. In our studies, the counter electrode is platinum wire. In order to make sure there will be no contamination from the wire in the system, it was annealed before each experiment with hydrogen flame. Saturated Calomel electrode (SCE), Mercury Sulfate Electrode (MSE), and Ag/AgCl reference electrodes are used for different electrochemical experiments. All solutions for electrochemical studies, STM, and infrared studies are prepared from chemicals with high purity (99%) and ultrapure DI water (>18.2 M\Omega). Solutions are de-aerated before each experiment for 1 hour with ultra-pure argon gas to reduce the concentration of the dissolved oxygen from air.

## 6.5. Underpotential Deposition Process

The Pd UPD experiment is proceeded in 0.1 M H<sub>2</sub>SO<sub>4</sub>+1mM H<sub>2</sub>pdCl<sub>4</sub> electrolyte. During the cyclic voltammetry (CV) study, Pt wire is used as the counter electrode (CE), saturated calomel electrode (SCE) is used as the reference electrode (RE), while Au (111) and Ru (0001) single crystals are used as the working electrodes (WE). The sweep limits for CV are 0.5 V to 0.9 V Vs. SCE and 0.37 V to 0.75 V vs. SCE for Au (111) and Ru (0001) single crystals respectively, with sweep rate of 1mV/s. After the monolayer of Pd was deposited on Au (111) and Ru (0001) single crystals, the crystals are washed with DI water and transferred to 0.05 M H<sub>2</sub>SO<sub>4</sub> as an electrolyte for the H<sub>2</sub> UPD experiment. Pt wire is the counter electrode and mercury sulfate electrode (MSE) is the reference electrode. The sweep limits for Pd<sub>ML</sub>/Au (111) and Pd<sub>ML</sub>/Ru (0001) are -0.62V to -0.25V vs. MSE with sweep rate of 5 mV/s.

## 6.6. Subtractively Normalized Interfacial Fourier Transform Infrared Spectroscopy (SNIFTIRS) Experiments

SNIFTIRS measurements are done by NICOLET 6700 FTIR apparatus which is equipped with a MCT-A detector. The detector is cooled down with liquid nitrogen and is set in the operation box on the optical table. The optical window for in-situ FTIR study is a custom-made Teflon cell with hemispherical  $CaF_2$  window on the bottom that serves as the ATR window. The optical path of the IR radiation is shown in Figure 30.



Figure 30 - Schematic of SNIFTIR setup

The optical path is guided with parabolic (f=6") and flat mirrors. In order to get ATR, the optical material has to have a higher refractive index than the electrolyte which is considered for calculation of critical angle. The critical angle is calculated from equation 42. Refraction index of CaF<sub>2</sub> is 1.43 (n<sub>1</sub>) and for water it is 1.37 (n<sub>2</sub>) and the incident angle is set  $2^{0}$  above the critical angle of the water/CaF<sub>2</sub> interface (75<sup>0</sup>).

Compressed air is purged from a Parker Ballston Purge Gas Generator with inlet pressure of 60 psi and flow rate of 9 Lmin<sup>-1</sup> into the operation box, in order to minimize

the noises, caused by H<sub>2</sub>O and CO<sub>2</sub>. The potential for the electrochemistry is controlled by BAS CV-27 Potentiostat.

For holding and pressing the working electrode against the  $CaF_2$  window, a glass tube is used. Pt wire is used as the counter electrode and MSE is used as the reference electrode. When the solution (0.5 M H<sub>2</sub>SO<sub>4</sub> or 0.5M D<sub>2</sub>SO<sub>4</sub>) is transferred into the Teflon cell, the value of the measured interferogram peak-to-peak is around 1. After placing the WE (Single crystal electrode) into the cell, there will be an immediate increase in the interferogram signal. The potential ranges from -560 mV to -680 mV vs. MSE are applied to study adsorbed H/D on the electrode surfaces.

#### 6.7. Gas Phase Mass Spectrometry

Mass spectrometer (SRS RGA200) was used for our gas phase mass spectrometry studies. The gas sampling chamber (30 mTorr) is connected to the high vacuum gas chamber which is evacuated to 10<sup>-7</sup> Torr. A gas leak valve is connecting the gas sampling chamber to the high vacuum gas chamber. The high vacuum chamber is connected to the mass spectrometer. Gas samples enter from gas injection port to the sampling chamber. After the gas enters the gas sample chamber, the pressure inside this chamber increases and gas molecules get diffused to the high vacuum chamber and detected by RGA. The partial pressure of the gas in RGA depends on the gas pressure in the gas sampling chamber. The details of the mass spectrometer can be seen in Figure 31.



Figure 31 - Schematic of Mass spectrometer for gas analyzing system

The Hoffman cell is used for direct mass spectroscopy measurements of H/D ratio in gas products. The hydrogen to deuterium ratio is calculated based on the data from mass spectrometer. In order to be at low over potential regions, where the recombination of atoms is the rate determining step, overpotential of -100 mV vs MSE was applied. The electrolyte is 1 M H<sub>2</sub>SO<sub>4</sub>+ %20 (0.05 M D<sub>2</sub>SO<sub>4</sub>), which gives H<sub>2</sub>O/D<sub>2</sub>O solution mixture of 80:20 Vol. On one side we have the platinum wire as the anode and on the other side there is the electrode under study which acts as cathode (Pd<sub>ML</sub>/Au (hkl), Pd<sub>ML</sub>/Ru(hkil) and bulk Pd(hkl)). When the current is applied through the cell, the solution is oxidized at the anode and produce oxygen gas and at the cathode the reduction reaction occurs and produces H<sub>2</sub>, HD and D<sub>2</sub> gas. The cathode side will connect to the gas injection port of the gas spectrometer system. Figure 32 shows the Hoffman setup for hydrogen isotope separation. More than 50 measurements of H/D ratio in the gas phase were done using mass spectrometer for all the catalysts under study.



Figure 32 - Hoffman cell setup used for hydrogen isotope separation efficiency measurement

# 7. Results and Discussion

### 7.1. Pd UPD on Au (111)

In this section the Pd UPD on Au (111) was studied by cyclic voltammetry and in situ scanning tunneling microscopy methods. Pd UPD on Au (111) is studied to get information regarding Pd monolayer deposition on Au (111), which is considered as an electrocatalyst in the field of electrocatalysis and catalyst design. This technique helps to study the formation of bimetallic catalyst monolayers with well-defined surface and particular surface composition, that show different chemisorption properties, compared to the substrate metal <sup>[109,110]</sup>. The cyclic voltammetry for Pd UPD on Au (111) in 0.1 M  $H_2SO_4 + 1mM H_2PdCl_4$  solution is shown in Figure 33 with its characteristic peaks.



**Figure 33** - Cyclic voltammetry of Pd UPD on Au (111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 1 mM H<sub>2</sub>PdCl<sub>4</sub> with scan rate 1 mV/s.

The Pd monolayer was deposited on the freshly annealed Au (111) surface. At potential values, more negative than the 0.49 V vs. SCE reference electrode, the bulk deposition will start. At potentials, more positive than 0.5 V vs. SCE, we can see two underpotential cathodic peaks. The main deposition peak (C<sub>1</sub>) is around 0.53 V vs. SCE, which shows the deposition is started at the steps, while the second cathodic peak (C<sub>2</sub>) at 0.5 V vs. SCE, shows the deposition continuous at the terraces to form a full monolayer. The anodic scan shows that the process is reversible, as first anodic peak (A<sub>1</sub>) at 0.58 is the UPD stripping peak at steps and the second anodic peak at 0.6 V vs. SCE is due to stripping from terraces. The Pd<sub>ML</sub>/Au (111) is a potential catalyst in the field of electrocatalysis. The electrochemical and specially the electrocatalytic properties of which have been thoroughly investigated <sup>[66]</sup>.

Pd monolayer is deposited on Au (111) at 510 mV vs. SCE. Figure 34 shows the linear sweep voltammetry for corresponding cathodic charge of Pd layer on Au (111). The



Figure 34 - linear sweep voltammetry for corresponding cathodic charge of Pd layer on Au (111).

formation of a complete pseudomorphic pd layer is equal to the cathodic charge around 460  $\mu$ C cm<sup>-2</sup>, which requires two electrons per Au surface atom. The calculated value for cathodic charge of a full pseudomorphic pd layer is expected to be around 450  $\mu$ C cm<sup>-2</sup> <sup>[76]</sup>. There is a good agreement between the calculated and measured cathodic charge, showing that during the deposition process no major changes in the anion adlayer happens.

The crystal is then transferred to 0.05 M  $H_2SO_4$  solution that is deoxygenated to study  $H_2$  UPD at Pd<sub>ML</sub>/Au (111), without the oxygen reduction reaction disturbance. The CV for  $H_2$  UPD on Pd<sub>ML</sub>/Au (111) is shown in Figure 35.



Figure 35 - Cyclic voltammetry for H<sub>2</sub> UPD on Pd<sub>ML</sub>/Au (111) with sweep rate 5 mV/s

Cathodic and anodic peaks, related to hydrogen adsorption and hydrogen desorption, can be seen at hydrogen regions of  $H_2$  UPD CV. At potential values, positive of the reversible potential of the  $H^+/H_2$  redox couple, hydrogen adsorption process starts and as potential goes toward more negative potentials, molecular hydrogen evolution reaction starts to begin (cathodic sweep). During the anodic sweep, the desorption of the H atoms occurs. This process is fast and electrochemically reversible and by sweeping potential, the equilibrium surface coverage is changing.

# 7.2. STM images of Pd UPD on Au (111)

Before the UPD process starts, the bare Au (111) surface at the air is shown in Figure 36.



In the following section, the in-situ STM images for Pd deposition onto Au (111) from  $0.1 \text{ M H}_2\text{SO}_4 + 0.1\text{mM H}_2\text{PdCl}_4$  are shown. Figure 37 shows bare gold surface at 800 mV with monoatomic high steps and islands. By moving in the cathodic direction, there



Figure 37 - STM images of Pd deposition on Au (111) and cyclic voltammetry in 0.1 M  $H_2SO_4 + 1mM H_2PdCl_4$ 

will be an increase in the cluster population at the edge of steps. Around 550 mV, a layer of [PdCl<sub>4</sub>]<sup>2-</sup> covered the Au surface due to strong adsorption. This increase in the population of the clusters at edges of steps shows that the UPD process begins at the defects of the Au surface. By getting closer to the main UPD peak (C<sub>1</sub>), nucleation and cluster density start to increase at terraces. Moving more toward the cathodic direction (bottom of the C<sub>1</sub> peak) there is a higher increase in the cluster density on the terraces. By moving toward second UPD peak ( $C_2$ ) and going beyond, the UPD layer completely covers the terraces. The Pd deposition on Au surface starts at the defects and gradually covers the whole surface and forms a complete layer. As expected, by UPD process, only one Pd monolayer is deposited on Au (111). If we go to more negative potentials (490 mV vs. SCE), the second Pd monolayer starts to deposit on the defects and is flat and like the first layer. The third layer starts to deposit on top of the islands of the second layer while the second layer is not completed yet. In situ STM images shows that after third layer, the growth becomes dendritic and while the third Pd layer is not formed completely the fourth layer starts to grow and has (111) orientation. The initial and final surfaces of Pd UPD on Au (111) are presented in Figure 38. The deposited Pd monolayer on Au (111) shows the



Figure 38 - Initial and final STM images of Au (111) Surface

topography of the Au (111) substrate and only one monolayer is created in the underpotential region.

The positive strain in  $Pd_{ML}/Au$  (111), shifts the d-band centers up, becoming closer to the Fermi level (Pd atoms are in positive strain). The decrease in the bandwidth of Pd atoms, shifts the d-band center closer to Fermi level, which in turn increases the reactivity and changes the adsorption properties of the system, compared to bare Au substrate. This increase in the activity of the surface due to tensile strain is studied in the following chapters with the help of SNIFTIR, MS and kinetic measurements studies.

Scaling analysis for Pd monolayer on Au, shows saturation roughness of the bare Au surface is almost close to Pd monolayer on Au. Figure 39 shows deposition at steps



Figure 39 - Scaling analysis for Pd monolayer on Au and Au surface

increase the roughness until the clusters start to merge at terraces, which cause a decrease in the roughness.

#### 7.3. Pd Deposition on Ru (0001)

Pd deposition on Ru (0001) is presented in this section. This bimetallic system is a unique Ru-based electrocatalyst. By depositing Pd monolayer on Ru we can gain a Pd-Ru electrocatalyst with desired qualities and low Pd content. Figure 40 shows cyclic voltammetry for Pd UPD on Ru (0001) in 0.1 M H<sub>2</sub>SO<sub>4</sub>+1 mM H<sub>2</sub>PdCl<sub>4</sub> solution.

Pd has low surface energy and form 2D layer on Ru (0001), the first monolayer is flat. The scanning (STM) is used to calculate the time and potential where the full



Figure 40 - Cyclic voltammetry for Pd UPD on Ru (0001) in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 1 mM H<sub>2</sub>PdCl<sub>4</sub> with scan rate 5 mV/s

monolayer is formed. Figure 41 shows the STM image for Pd deposition on Ru (0001). Pd deposition on Ru (0001) shows that cathodic and anodic peaks are indicative of overpotential deposition and underpotential dissolution process. Based on the CV for Ru (0001) and STM images, we can see cathodic peak around 0.4 V vs. SCE. On the anodic scan, the UPD stripping peak is shifted around 150 mV, towards more positive potential. Based on the charge stripping measurements and STM, the time to form full monolayer on Ru (0001) is faster, compared to Au (111).



Figure 41 - STM Image for Pd deposition on Ru (0001)

Figure 41 shows formation of the monolayer deposit on Ru (0001). Monolayer formation on Ru (0001) is a fast and as can be seen in this image, there is a point where potential (650 mV vs. SCE) is stepped from clean Ru (0001) surface to potential (420 mV vs. SCE), where a monolayer is formed. For depositing Pd monolayer on Ru (0001), 420

mV vs. SCE was applied to form a monolayer, and after that the crystal was transferred to the 0.05 M  $H_2SO_4$  solution that is deoxygenated, to study  $H_2$  UPD at  $Pd_{ML}/Ru$  (0001). Figure 42 shows the cyclic voltammetry for  $H_2$  UPD on  $Pd_{ML}/Ru$  (0001).



Figure 42 - Cyclic voltammetry for H<sub>2</sub> UPD on Pd<sub>Ml</sub>/Ru (0001) in 0.05 M H<sub>2</sub>SO<sub>4</sub> with scan rate 5 mV/s.

Hydrogen adsorption and desorption of the H UPD starts at potentials more positive than the  $H^+/H_2$  reversible potential (-0.64 V vs. MSE). By sweeping the potential in the cathodic sweep (going toward negative potential), the H adsorption starts and in anodic sweep (going toward more positive potentials), the H desorption will happen.

## 7.4. Pt (111) Single Crystal

Platinum is one of the most used and efficient electrocatalysts in studying hydrogen evolution reaction. The single crystal electrode surface defines the reaction kinetics for electrocatalytic reactions. The plane exposed on top of the single crystal determines the coordination number of surface atoms and distance between adsorption sites. These planes are bridge, atop, threefold and fourfold hollow sites and behave differently toward the adsorbates, due to the differences in their coordination numbers. Single crystal electrodes are used widely for studying basics of the electrocatalytic reactions, as they enable us to study surface crystallography effects on kinetics of the reactions and active sites for adsorbates-substrates interactions.

Figure 43 shows cyclic voltammetry study of Pt (111). At negative potentials, hydrogen adsorption happens before hydrogen evolution. Based on Figure 43, UPD of H happens at potential values more negative than -300 mV. vs MSE, and by going toward more negative potentials (around -580 mV vs. MSE), the adsorption of H atom at top site begins. The butterfly peaks are due to adsorption and desorption of hydrogen atoms. The hydrogen adsorption that produces the hydrogen gas was first detected with the help of cyclic voltammetry on Pt electrode, and it was on different metallic sites than H<sub>UPD</sub>.



Figure 43 - Cyclic voltammetry for Pt (111) single crystal in 0.05 M H<sub>2</sub>SO<sub>4</sub> with scan rate 20 mV/s

#### 7.5. Pd Multilayer Deposition on Ru (0001)

Pd layers were deposited on Ru (0001) single crystal to act as bulk palladium due to the sensitivity of the Pd single crystal surface, as it can easily get contaminated by surrounding air and oxidized. Another advantage of using pd multilayers on Ru (0001) is to minimize absorption issues during SNIFTIR of using Pd (111) single crystals. Ruthenium single crystal is getting ready by mechanical polishing and annealing, followed by deposition of Pd layers. Cyclic voltammetry for freshly annealed Ru (0001) single crystal is shown in Figure 44 in 0.1 M H<sub>2</sub>SO<sub>4</sub>+ 1 mM H<sub>2</sub>PdCl<sub>4</sub> solution.



**Figure 44 -** Cyclic voltammetry for Ru (0001) single crystal in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 1 mM H<sub>2</sub>PdCl<sub>4</sub> with scan rate 5 mV/s

In order to deposit four layers of palladium on Ru (0001), linear sweep voltammetry for corresponding cathodic charge of Pd layer on Ru (0001) was studied and can be seen

in Figure 45. Cathodic charge of 1920  $\mu$ C cm<sup>-2</sup> was observed for depositing four layers, based on the fact that the cathodic charge of a full pseudomorphic Pd layer is around 450  $\mu$ C cm<sup>-2</sup>. The electronic and strain effect from the Ru (0001) substrate are effective up to the second layer, and after the third layer is deposited, the Pd layer on top starts to act as bulk palladium.



Figure 45 - Linear sweep voltammetry for corresponding cathodic charge for 4 layers of Pd on Ru (0001)

# 7.6. Subtractively Normalized Interfacial Fourier Transform Infrared Spectroscopy Results

#### 7.6.1. Terminal H and D Adsorption on Pt (111)

The adsorption strength of the hydrogen on single crystal electrodes is studied by in-situ SNIFTIRS. Figure 46 shows SNIFTIRS spectrum observed in  $0.05M H_2SO_4$  for Pt (111)- single crystal, at sample potential equal to -600 mV and -300 mV vs. MSE reference

potential. Based on the SNIFTIRS spectrum, the stretching frequency of H adsorption appears at 2137 cm<sup>-1</sup>. This band is assigned to the v (Pt-H) mode of terminal H. The SNIFTIRS spectrum observed in 0.05 M H<sub>2</sub>SO<sub>4</sub>, at E= -600 mV vs. MSE, demonstrated in Figure 46, showed an increase or decrease in the intensity of the peaks. With respect to reference potential, the peaks may be upward or downward. The upward bands between 1219 and 1000 cm<sup>-1</sup> are due to sulfate or bisulfate ions adsorption at the reference potential. By applying the sample potential, these ions will be desorbed from the surface. At the interface due to the OH stretching (v (OH)) and HOH bending ( $\delta$ (HOH)) modes of water molecules, bipolar bands at 3700-2500 and 1620 cm<sup>-1</sup> can be seen, respectively. The band around 1700 cm<sup>-1</sup> is attributed to the asymmetric  $\delta$ (HOH) mode of H<sub>3</sub>O<sup>+</sup> ion and by going toward more negative potentials, this band merged in to the  $\delta$ (HOH) mode of H<sub>3</sub>O<sup>+</sup> ion with  $\delta$ (HOH) mode of water, proposes that forerunner for hydrogen absorption is the adsorption of H<sub>3</sub>O<sup>+</sup> on the electrode surface.



Figure 46 - SNIFTIRS spectrum of the Pt electrode surface observed in 0.05 M H<sub>2</sub>SO<sub>4</sub> at -600 mV with respect to -300 mV vs. MSE reference potential

H underpotential deposition starts at less negative potentials than -0.4 V vs. MSE, while terminal H occurs at potentials more negative than -0.65 V vs. MSE (Figure 43). An increase in the peak intensity is observed by getting close to the H overpotential regions. Adsorption bond frequency is changed by changing the value of applied potential, which shows these bands arise from adsorbed species. Figure 47, shows how the frequency value is changing by changing potential in the H-UPD and H-OPD regions for Pt (111)- single crystal electrode.



**Figure 47** - SNIFTIRS spectra for Pt electrode surface in 0.05 M H<sub>2</sub>SO<sub>4</sub>, by going to more negative value of the potential the frequency of adsorbed H moves to lower values.

Based on Figure 47, these bands are very broad and almost symmetric.  $\nu$  (Pt-H) band is intrinsically broad, due to terminal H vibrations and the high mobility of the H atoms on metal surfaces<sup>[111]</sup>. The Pt-H bond strength is affected by values of the potential. By changing the potential, the bond strength will change.

In order to study adsorption strength of the deuterium on Pt (111) surface, 0.05 M  $D_2SO_4$  was used for SNIFTIRS study. Figure 48 shows SNIFTIR spectrum, observed in 0.05M  $D_2SO_4$  for Pt (111)- single crystal at potentials equal to -600 mV and -300 mV vs. MSE reference potential. Based on the SNIFTIRS spectrum, the stretching frequency of D adsorption appears at 1431 cm<sup>-1</sup>. This band is assigned to the v (Pt-D) mode of terminal D.



**Figure 48** - SNIFTIRS spectrum of the Pt electrode surface observed in 0.05 M D<sub>2</sub>SO<sub>4</sub> at -600 mV with respect to -300 mV vs. MSE reference potential.

By changing the solution from  $H_2SO_4$  to  $D_2SO_4$ , the band in the 2137 cm<sup>-1</sup> is disappeared and new band is appeared at 1431 cm<sup>-1</sup>. The frequency ratio of the two bands can be calculated by

frequency ratio = 
$$\frac{\nu_{(M-H)}}{\nu_{(M-D)}}$$
. (45)

This value is expected to be close to the theoretically predicted value for  $v_{(M-H)}$  and  $v_{(M-D),}$  (= $\sqrt{\frac{m_D}{m_H}} \approx \sqrt{2}$ , where  $m_D$  and  $m_H$  are the masses of H and D atoms, respectively). Based on equation 45 for Pt (111) single crystal, the frequency ratio is 1.49. The bands for D adsorption are shown in Figure 48. By using D<sub>2</sub>SO<sub>4</sub> solution, asymmetric  $\delta$ (DOD) mode of D<sub>3</sub>O<sup>+</sup> can be seen around 1230 cm<sup>-1</sup> and v (OD) observed around 2500 cm<sup>-1</sup>.

The shift in the vibration frequency for D-bond as compared to H- bond for Pt (111) is 706 cm<sup>-1</sup>. If we apply more negative potentials, the bands are shifting toward lower wavenumber, by applying more negative potential, showing that these bands are arose from adsorbed species and are due to the change in the Pt-D bond strength. Figure 49 shows the change in the frequency value by changing the potential.



**Figure 49** - SNIFTIRS spectra for Pt electrode surface in 0.05 M D<sub>2</sub>SO<sub>4</sub>, by going to more negative value of the potential (D-OPD regions) the frequency of adsorbed D moves to lower frequency values

The Pt-H and Pt-D bond strength are dependent to the potential value and are the main reason for this shift in the peak positions. The reaction intermediate in the hydrogen evolution reaction is the terminal H atom. The HER happens with the Volmer-Tafel mechanism at low overpotential regions, where the recombination of H/D atoms is the rate determining step.

In a study done by Kunimatsu et. al <sup>[27]</sup> they studied hydrogen evolution reaction (HER) on Pt electrode in acid solutions, with the help of surface enhanced infrared absorption spectroscopy (SEIRA). The vibrational mode for terminal H was detected at 2080-2095 cm<sup>-1</sup> at 0.1 V (vs RHE) and shifted to more negative values by increasing the hydrogen evolution current. By changing the solution from H2SO4 to D2SO4, they observed that H band disappeared and new band at 1498 appeared. The calculated frequency ratio was 1.39. Figure 50 shows SEIRA spectra for Pt electrode surface.



Figure 50 - SEIRA spectra of H and D adsorption on polycrystalline Pt electrode in H<sub>2</sub>SO<sub>4</sub> (a) and D<sub>2</sub>SO<sub>4</sub> (b). Taken from ref <sup>[27]</sup>.

If we compare our data from figure 46 and 48 with Figure 50, it can concluded that our data are in great agreement with data form literature <sup>[25,26,28,37,98,99,108]</sup>, which is

remarkable. We observed H adsorption in Otto Configuration for the first time, where as in other studies, surface enhanced infrared spectrometry with Kretschmann configuration was used for studying H adsorption. Also, we studied single crystal electrodes, whereas in other studies, polycrystalline Pt was used, due to difficulties of preparing single crystals. Despite the difficulties in the measurement of H adsorption with Otto configuration, our experiments were successful and showed required resolution and sensitivity for measuring H and D bond frequency change.

#### 7.6.2. Terminal H and D Adsorption on Pd multilayers on Ru (0001)

Palladium surface can act as an active electrocatalyst for studying H isotope separation. In order to have bulk palladium, we deposited 4 layers of palladium on Ru (0001). Pd multilayer on Ru (0001) electrode SNIFTIR spectrum observed in 0.5 M H<sub>2</sub>SO<sub>4</sub> at -600 mV sample potential and -200 mV vs. MSE reference potential is shown in Figure 51. The stretching frequency of H adsorption appears at 2128 cm<sup>-1</sup>, which is the v (Pd-H) mode of terminal H. Change in the intensity of the peaks with respect to the reference potential can cause upward or downward peaks. Sulfate or bisulfate ions, adsorbed at reference potential and showed upward bands around 1000- 1219 cm<sup>-1</sup>, which would be desorbed from surface by applying sample potential. At the interface of the electrode, due to the OH stretching (v (OH)) and HOH bending ( $\delta$ (HOH)) modes of water molecules, bipolar bands at 3700-2500 and 1620 cm<sup>-1</sup> can be seen, respectively. The band around 1700 cm<sup>-1</sup> is attributed to the asymmetric  $\delta$ (HOH) mode of H<sub>3</sub>O<sup>+</sup> ion, and by going to more negative potentials this band merged in to the  $\delta$ (HOH) mode of water by shifting to lower frequencies. Merging of the asymmetric  $\delta$ (HOH) mode of H<sub>3</sub>O<sup>+</sup> ion with  $\delta$ (HOH) mode of water, proposes that forerunner for hydrogen absorption is the adsorption of  $H_3O^+$  on the electrode surface. Applying potentials in the range of H UPD, results in the change in the value of frequency and confirms that the bands arise from adsorbed species. By changing the potential, the bond strength of Pd-H will change as well.



Figure 51 - SNIFTIRS spectrum of the Pd multilayer on Ru (0001) electrode surface observed in 0.5 M  $H_2SO_4$  at -600 mV with respect to -200 mV vs. MSE reference potential.

The peak intensity of the hydrogen IR spectra increases when potential values get closer to the H-OPD region. Figure 52, shows the shift in the adsorption bond frequency as a function of applied potential.



Figure 52 - SNIFTIRS spectra for Pd multilayers on Ru (0001) electrode surface in 0.05 M H<sub>2</sub>SO<sub>4</sub>

Adsorption strength of the deuterium on Pd multilayer on Ru (0001) surface was measured in 0.5 M D<sub>2</sub>SO<sub>4</sub> with SNIFTIRS. Figure 53 shows SNIFTIR spectrum observed in 0. 5 M D<sub>2</sub>SO<sub>4</sub> for Pd multilayer on Ru (0001), at potentials equal to -600 mV and -200 mV vs. MSE reference potential. The stretching frequency of D adsorption appears at 1461 cm<sup>-1</sup>. This band is assigned to the v (Pd-D) mode of terminal D. Asymmetric  $\delta$ (DOD) mode of D<sub>3</sub>O<sup>+</sup> can be seen around 1230 cm<sup>-1</sup> and stretching mode of v (OD) appears at frequency equal to 2700 cm<sup>-1</sup>.



Figure 53 - SNIFTIRS spectrum of the Pd multilayer on Ru (0001) electrode surface observed in 0. 5 M  $D_2SO_4$  at -600 mV with respect to -200 mV vs. MSE reference potential.

The results from SNIFTIRS showed that by using D<sub>2</sub>SO<sub>4</sub>, the band at 2128 cm<sup>-1</sup> disappeared and new band at 1461 cm<sup>-1</sup> appeared. Based on the frequency ratio for the two bands (equation 45), the frequency ratio is 1.45 cm<sup>-1</sup>. This value is close to the theoretically calculated value ( $\sqrt{2}$ ) for  $\nu_{(M-H)}$  and  $\nu_{(M-D)}$ . The peak intensity of the IR spectra is

increased, when potential values get closer to the H-OPD region. Also, the shift in the adsorption bond frequency as a function of applied potential can be seen in Figure 54.



Figure 54 - SNIFTIRS spectra for Pd multilayers on Ru (0001) electrode surface in 0.05 M D<sub>2</sub>SO<sub>4</sub>.

#### 7.6.3. Terminal H and D adsorption on Pd<sub>ML</sub>/Au (111)

Bimetallic systems give us the ability to have surface with desired composition that can affect the catalytic properties of the surface. It is very important to understand the electronic factors, when a catalytically active material like palladium is placed on a conductive substrate such as gold. During the pseudomorphic deposition of palladium on gold, the reactivity of the system is influenced by two factors, the electronic interaction between Pd overlayer and gold, which is a small interaction. The other factor is due to the difference in the lattice constant of the Palladium ( $a=3.96 \text{ A}^0$ ) and gold ( $a=4.18\text{ A}^0$ ). As a result, pseudomorphic pd films are expanded by 5%. The expansion in the Pd overlayer films results in the larger hydrogen binding energies. In the case of Pd on gold, a transition metal is deposited on an inert noble metal electrode (2D monolayer), with the help of electrochemical techniques and in-situ STM. The activity of the surface is examined with in-situ FTIR for H/D adsorption bond strength. The data from SNIFTIR can be used to calculate the isotope separation and compare the results to bulk palladium and platinum.

Pd<sub>ML</sub>/Au (111) electrode SNIFTIR spectrum observed in 0.5M H<sub>2</sub>SO<sub>4</sub> at -600 mV sample potential and -350 mV vs. MSE reference potential is shown in Figure 55. The stretching frequency of H adsorption appears at 2138 cm<sup>-1</sup>, which is the v (Pd<sub>ML</sub>-H) mode of terminal H. The peaks may appear upward or downward based on the intensity of the peaks, with respect to reference potential. Sulfate or bisulfate ions bands appear around 1000-1219 cm<sup>-1</sup>, due to the adsorption at reference potential. By applying sample potential, these ions will desorb from the surface. At the interface of the electrode, due to the OH stretching (v (OH)) and HOH bending ( $\delta$ (HOH)) modes of water molecules, bipolar bands at 3700-2500 and 1620 cm<sup>-1</sup> can be seen, respectively. Asymmetric  $\delta$ (HOH) mode of H<sub>3</sub>O<sup>+</sup> ion shows band around 1700 cm<sup>-1</sup>, and applying more negative potentials merged this band in to the  $\delta$ (HOH) mode of water by shifting to lower frequencies. Merging of the



**Figure 55** - SNIFTIRS spectrum of the Pd<sub>ML</sub>/Au (111) electrode surface observed in 0. 5 M H<sub>2</sub>SO<sub>4</sub> at -600 mV with respect to -350 mV vs. MSE reference potential.

asymmetric  $\delta(\text{HOH})$  mode of  $\text{H}_3\text{O}^+$  ion with  $\delta(\text{HOH})$  mode of water, proposes that forerunner for hydrogen absorption is the adsorption of  $\text{H}_3\text{O}^+$  on the electrode surface.

Based on Figure 35, H UPD regions for  $Pd_{ML}/Au$  (111) are at potential values more positive than -640 mV vs. MSE. Figure 56 shows that if potentials in the range of H-UPD and H-OPD are applied to the electrode, the SNIFTIR spectra shows change in the value of the frequency, which confirms that these bands arise from adsorbed species.



**Figure 56** - SNIFTIRS spectra for Pd<sub>ML</sub>/Au (111) electrode surface in 0.5 M H<sub>2</sub>SO<sub>4</sub>, by going to more negative value of the potential the frequency of adsorbed H moves to lower frequency values.

Based on the d-band model, due to the expansion of the palladium overlayer on top of gold and also weak coupling between d-bands of gold and palladium, an upshift in the d-band is expected, causing an increase in the activity of the surface for H adsorption. If we compare SNIFTIR results from Pd (111), Pt (111) and Pd<sub>ML</sub>/Au (111), it is clear that in the case of Pd<sub>ML</sub>/Au (111), the stretching frequency for H adsorption is at 2138 cm<sup>-1</sup>, which is higher value compared to Pt (111) and Pd (111), which are at 2137 cm<sup>-1</sup> and 2130 cm<sup>-1</sup>,
respectively. This shows that  $Pd_{ML}/Au$  (111) has higher surface reactivity for hydrogen adsorption, compared to bulk palladium and platinum.

In order to study the adsorption strength of deuterium with SNIFTIRS on  $Pd_{ML}/Au$  (111), the experiment was done in 0.5 M D<sub>2</sub>SO<sub>4</sub>. Figure 57 shows SNIFTIR spectrum observed in 0.5 M D<sub>2</sub>SO<sub>4</sub> for  $Pd_{ML}/Au$  (111) at potentials equal to -600 mV and -200 mV vs. MSE reference potential. The stretching frequency of D adsorption appears at 1414 cm<sup>-1</sup>. This band is assigned to the v (Pd-D) mode of terminal D. Asymmetric  $\delta$  (DOD) mode of D<sub>3</sub>O<sup>+</sup> can be seen around 1230 cm<sup>-1</sup> and stretching mode of v (OD) appears at 2500 cm<sup>-1</sup>.



Figure 57 - SNIFTIRS spectrum of the Pd<sub>ML</sub>/Au (111) electrode surface observed in 0.5 M D<sub>2</sub>SO<sub>4</sub> at -600 mV with respect to -350 mV vs. MSE reference potential.

Based on SNIFTIRS spectrum at Figure 57, by using D<sub>2</sub>SO<sub>4</sub> instead of H<sub>2</sub>SO<sub>4</sub>, the H band at 2138 cm<sup>-1</sup> is disappeared and a new band at 1414 appeared. The frequency ratio for these two bands ( $\nu_{(Pd_{ML}-H)}$  and  $\nu_{(Pd_{ML}-D)}$ ) based on equation 45 is 1.5. The frequency ratio observed for Pd<sub>ML</sub>/Au (111) is higher, compared to bulk palladium and platinum, which indicates the ability of this electrode to act as an ideal electrocatalyst for studying H isotopes, showing high efficiency for electrolytic hydrogen isotope separation, which will

be discussed in the following chapter. The difference in the band frequency for H and D is 724 cm<sup>-1</sup> at -600 mV vs MSE. If we go to OPD regions (-680 mV.vs MSE) this difference in the band frequency is 720 cm<sup>-1</sup>.

Applying potentials in the UPD and OPD regions shows a shift in bands to lower wave number, by applying more negative potential. This indicates that these bands are arose from adsorbed species and are due to the change in the Pd-D bond strength. Figure 58 shows the change in the frequency value by changing the potential.



**Figure 58** - SNIFTIRS spectra for Pd<sub>ML</sub>/Au (111) electrode surface in 0.5 M D<sub>2</sub>SO<sub>4</sub>, by going to more negative value of the potential the frequency of adsorbed H moves to lower frequency values.

#### 7.6.4. Terminal H and D adsorption on PdML/Ru (0001)

Surface structure of the electrode material can affect the catalytic activity, making it important to understand the structure-reactivity relationships. Surface strain effects on catalytic activity can be studied by deposition of second metal, such as palladium on substrate with different lattice constants. In the case of  $Pd_{ML}/Ru$  (0001), palladium atoms with lattice constant of 3.96 A<sup>0</sup>, are deposited on Ru (0001) with lattice constant of 2.9 A<sup>0</sup>.

The differences in the lattice constant of the overlayer metal (Pd) and the substrate (Ru), cause a compression strain in the palladium overlayer, which can affect the activity of the electrode surface due to the strain effect. The shift in the d-band center and changes in the surface lattice affect the bond strength of the adsorbate H/D atoms on the electrode surface. If the d-band center becomes low, the binding of adsorbates to surface decreases. The shift in the d-band center for pd deposition on Ru is -0.82 eV.

The adsorption strength of H isotopes on  $Pd_{ML}/Ru$  (0001) electrode was studied with SNIFTIRS. Spectrum was observed in 0.5 M H<sub>2</sub>SO<sub>4</sub> at -600 mV sample potential and -200 mV vs. MSE reference potential and is shown in Figure 59. H adsorption stretching frequency shows a band for v (Pd<sub>ML</sub>-H) mode of terminal H at 2108 cm<sup>-1</sup>. The peaks may appear upward or downward based on the intensity of the peaks, with respect to reference potential. Bands around 1000-1219 cm<sup>-1</sup> are due to the adsorption of sulfate or bisulfate ions at the refence potential, which will eventually be desorbed from the surface by



**Figure 59** - SNIFTIRS spectrum of the Pd<sub>ML</sub>/Ru (0001) electrode surface observed in 0.5 M H<sub>2</sub>SO<sub>4</sub> at -600 mV with respect to -200 mV vs. MSE reference potential.

applying sample potential. At the interface of the electrode, due to the OH stretching (v (OH)) and HOH bending ( $\delta$ (HOH)) modes of water molecules, bipolar bands at 3700-2500

and 1620 cm<sup>-1</sup> can be seen, respectively. Asymmetric  $\delta$ (HOH) mode of H<sub>3</sub>O<sup>+</sup> ion shows band around 1700 cm<sup>-1</sup>. Applying more negative potentials, merged this band in to the  $\delta$ (HOH) mode of water by shifting to lower frequencies. Merging of the asymmetric  $\delta$ (HOH) mode of H<sub>3</sub>O<sup>+</sup> ion with  $\delta$ (HOH) mode of water proposes that forerunner for hydrogen absorption is the adsorption of H<sub>3</sub>O<sup>+</sup> on the electrode surface.

Changing potentials from H-UPD region to OPD-region, shows a shift in the bands value. The change in the frequency values by changing potential shows that these bands are arose from adsorbed species and are due to the change in the Pd-H bond strength. Figure 60 shows how the bands value is changing by changing applied potential.



Figure 60 - SNIFTIRS spectra for  $Pd_{ML}$ / Ru (0001) electrode surface in 0.5 M H<sub>2</sub>SO<sub>4</sub>, by going to more negative value of the potential the frequency of adsorbed H moves to lower frequency values.

The compression strain in the palladium overlayer on ruthenium electrode, shifts the d-band center down and decreases the activity of the surface for H adsorption. Comparing SNIFTIRS data from Pd (111), Pt (111), Pd<sub>ML</sub>/Au (111) and Pd<sub>ML</sub>/Ru (0001),

reveals that stretching frequency for H adsorption on Pd<sub>ML</sub>/Ru (0001) shows the lowest value among all the electrode surfaces at 2108 cm<sup>-1</sup> at potential value of -600 mV vs. MSE. This proves that compression strain effect in the Pd overlayer, decreases the strength of adsorbed hydrogen bond. During the hydrogen evolution reaction, the rate determining step is the recombination of the two hydrogen atoms at low overpotential regions. If the strength of the adsorbed hydrogen bond is decreased in the overpotential region, the hydrogen isotope separation efficiency will also be affected.

Figure 61, shows SNIFTIRS data for  $Pd_{ML}/Ru$  (0001) in 0. 5 M D<sub>2</sub>SO<sub>4</sub>, for studying the adsorption strength of deuterium. The sample potential is at -600 mV and reference potential is -200 mV vs. MSE. For  $Pd_{ML}/Ru$  (0001) the stretching frequency of D adsorption appears at 1425 cm<sup>-1</sup>, which is due to the v (Pd-D) mode of terminal D. The peak around 1230 cm<sup>-1</sup> is due to the asymmetric  $\delta$ (DOD) mode of D<sub>3</sub>O<sup>+</sup> and stretching mode of v (OD) appears around 2600 cm<sup>-1</sup>.



**Figure 61** - SNIFTIRS spectrum of the Pd<sub>ML</sub>/Ru (0001) electrode surface observed in 0.5 M D<sub>2</sub>SO<sub>4</sub> at -600 mV with respect to -200 mV vs. MSE reference potential.

Using  $D_2SO_4$  for studying SNIFTIRS spectrum instead of  $H_2SO_4$ , shows that a new band appears at 1425 cm<sup>-1</sup> while H band is disappeared at 2108 cm<sup>-1</sup>. The calculated value

for frequency ratio for these two bands ( $\nu_{(Pd_{ML}-H)}$  and  $\nu_{(Pd_{ML}-D)}$ ) is 1.47. The frequency ratio observed for Pd<sub>ML</sub>/Ru (0001) is lower, compared to Pd<sub>ML</sub>/Au (111), bulk platinum. However, this value is higher, compared to bulk palladium. The difference in the band frequency for H and D at-600 mV vs. MSE is ( $\Delta \nu_{Pd_{ML},Ru(0001)} = \nu$  (*H*) –  $\nu$  (*D*) = 683).

If potentials in the D-UPD region are applied to the surface and going toward D-OPD, we can see a shift in bands. By going toward more negative values of potentials, bands also are shifted toward lower wavenumber values. This indicates that these bands are arose from adsorbed species, due to the change in the Pd-D bond strength. The change in the frequency value by changing the potential can be seen in Figure 62.



Figure 62 - SNIFTIRS spectra for Pd<sub>ML</sub>/Ru (0001) electrode surface in 0.05 M D<sub>2</sub>SO<sub>4</sub>.

Based on the SNIFTIRS spectra for all the electrodes under study, all the bands appear symmetrically, which is due to the repulsive interaction between H/D atoms. This suggests that the terminal H/D atoms are homogenously distributed on the surface, and an increase in the inter-atomic distance in observed. In some cases when the H/D atoms are randomly distributed on the electrode surfaces, the band shapes will be asymmetric. Surface strain is one of the critical factors that can affect the activity of the electrode surfaces. In the case of  $Pd_{ML}/Au$ , tensile strain in Pd overlayer, shifts the d-band center toward fermi level by 0.35 eV and increases the activity of the surface. Tensile strain in the Pd overlayer on gold, results in placing adsorbed H atoms in the surface adsorption sites, and not on the surface. However, compressive strain in the Pd overlayer on Ru, shifts the position of the d-band center to lower values and decreases the activity of the surface. In this situation, hydrogen-metal interaction on the surface gets easier.

The SNIFTIRS spectra of on all the electrodes under study is plotted on Figure 63. Potential value of -600 mV vs. MSE was chosen for all single crystal electrodes to compare their band positions. As Figure 63 shows, the chemisorption properties of Pd monolayer (i.e.  $Pd_{MI}/Au$  (111) and  $Pd_{MI}/Ru$  (0001)) is different from bulk Pd (111) and Pt (111) single crystals. Based on Figure 62, At -600 mV vs. MSE,  $Pd_{MI}/Au$  (111), H adsorption band appears at 2138 cm<sup>-1</sup>, while for  $Pd_{multilayer}/Ru$  (0001) band is at 2128 cm<sup>-1</sup> and for  $Pd_{MI}/Ru$ 



Figure 63 - SNIFTIRS spectra of all electrodes at -600 mV vs. MSE in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

(0001) appears at 2108 cm<sup>-1</sup>. One reason can be the difference between the average bond length of Pd monolayer deposited on Au (111) and Ru (0001) with the substrate metal, which results in strain in the Pd monolayer. The ligand effect can also change the chemisorption property by changing the surface electronic structure of the bimetallic systems.

Effect of strain in the Pd monolayer is an important parameter in describing the catalytic activity of the electrodes. For example, the adsorption of H on Pd<sub>ML</sub>/Au (111) surface is more favored, compared to Pd<sub>ML</sub>/Ru (0001) surface. For Pd<sub>ML</sub>/Au (111), the Pd atoms are in positive strain (tensile strain) and the bandwidth of the Pd atoms are decreased. This decrease causes an up-shift in the d-band center toward Fermi level, increases the average energy of the d-states, and as a result, increases the reactivity of the over layer metal, which can also change the chemical properties of the substrate metal. In the case of Pd<sub>ML</sub>/Ru (0001), negative strain caused by the compression of the Pd atoms on top, increases the bandwidth of the Pd atoms. As a result, a downshift in the d-band center is expected to keep the same number of electrons. So, the average energy of the d-states decrease in the reactivity of overlayer metal.

Better understanding of the trends in D-adsorption is possible by comparing the bands for all single crystals at same potential. Figure 64 shows this comparison at -600 mV vs. MSE. Positive strain in  $Pd_{ML}/Au$  (111) affects the D adsorption bond strength in the overpotential region (RDS is the recombination of the D atoms). The diffusion barrier for H atoms adsorption rises due to this positive strain, which improves recombination of isotopes with smaller mass. As a result of the positive strain in  $Pd_{ML}/Au$  (111), the



Figure 64 - SNIFTIRS spectra of all electrodes at -600 mV vs. MSE in 0.5 M D<sub>2</sub>SO<sub>4</sub>.

adsorption sites separate from each other, making it more difficult for D (heavier isotope) to recombine, due to the separation in adsorption sites. The value of D adsorption peak shifts to lower values for  $Pd_{ML}/Au$  (111).

The differences in the frequencies of H and D adsorption on  $Pd_{ML}/Au$  (111),  $Pd_{ML}/Ru$  (0001) and Pd multilayer on Ru (0001) at low overpotential region (-680 mV vs. MSE), where H/D atoms recombination is the rate determining step is summarized in table 2.

Catalyst electrode	$\Delta v = v_{H-}v_{D}/cm^{-1}$
Pd <sub>ML</sub> /Au (111)	719
Pd <sub>ML</sub> /Ru (0001)	653
Pd multilayer /Ru (0001)	665

**Table 2** - summary of differences in the frequencies of adsorbed hydrogen and deuterium on electrode surfaces

The differences in the band frequency for H and D for Pd monolayer under the tensile strain forced by epitaxy with Au substrate shows the highest value, while the band frequency for Pd monolayer under compressive strain induced by Ru substrate shows the lowest value. Figure 65 shows the SNIFTIR spectra of adsorption bond frequencies between H and D for all the substrates at -100 mV overpotential region, where RDS is the recombination of atoms.



Figure 65 - SNIFTIRS spectra of all electrodes at -600 mV vs. MSE in 0.5 M D<sub>2</sub>SO<sub>4</sub> and 0.5 M D<sub>2</sub>SO<sub>4</sub>.

The differences in the adsorption bond frequencies between H and D gained from SNIFTIR data, were used to calculate the  $S_k$  values. Considering all the results, it can be concluded that the positive strain in the Pd ML, deposited on Au (111)-single crystal, increases the strength of the H adsorption bonds in overpotential region. As a result, bonds

will vibrate at higher frequency. This increase in the reactivity of the surface caused by positive strain ( $Pd_{ML}/Au$  (111)), affects the recombination of the isotopes with smaller mass (H), more than isotopes with higher mass (D). Stretching the surface separates the neighboring adsorption sites from each other and has an impact on the heavier isotopes, by lowering the probability of their recombination. This results in an increase in the separation factor. The compressive strain, decreases the diffusion barrier value for adsorbed hydrogen atoms and results in less recombination of H isotopes with smaller mass (H). In Pd<sub>ML</sub>/Ru (0001), due to the surface compression, the neighboring adsorption sites get closer and it can improve the recombination of heavier isotope (D). So, a higher probability for recombination of D atoms is expected. The strain in the Pd overlayer changes the value of the separation factor, compared to bulk electrodes. The experimentally observed frequency difference on various surfaces between H and D can be used to predict value of separation factor for different substrates. Theoretical calculation of the separation factor among the catalysts under study confirms our finding. Hydrogen isotope separation factor can be expressed as

$$S_{k} = 1 + 2 \left(\frac{R_{H_{2}}}{R_{D_{2}}}\right) \approx 1 + \frac{8}{3} exp\left(\frac{0.5hC(v_{0,H} - v_{0,D})}{k_{b}T}\right).$$
 (46)

Higher fundamental frequency of bond vibration due to the stain effect, increases the value of the (v<sub>0,H</sub> - v<sub>0,D</sub>). While  $\Delta v$  increases, it can affect the value of the separation factor in equation 46. In our calculations, H and D adsorption bond zero-point energy is replaced by the energy of H and D adsorption bond. Based on equation 46, the separation factor value for different catalysts under study can be calculated as  $S_{k(Pd(multilayer)/Ru)} = 14.2$ ,  $S_{kPd_{ML}/Au(111)} = 16.1$  and  $\Delta v_{Pd_{ML}/Ru(0001)} = 13.9$ .

The ratios of hydrogen isotope separation factors between Pd MLs and Pd bulk can be calculated based on SNIFTIRS data as followed:

$$\frac{S_{k(Pd_{ML}/Au(111))}}{S_{k(Pd(bulk)}} \infty \frac{1 + \frac{8}{3}exp\left(\frac{0.5hC}{k_bT} \cdot \left(\Delta v_{Pd_{ML}/Au(111)}\right)\right)}{1 + \frac{8}{3}exp\left(\frac{0.5hC}{k_bT} \cdot \left(v_{Pd(bulk)}\right)\right)} = 1.14,$$
(47)

$$\frac{S_{k(Pd_{ML}/Ru(0001)}}{S_{k(Pd(bulk))}} \infty \frac{1 + \frac{8}{3} exp\left(\frac{0.5hC}{k_b T} \cdot \left(\Delta v_{PPd_{ML}/Ru(0001)}\right)\right)}{1 + \frac{8}{3} exp\left(\frac{0.5hC}{k_b T} \cdot \left(v_{Pd(bulk)}\right)\right)} = 0.98,$$
(48)

and

$$\frac{S_{k(Pd_{ML}/Au(111))}}{S_{k(Pd_{ML}/Ru(0001)}} \infty \frac{1 + \frac{8}{3} exp\left(\frac{0.5hC}{k_b T} \left( \Delta v_{Pd_{ML}/Au(111)} \right) \right)}{1 + \frac{8}{3} exp\left(\frac{0.5hC}{k_b T} \left( v_{Pd_{ML}/Ru(0001)} \right) \right)} = 1.16$$
(49)

As data suggests, stronger binding for stretched surface is seen. For compressed surface however, this value is lower. The increase in the separation factor for bimetallic systems shows that H evolution reaction is improved by strain effect. Table 3 shows the summary of  $S_K$  calculation and shows that efficiency of the hydrogen isotope separation is improved for Pd ML under tensile strain, induced by underlying Au substrate, compared to bulk Pd.

 Table 3 - theoretical separation factor value, calculated based on SNIFTIR data

At -100 mV overpotential	$\frac{S_{k(Pd_{ML}/Au(111))}}{S_{k(Pd(bulk))}}$	$\frac{S_{k(Pd_{ML}/Ru(0001)}}{S_{k(Pd(111))}}$	$\frac{S_{k(Pd_{ML}/Au(111))}}{S_{k(Pd_{ML}/Ru(0001)}}$
S <sub>k</sub> ratios calculated based on the SNIFTIR data	1.14	0.98	1.16

### 7.7. Mass Spectrometry Data

In order to study the H/D ratio in gas products, acidic water with pre-defined  $H_2O/D_2O$  was electrolyzed. Mass spectroscopy measurements were done using RGA 200

Residual Gas Analyzer which can detect all the isotopes in the range of 1-200 au. At each experiment around 5-7 cm<sup>3</sup> of hydrogen gas is generated which gives large quantity of gas for analysis. The mass spectrometry was performed at low overpotential regions for hydrogen/deuterium evolution reaction (-100 mV), where H/D atom recombination is the rate determining step.

The catalysts monolayers that were used for mass spectrometry experiments were  $Pd_{ML}/Au(hkl)$ ,  $Pd_{ML}/Ru(hkil)$  and bulk Pd(hkl). For each surface more than 50 spectrometry measurements of H/D ratio in gas phase were performed. Figure 66 shows the averages and calculated values for separation factor.



Figure 66 - Representative averages of almost 50 mass spectrometry for each catalyst and calculated values of S<sub>k</sub>

The  $H_2O/D_2O$  solution for electrolysis was prepared as 80:20 volume which gives molar ratio of H/D in solution phase to be around 4. The calculated values of  $S_k$  and representative averages can be seen in table 4.

Electrode	(H/D) <sub>Sol</sub>	(H/D)gas	SK=(H/D)gas/(H/D)Sol
Pd (hkl)	4	37	9.3
Pd <sub>ML</sub> /Ru(hkil)	4	38.5	9.6
Pd <sub>ML</sub> /Au(hkl)	4	43	10.8

Table 4 - separation factor value, calculated from mass spectrometry data

The data shows that  $S_K$  (Pd<sub>ML</sub>/Au (111)) is around 20% higher than  $S_k$  (Pd (111)) electrode, and almost 10% higher than  $S_k$  (Pd<sub>ML</sub>/Ru (0001)).  $S_k$  (Pd<sub>ML</sub>/Ru (0001)) is also larger than  $S_k$  (Pd (111) due to the fact that at potentials where Pd monolayer is deposited on Ru (0001), the Ru surface is covered by hydroxide or oxide layer that prevents the epitaxial growth, and the Pd monolayer on top could be strain free. Also, Pd bulks are expected to be under compressive strain due to the formation of hydride on the surface at the overpotential regions. Table 5 shows  $S_K$  ratios based on mass spectrometry experiments.

Table 5 - SK Ratios calculated based on mass spectrometry data

At -100 mV overpotential	$\frac{S_{k(Pd_{ML}/Au(111))}}{S_{k(Pd(111))}}$	$\frac{S_{k(Pd_{ML}/Ru(0001))}}{S_{k(Pd(111))}}$	$\frac{S_{k(Pd_{ML}/Au(111))}}{S_{k(Pd_{ML}/Bu(0001))}}$
S <sub>k</sub> ratios calculated based on the Mass Spectrometry data	1.16	1.03	1.13

#### 7.8. Hydrogen Evolution Reaction Kinetic Measurements

In order to do theoretical analysis and comparing with experimental data for hydrogen isotope separation, the kinetic measurements of hydrogen and deuterium evolution reaction (HER and DER) was performed. The measurements were done in pure isotopic 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.05 M D<sub>2</sub>SO<sub>4</sub> solutions. MSE was used as reference electrode filled with isotopic solutions in order to make sure no differences in overpotential is applied. Pd<sub>MI</sub>/Au (111) and Pd<sub>MI</sub>/Ru (0001) were used as WE. Potentiostatic method was used for measuring current densities at relevant overpotential region. The potential was applied in the range of -600 mV to -680 mV vs. MSE. The potential was applied for 20 seconds until we get to the steady state and the current values were recorded. For preventing D<sub>2</sub>O solution contamination by external moisture in the air, all the experiments were

performed in the dry box which was purged with high purity  $N_2$  during the whole experiment time. Each current density value is for the steady state case and the hanging meniscus configuration was used. Figure 67 shows current measurements in 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.05 M D<sub>2</sub>SO<sub>4</sub> solutions for Pd<sub>ML</sub>/Au (111) and Pd<sub>ML</sub>/Ru (0001).



Figure 67 - Current measurements in 0.05 M  $H_2SO_4$  and 0.05 M  $D_2SO_4$  solutions for  $Pd_{ML}/Au$  (111) and  $Pd_{ML}/Ru$  (0001).

Kinetic measurement of HER and DER data for  $Pd_{ML}/Au$  (111) in 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.05 M D<sub>2</sub>SO<sub>4</sub> are shown in figure 68. At over potential regions, the ratio between rates of HER and DER for  $Pd_{ML}/Au$  (111) was calculated as  $R_{HER}$  and  $R_{DER}$ , and used for calculating hydrogen isotope separation factor. The  $R_{HER}/R_{DERratio}$  for  $Pd_{ML}/Au$  (111) calculated as 13.



**Figure 68** - HER and DER for Pd<sub>ML</sub>/Au (111), in 0.05 M H<sub>2</sub>SO<sub>4</sub> and D<sub>2</sub>SO<sub>4</sub>. Each current density readings at each potential is for steady state case.

Figure 69 shows the detail for  $Pd_{ML}/Ru$  (0001) kinetic measurements details and calculations. This ratio between rates of HER and DER for  $Pd_{ML}/Ru$  (0001) at -100 mV overpotential regions was 11. The kinetic measurements data are comparable with the data gained from mass spectroscopy and shows that  $S_K$  ( $Pd_{ML}/Au$  (111)) is larger than  $S_K$ 

 $(Pd_{ML}/Ru(0001))$ . The qualitative trend from calculated separation factor shows  $S_k$  for  $Pd_{ML}/Au$  (111) is %20 larger than  $Pd_{ML}/Ru(0001)$  at -100 mV overpotential regions.



**Figure 69** - HER and DER for PdML/Ru (0001), in 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.05 M D<sub>2</sub>SO<sub>4</sub>. Each current density readings at each potential is for steady state case.

Theoretical calculation of Sk based on the SNIFTIR data for H and D vibrational frequencies, the data obtained from mass spectrometry, HER/DER kinetic measurements of Pd ML on Au and Ru substrate and Pd bulk electrode are all summarized in table 6. The results show a perfect agreement between theory and experimental results.

	$S_{k(Pd(bulk))}$	$S_{k(Pd_{ML}/Ru(0001))}$	$S_{k(Pd_{ML}/Au(111))}$
Calculation+ SNIFTIRS	14.2	13.9	16.1
Mass Spectrometry	9.3	9.6	10.8
Kinetics Measurements	-	11	13
	$\frac{S_{k(Pd_{ML}/Au(111))}}{S_{k(Pd(111))}}$	$\frac{S_{k(Pd_{ML}/Ru(0001))}}{S_{k(Pd(111))}}$	$\frac{S_{k(Pd_{ML}/Au(111))}}{S_{k(Pd_{ML}/Ru(0001))}}$
Calculation+ SNIFTIRS	1.14	0.98	1.16
Mass Spectrometry	1.16	1.03	1.13
Kinetics Measurements	-	-	1.18

 Table 6 Summary of theoretical calculation and experimental measurements for separation factor

The data suggests an agreement between results from electrolysis of H<sub>2</sub>O/D<sub>2</sub>O solution mixture and kinetic measurements of HER and DER rates with theoretical calculations. The epitaxial growth of Pd monolayer on Au substrate showed the highest hydrogen isotope separation factor, compared to bulk palladium and Pd monolayer on Ru, in which Pd atoms are under compressive strain, induced by Ru substrate. Two different sets of experimental approaches confirmed this observation. First one was direct measurement during the electrolysis of water and the second one was indirect by measuring the rates of HER and DER. This agreement of the data, lay out the advantage of Pd monolayer catalyst for efficient hydrogen isotope separation and confirms the fact that tensile strain in Pd monolayer on Au substrate, significantly improves the hydrogen isotope separation efficiency by 10-20 % compared to Pd bulk electrode.

## 8. Conclusion

Pd monolayer on Au (111), Ru (0001) and Pd bulk surfaces were studied, as Pd surface is one of the most efficient and active cathodes for hydrogen isotope separation. An understanding of the metal surface properties helps to determine the reactivity of the catalyst surface. The results revealed some important conclusions which can help to identify fundamental advantages of strain and monolayer morphology. The results enable us to predict the reactivity of a particular surface. We first studied the formation of 1x1 adlayer structure of Pd on Au (111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> solutions, containing 10<sup>-3</sup> {PdCl<sub>4</sub>}<sup>2-</sup>, which was preceding a multilayer Pd growth. The deposition of Pd on to gold single crystal substrate with different lattice constant, results in strained surface. The reduction process of Pd monolayer on gold was observed to be slow, and psedumorphic monolayer was formed. We also studied formation of Pd monolayer on Ru (0001) in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution, containing 10<sup>-3</sup> {PdCl<sub>4</sub>}<sup>2</sup>, which showed very fast kinetics. The differences in the lattice parameter of the Pd overlayer with the bulk metal surface (Au and Ru), change the metalmetal bonding in the Pd overlayer. Successful design and synthesis of Pd monolayer catalyst on Au and Ru substrates were achieved by studying the initial stages of pd deposition on Au and Ru substrate with help of in-situ STM, underpotential deposition process (UPD), charge stripping and linear sweep voltammetry (LSV) measurements. The initial stages of metal deposition affect the growth behavior and morphology of the Pd overlayer.

At the next step, SNIFTIR was used to study the effect of the surface strain on catalyst activity by studying  $H_{OPD}$  and  $D_{OPD}$  adsorption strength for continuous  $Pd_{ML}/Au$  (111) and  $Pd_{ML}/Ru$  (0001), and corresponding bulk Pd (111) in Ar-purged acidic solutions.

A vibrational band was observed and assigned to the hydrogen or deuterium atom, adsorbed at atop sites of Pd monolayer, based on the vibrational frequency. The difference in the position of the H and D adsorption bands between monolayer catalysts and bulk electrode, as a result of difference in the adsorption energy differences, is due to the coherent strain. The frequency of the bond is proportional to the energy of the H and D adsorption bond. Good signal to noise ratio of the SNIFTIR spectra makes it possible to gain a quantitative relation between coverage of terminal H and kinetics of hydrogen /deuterium evolution reaction. This shows that the reaction intermediate is the terminal H atom and rate determining step is the recombination of two H or D atoms. We observed that monolayer catalyst behaves differently than the bulk, due to the different structural and quantum effects. The energy of the d-band center affects the monolayer catalyst behavior. While we have a substrate with weak electronic effects (ligand effect), the coherent strain is mainly affecting the energy of the d-band center for continuous metal monolayer. The epitaxial relation between the metal monolayer and the substrate, affects the coherent strain directly. In the case of  $Pd_{ML}/Au$  (111), large positive strain (tensile) in Pd monolayer ( $\sim 4.6\%$ ), induced by epitaxy with Au substrate, causes positive shift in the d-band center toward the fermi level and increases the reactivity of the monolayer catalyst. It makes  $Pd_{ML}/Au$  (111), one of the most efficient surfaces for hydrogen isotope separation, compared to bulk Pd (111) or Pd monolayer under compressive strain, induced by epitaxy with Ru substrate (Pd<sub>MI</sub>/Ru (0001)). In cases where the position of the d-band center becomes low, like Pd<sub>ML</sub>/Ru (0001), weaker binding of the adsorbed spices is expected, as well as reduction of their coverage on the surface.

The SNIFTIR data showed that when surface is stretched, a stronger binding is observed, compared to compressed surfaces. The catalytic activity for Pd monolayer catalyst was determined by substrate and the morphology on the Pd monolayer on top. Maximum catalytic activity of the Pd monolayer is expected, when Pd surface binds to adsorbates not too weak nor too strong. The energy of the hydrogen adsorption bond in the hydrogen evolution region was investigated. The increase in the strength of the H<sub>OPD</sub> and  $D_{OPD}$  on  $Pd_{ML}/Au$  (111) was observed, due to the increased catalytic activity of the surface, causing higher zero-point energy for adsorbed species on the surface and higher frequency for bonds' fundamental mode of vibrations. The higher adsorption bond energy, increases surface diffusion barrier for adsorbed species on the catalyst surface. The isotope with smaller mass shows large increase in frequency for diffusion jump. So, a higher probability for recombination of atoms is expected, as well as an increase in the  $S_{\rm K}$  (Pd<sub>ML</sub>) values, compared to  $S_K$  (Pd). Moreover, when the surface is stretched, the neighboring adsorption sites are separate from each other and this makes the recombination of two D atoms less likely, compared to H atoms, due to the fact that the atoms have to make large jump to reach the transition state. In the case of  $Pd_{ML}/Ru$  (0001), the compressive strain in the Pd monolayer, induced by Ru substrate, makes the neighboring adsorption sites getting closer. This can ease the recombination of atoms with heavier mass (D) and increase the probability for recombination of D atoms. The energy of H and D adsorption bond on  $Pd_{ML}/Ru$  (0001) shows weaker binding, compared to stretched surface. The strain in the overlayer plays an important role in changing the value of separation factor, compared to bulk electrodes.

Experimental results from direct mass spectrometry measurements of the H/D ratio in the gas products from electrolysis of H<sub>2</sub>O/D<sub>2</sub>O solution mixture at low overpotential regions (where rate determining step is the recombination of H/D atoms), give separation factor ratio of bulk Pd, Pd<sub>ML</sub>/Au and Pd<sub>ML</sub>/Ru. The results show qualitative agreement with calculations from SNIFTIR. Pd<sub>ML</sub>/Au (111) shows highest separation factor value, compared to bulk Pd and Pd<sub>ML</sub>/Ru (0001). S<sub>K</sub> (Pd<sub>ML</sub>/Ru (0001)) was also 10 % larger than bulk palladium S<sub>K</sub> (Pd (111). The reason relies on the fact that at potential where the Pd monolayer is deposited on Ru surface, hydroxide and oxide layers cover the surface and prevent the epitaxial growth of Pd on Ru (0001). This may cause the strain free Ru surface or surface with incommensurate layer. Moreover, Pd bulk is expected to be under compressive strain, as a result of Pd-hydride formation phase at overpotential regions (-100 mV) of HER and DER. Mass spectrometry results, confirm that lateral strain in catalyst monolayer can enhance the efficiency of hydrogen isotope separation.

The effects of strain in the 2D bimetallic catalyst can be further analyzed by help of kinetic measurements, in which the ratio between rates of HER and DER for Pd monolayer on Au and Ru were calculated as  $R_{HER}$  and  $R_{DER}$ . The  $\frac{R_{HER}}{R_{DER}}$  is used for calculating hydrogen isotope separation factor at low overpotential regions with H/D atom recombination as a RDS. The kinetic measurements reconfirm that  $S_k$  (Pd<sub>ML</sub>/Au (111) is larger than  $S_K$  (Pd<sub>ML</sub>/Ru (0001)). Comparing all the results from theoretical calculation and experimental methods showed a general agreement and proved the benefit of having Pd monolayer catalyst as an efficient catalyst for studying hydrogen isotope separation.

To conclude, we presented for the first time a catalyst monolayer with improved efficiency, that can be used for hydrogen isotope separation application. The electronic modification of Pd monolayer is affected by the geometric effect and changes in the metalmetal bonding within Pd monolayer is affecting the activity of the surface. Combination of theoretical calculation from SNIFTIR data for PdML/Au(111), PdML/Ru(0001) and bulk palladium with experimental results from electrolysis of H<sub>2</sub>O/D<sub>2</sub>O solution mixture and kinetic measurements, all confirmed that the Pd monolayer under tensile strain, induced by Au substrate is a more efficient catalyst for hydrogen isotope separation than Pd monolayer under compressive strain and bulk palladium.

### 9. Future works

To get full understanding of the 2D monolayer catalyst, more study beside Pd monolayer is needed. Other active catalysts like Pt can be studied to explore the effect of surface strain and electronic effect on the activity of the electrode catalyst. High activity of Pt catalyst for electrolysis of water and hydrogen isotope separation makes the Pt monolayer an ideal overlayer to be studied in more detail. The results from these studies can be compared with the strain effect data from Pd monolayer.

Due to difficulties of 2D deposition of Pt at room temperature, surface limited redox replacement (SLRR) can be an ideal approach for synthesis of Pt ML on noble metal substrates. The 2D-monolayer catalyst has higher surface activity due to the upward shift in the energy of the d-band center, relative to Fermi level. For substrates with weak electronic effect, the only parameter affecting the activity of the surface will be the strain effect in Pt overlayer.  $Pt_{ML}/Au$  can be studied for HER and the effects of strain in Pt monolayer for H isotope separation factor.

The substrate has a significant effect on defining the activity of the monolayer catalyst by inducing strain effect. In the case of  $Pd_{ML}/Au$  (111), the Pd monolayer deposited on Au, takes the lattice constant of the Au substrate. The positive strain in the Pd monolayer improves the catalytic activity of the surface. Other metal substrates such as Ag with lattice constants greater than Au, can induce more strain and can be a promising candidate for improving the bimetallic catalysts activity. Also, choosing substrates such as Ag which is cheaper than Au, helps to reduce the cost for effective bimetallic systems for hydrogen isotope separation.

Oxygen isotope separation can be studied in more details with the help of monolayer catalysts. Oxygen isotopes are very popular due to high stability of the isotopes. Improvement of separation factor with the help of monolayer catalyst can be investigated.

The promising results from  $Pd_{ML}/Au$  (111) and Pd <sub>ML</sub>/Ru (0001) on hydrogen isotope separation and the generality of this concept, can be used to study other isotopes production, where the recombination of atoms is the rate determining step. These bimetallic systems can be used for studying other isotope separations such as Cl evolution and Cl isotope separation, specifically for medical purposes, where Cl is very popular.

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