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Cyclic Voltammograms for H on Pt(111) and Pt(100) from First Principles

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Cyclic voltammetry is a fundamental experimental method for characterizing electrochemical surfaces. Despite its wide use, a way to quantitatively and directly relate cyclic voltammetry to *ab initio* calculations has been lacking. We derive the cyclic voltammogram for H on Pt(111) and Pt(100), based solely on density functional theory calculations and standard molecular tables. By relating the gas phase adsorption energy to the electrochemical electrode potential, we provide a direct link between surface science and electrochemistry.

In recent years electrochemical surface science has become an important tool in a number of diverse fields such as microelectronics, catalysis, and fuel cells [1]. A central technique in electrochemistry is cyclic voltammetry, where the current through an electrochemical cell is measured as the cell potential is cycled. The spectra obtained provide an abundance of quantitative information regarding electrochemical surface phenomena. For over 40 years, general and specific quantitative mathematical relationships have been developed to describe spectra recorded using cyclic voltammetry [2–8]. Such expressions are crucial in the interpretation of measured data; however, in and of themselves such expressions offer little, if any, predictive ability.

In the present Letter, we present a straightforward first principles method based on density functional theory calculations for generating theoretical cyclic voltammograms (CVs). The method is applied to a calculation of the CVs for hydrogen under-potential deposition (H-UPD) over Pt(111) and Pt(100) surfaces. The theoretical CVs show excellent agreement with experimental measurements, indicating that we have now a direct link between the energetics of adsorption processes on metal surfaces and experimental CVs.

The density functional theory calculations are performed using DACAPO, a plane-wave pseudopotential implementation [9,10] employing ultrasoft pseudopotentials [11] to represent the ionic cores. For all calculations the RPBE [12] exchange and correlation functional has been used. Three and four layer thick periodic 2×2 supercells were used to represent the Pt(111) and Pt(100) surfaces, respectively, all at the RPBE lattice constant of Pt (4.02 Å). For Pt(111) a 3×2 cell with three layers was also used to allow for calculations including a water bilayer. In all cases the bottom two layers were kept fixed while the top layers were allowed to relax. The plane-wave cutoff was 26 Ry, and the k points were sampled using a $4 \times 4 \times 1$ and $4 \times 6 \times 1$ Monkhorst-Pack reduced grids for the 2×2 and

3×3 cells, respectively. Dipole correction was used in all cases. Based on the density-functional theory (DFT) results a lattice model is developed for the H-H interaction. We solve the lattice model on a 50×50 lattice with periodic boundary conditions by use of standard Metropolis Monte Carlo calculations [13].

The process we study is the reaction of protons from aqueous solution with electrons at a Pt(111) or (100) surface (at a potential of U) to form adsorbed hydrogen:

$$H^+ + e^- \rightarrow H^*. \qquad (1)$$

The reaction is generally assumed to be fast [1], a conclusion supported by recent DFT calculations showing the barrier to be essentially zero [14]. In the case that reaction (1) is close to equilibrium at each electrode potential, U, the free energy difference associated with the reaction must be zero:

$$\Delta G(U, \theta) = 0. \qquad (2)$$

This determines the relationship between the coverage, θ, of H^* on the surface and the electrode potential, which in turn can be directly related to the current measured in a cyclic voltammogram.

In cyclic voltammetry the potential is ramped up to a certain value and turned back. At the same time, the current is measured. From the relation between U and θ implied by Eq. (2) we can obtain:

$$\frac{dU}{dt} = \frac{dU}{d\theta}\frac{d\theta}{dQ}\frac{dQ}{dt}. \qquad (3)$$

Here $\frac{dU}{dt}$ is the linear sweep rate of the experiment and $\frac{dQ}{dt}$ is the measured current. Assuming a transfer of one electron per adsorbed H, the relation between the charge transferred per area Q and the coverage θ is

$$Q = Q_{tot}\theta. \qquad (4)$$

Here Q_{tot} is e times the density of Pt atoms in the surface

layer and we use 241 and 209 $\mu C/cm^2$ for the (111) and (100) surfaces, respectively. Introducing $\pm K$ for the sweep rate and $i(t)$ for the current, we obtain:

$$i(t) = \pm K Q_{tot} \frac{1}{\frac{dU}{d\theta}} = \pm K Q_{tot} \frac{d\theta}{dU}. \qquad (5)$$

The key to calculating the voltammogram is therefore a calculation of the reaction free energy, $\Delta G(U, \theta)$, for reaction (1). To obtain this free energy we need to calculate the free energy of adsorbed H at the solid-liquid interface in the presence of an electrical field. We also need the free energy of the solvated protons and the electron in the electrode as a function of the electrode potential, U. The latter problem can be solved by introducing the theoretical counterpart to the standard hydrogen electrode (SHE) [15]. The SHE is defined so that when the electrode potential is measured relative to it, the reaction

$$1/2 H_2(g) \rightarrow H^+ + e^- \qquad (6)$$
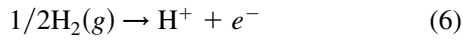
has a reaction free energy $\Delta G = 0$ eV at a potential $U = 0$ V at standard conditions, $T = 298$ K, $p = 1$ bar of H_2 and $pH = 0$. At another potential the chemical potential of the right side of Eq. (6) is changed by $-eU$ with respect to H_2 in the gas phase. Hence, the ΔG of Eq. (1) can be obtained by the Born-Haber cycle $H^+ + e^- \rightarrow 1/2 H_2(g) \rightarrow H^*$. Adding the changes in free energy during these steps the ΔG of reaction (1) can be related to the electrode potential via

$$\Delta G = \Delta G_0 + eU, \qquad (7)$$

where ΔG_0 is the reaction free energy for

$$1/2 H_2(g) \rightarrow H^* \qquad (8)$$
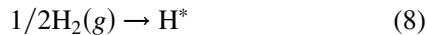
at standard conditions. This free energy can be directly calculated using DFT and standard molecular tables via

$$\Delta G_0 = \Delta E + \Delta ZPE - T\Delta S. \qquad (9)$$

Here ΔE and ΔZPE are the differential adsorption energy for H and the difference in zero point energy for reaction (8) as given by DFT. ΔS is the difference in entropy. The latter includes the loss of translational degrees of freedom during adsorption (taken from standard tables [16,17]) as well as the vibrational entropy of the adsorbed state as given by DFT. We use $\Delta ZPE = -0.008$ eV and $\Delta S = 0.00067$ eV/K.

In Eq. (9) the energy difference, ΔE, must be calculated for a H adsorbed at the solid-liquid interface in the presence of the electrical field set up by charge transferred to the surface and counter ions in the liquid, just outside the surface. For the case of H adsorption the effect of having a water layer above the surface and the effect of an applied electrostatic potential is very small, see Fig. 1(a). For this case we can therefore neglect effects due to the electrical double layer outside the surface. The small effect due to electric field and water layers is in agreement with previous
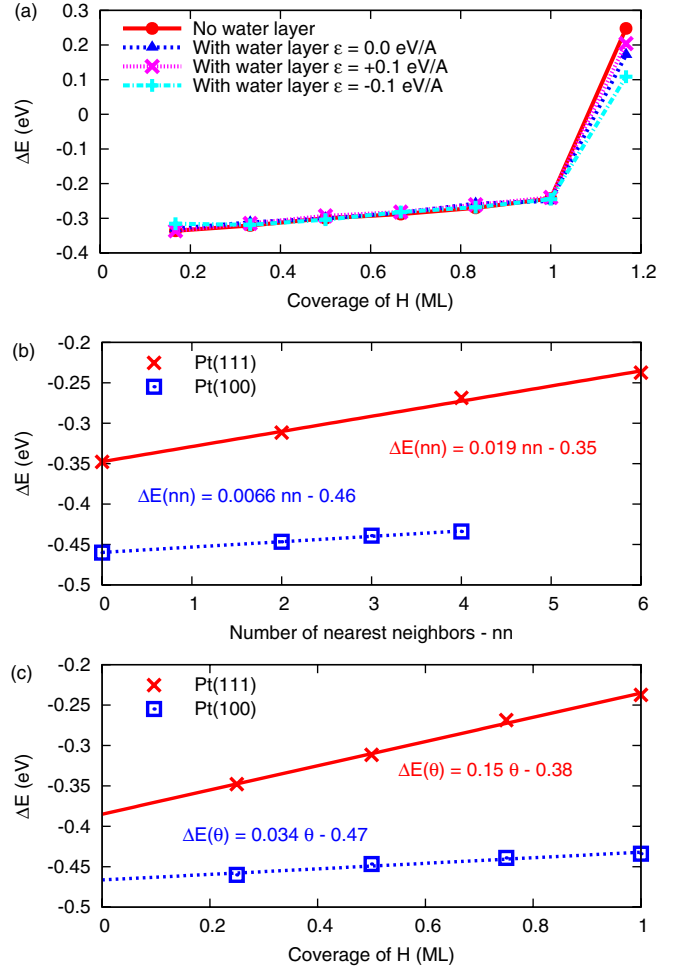

FIG. 1 (color online).   Differential adsorption energy ΔE for H on Pt(111) and Pt(100). Part (a) shows the effect of a water bilayer and electric field (ϵ) for the Pt(111) electrode. In parts (b) and (c) ΔE is plotted vs the number of H nearest neighbors on the surface and the H coverage, respectively.

investigations [18,19] and is assumed to be valid also for the Pt(100) surface.

In order to obtain the coverage dependence of ΔE, we have calculated the differential adsorption energy for H as a function of the hydrogen coverage on Pt(111) and Pt(100). For a coverage up to one hydrogen atom per surface atom, 1 monolayer (ML), on Pt(111) the threefold hollow fcc site is the most stable. Of the possible remaining adsorption sites, the on-top site is most stable. On Pt(100) the twofold bridge site is the most stable site both below and above a coverage of 1 ML.

An important feature to note in Fig. 1(a) is the jump in ΔE as the coverage becomes larger than 1 ML. This jump is due to the increased H-H interaction when a new high symmetry site becomes occupied. A similar but less pronounced jump can be observed for the Pt(100) surface (not shown), where ΔE goes from -0.43 eV at 1 ML to -0.19 eV at 1.25 ML. Because of these jumps in interaction energy, the analysis that follows will only focus on

coverages less than or equal to 1 ML of H. The high interaction energies at $\theta > 1$ ML correspond to potentials where the experimental CV is dominated by hydrogen evolution.

The first step towards generating a CV is to obtain the coverage of H as a function of potential at a given temperature. We obtain this with Metropolis Monte Carlo simulations of the electroadsorption and desorption of H based on Eq. (7). In this simulation a H atom is adsorbed in (desorbed from) an empty (filled) site if $\Delta G(U)$ for that process is negative. If the ΔG for that process positive it can still occur with a probability proportional to $\exp(-\Delta G(U)/k_BT)$. The local differential adsorption energy is evaluated using a lattice model and a model Hamiltonian. We use a simple model Hamiltonian including only pairwise nearest neighbor interaction:

$$\Delta E(\theta) = \Delta E_0 + \sum_i J\sigma_i, \qquad (10)$$

where ΔE_0 is the differential adsorption energy without any nearest neighbors, J is the interaction parameter, and σ_i is an occupation number. As can be seen from Fig. 1(b) the H-H interaction is well described by a pairwise nearest neighbor interaction on both Pt(111) and Pt(100).

Another less rigorous but more simple and transparent way to make the CV is to express the differential adsorption energy ΔE as a function of coverage directly from the DFT data, see Fig. 1(c). Equation (9) then needs to be corrected for the configurational entropy, which in the case of the Monte Carlo method was included *a priori*. We include this by adding the differential configurational entropy of noninteracting particles,

$$\Delta S_{\text{conf}} = k_B \ln\left(\frac{1-\theta}{\theta}\right), \qquad (11)$$

to Eq. (9). Combining Eq. (2) and (7) we obtain an expression relating the potential to the differential free energy of adsorption

$$U = -\frac{\Delta G_0(\theta)}{e}. \qquad (12)$$

This relation, analogous to the Nernst equation at $p\text{H} = 0$, can then be differentiated to give:

$$\frac{dU}{d\theta} = -\frac{1}{e}\left(a + k_BT\frac{1}{\theta(1-\theta)}\right), \qquad (13)$$

where a is the slope of the $\Delta E(\theta)$ curve given in Fig. 1(c). Inserting Eq. (13) into Eq. (5) one clearly sees how both the H-H interaction and the configurational entropy affects the CV curve for H adsorption and desorption. Although explicit use of Eq. (13) requires a numeric inversion of the $U(\theta)$ function, it is henceforth termed "analytic" to distinguish it from the Monte Carlo approach.
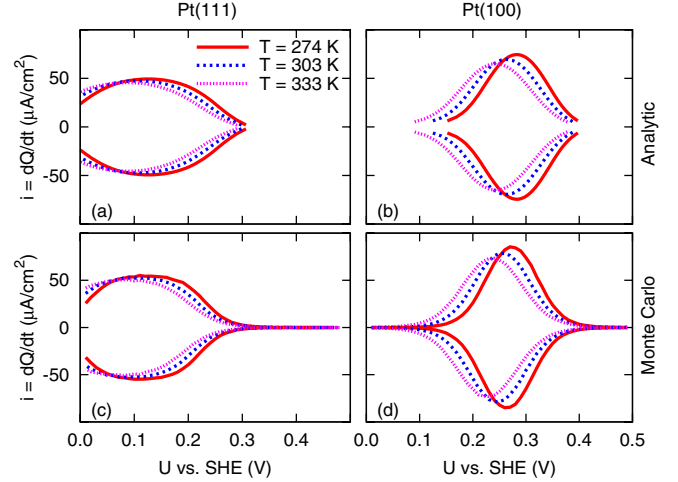

FIG. 2 (color online).   Cyclic voltammograms for H adsorption and desorption from Pt(111) and Pt(100) surfaces at different temperatures. The top panels show the result from the analytical model and the bottom two show results from a Metropolis Monte Carlo simulation.

The theoretical CVs obtained both by the "analytic" and Monte Carlo methods are shown in Fig. 2 for three different temperatures. For both Pt(111) and Pt(100) the i-V characteristics show qualitative agreement with the experimental CVs presented in Ref. [20]. Also the temperature dependence of the theoretical CVs agrees well with what is observed the experiments.

In order to compare quantitatively to experiments, we need to exclude from the experimental data effects which are not included in our first principles model, such as current from anion adsorption, charging of the double layer, and hydrogen evolution. Based on the accumulated knowledge in electrochemistry, a deconvolution of the CV peak related to H can be made for both Pt(111) and Pt(100). Such a deconvolution was made by Markovic, Grgur, and Ross [20] and we reproduce their data in Fig. 3(a). In Fig. 3(b) we show the theoretical charge versus potential curves (integrated CV) for the two facets as calculated using the Monte Carlo and the "analytical" method. As can be seen the agreement is very good regarding both the potential axis and the charge axis.

The good agreement between our DFT calculations and the electrochemical data suggest a close correlation between surface science and electrochemistry. In fact, solving for ΔE from Eq. (9) and (11) an estimate of the differential binding energy for hydrogen at a given H coverage $\theta = Q/Q_{\text{tot}}$ can be obtained from experimental data through

$$\Delta E(Q, U) = eU - \Delta\text{ZPE} + T\Delta S - k_B \ln\left(\frac{Q_{\text{tot}} - Q}{Q}\right). \qquad (14)$$

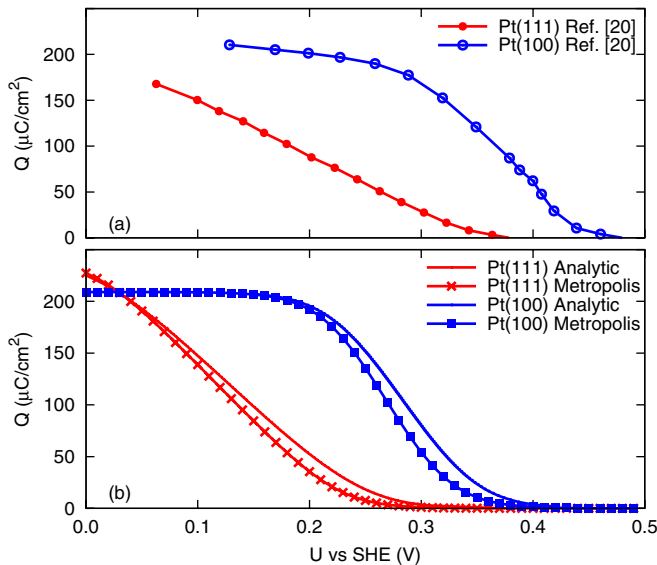Applying this relation we can estimate the differential

FIG. 3 (color online). Charge deposition due to hydrogen adsorption vs potential from (a) experiments presented in Ref. [20] and (b) theoretical calculations based only on DFT and molecular tables. The theoretical data are obtained from Eq. (4) and the calculated coverage vs potential. Two different approaches have be used to calculate the theoretical values, see text.

binding energy for H at 0.25 ML to be −0.45 eV and −0.60 eV for Pt(111) and Pt(100) surfaces, respectively. These numbers are similar to other estimates based on CVs [8,21,22]. Comparing with the calculated values presented in Fig. 1 this implies an error in the DFT calculations of about 0.1 eV, illustrating the current level of accuracy of generalized-gradient-approximation-type exchange-correlation functionals.

In summary, we have shown how to calculate both the electroadsorption isotherm and the cyclic voltammogram for H adsorption on Pt(111) and Pt(100) directly from density functional theory calculations and standard molecular tables. The agreement with experiments is excellent. The systems we have considered are the simplest possible: homogeneous surfaces with only one adsorption site and a process operating close to equilibrium. The present approach can, however, be generalized to include inhomogeneities, phase transitions, and dynamic effects [23]; the important ingredient introduced here is the use of the theoretical standard hydrogen electrode that gives us a direct and computationally simple link to experimental potential scales.

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