

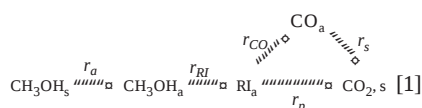
Potential Dependent Dynamics of Methanol Electrooxidation on Pt(111)

A Summary Report to the Electrochemical Society for the 1998 Department of Energy Summer Research Fellowship

by Suresh Sriramulu

Efficient methanol electrooxidation is crucial to the commercial development of the direct methanol fuel cell. The electrooxidation reaction, however, is plagued by low rates of oxidation and poor selectivity to the complete oxidation product CO_2 . Poor selectivity leads to the accumulation of partial decomposition products (mostly CO) which poison the surface.¹⁻⁶ One obvious consequence of poisoning is the decreased rate of methanol dissociative adsorption on the electrode surface due to fewer adsorption sites.⁷ In addition, by blocking sites required for other surface reactions, adsorbed residue may also influence the course of the surface reactions.

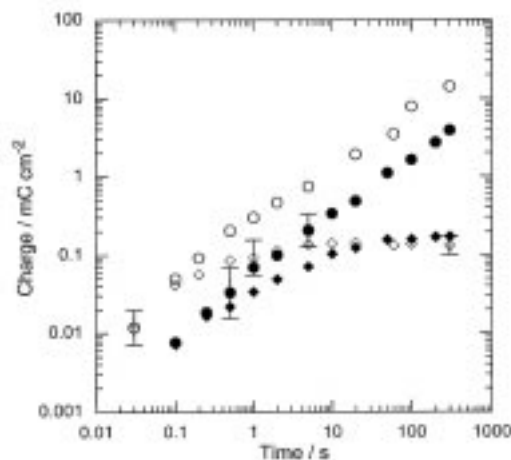
Based on available experimental evidence, we proposed the following mechanism for methanol electrooxidation on Pt(111):⁸



where the subscripts *a* and *s* denote adsorbed and solution phase species respectively. The site balance for this model was written using the Langmuir-Hinshelwood description of the surface chemistry⁷ and the unknown parameters in the model estimated by comparing model predictions with experimental data for reaction at 0.6 V_{RHE} .⁸ The model provided an excellent fit to the data and showed that, for reaction on an initially clean electrode surface, the most abundant surface species was H:C:O (RI) at short time scales and CO at longer time scales. With residue accumulation, kinetic control of the overall reaction transferred from RI oxidation to methanol adsorption and finally to CO oxidation. Furthermore, the rate of the non-CO pathway r_p was always higher than the rate of CO oxidation r_s .⁷ The non-CO path was shown to be active on Pt(111) even at potentials where CO does not oxidize.⁹

Here, new data for the methanol reaction at 0.5 V_{RHE} on Pt(111) is compared with data obtained previously at 0.6 V_{RHE} . The influence of potential on the rate of the non-CO pathway is estimated and compared to the effect of adsorbed residue on surface reactions at these two potentials.

FIG. 1. Comparison of experimental reaction q_r (circles) and stripping q_s (diamonds) charges measured on Pt(111) at 0.6 V_{RHE} (open symbols) and 0.5 V_{RHE} (filled symbols). The electrolyte composition was 0.1 M CH_3OH + 0.1 M HClO_4 for the q_r measurement and 0.1 M HClO_4 for the q_s measurement. Error bars are shown at twice the relative standard deviation.

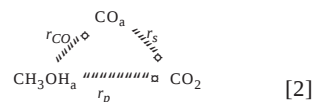


Complete details of the experimental procedure are given elsewhere.¹⁰ Briefly, the experiments were performed under anaerobic conditions in a dual cell apparatus at room temperature. All potentials are quoted with respect to the reversible hydrogen electrode (RHE) in the same electrolyte. The reaction charge q_r is the charge passed following a potentiostatic step to the reaction potential E_r on an initially clean Pt(111) electrode in methanol-bearing electrolyte. Subsequently, stripping voltammetry in neat electrolyte was used to oxidize the adsorbed residue formed during the methanol reaction. The charge required to oxidize the adsorbate is the stripping charge q_s . For the measurements reported E_r was fixed at 0.5 V or 0.6 V, and the duration of the potential step, i.e., the reaction time, varied.

Figure 1 shows the reaction and stripping charges for reaction of 0.1 M methanol at 0.6 V and 0.5 V on a Pt(111) electrode as a function of the reaction time. Note that CO oxidation occurs at a finite rate only at potentials positive of 0.55 V. This limits the q_s value for reaction at 0.6 V, whereas q_s continues to increase for reaction at 0.5 V. The q_r and q_s values are consistently greater for reaction at 0.6 V suggesting that the surface reactions occur at faster rates at higher potentials. With reference to Eq 1, all reaction steps, with the exception of molecular adsorption of methanol, will be accompanied by charge transfer.

From the data in Fig. 1 it cannot be determined which reaction step is most affected by potential. However, if either methanol adsorption or dissociation on Pt(111) is activated by potential,⁹ then r_{CO} and r_p will also occur at a lower rate because of the reduced supply of RI at 0.5 V.

From the data presented in Fig. 1, the rate of the non-CO pathway at the two potentials can be calculated. At long times, when CO is the most abundant surface species, the over all reaction is adequately represented by⁷:



with the understanding that $r_s = 0$ for potentials less than 0.55 V. Since CO formation results in the flow of four electrons, CO oxidation in the flow of two electrons, and complete oxidation of methanol in the flow of six electrons, the following expression for the reaction current when $r_s = 0$ can be written:

$$i_r = 2i_s + 6eM r_p \quad [3]$$

where i_r is given by the slope of q_r vs time and i_s by slope of q_s vs time; e is the charge on an electron, M the surface atom density of Pt(111) and r_p the rate of CO_2 production by the non-CO pathway. For reaction at 0.5 V, when q_s equals 0.14 $\text{mC}\cdot\text{cm}^{-2}$, the estimated value of r_p from Eq. 3 is 0.010 s^{-1} . A

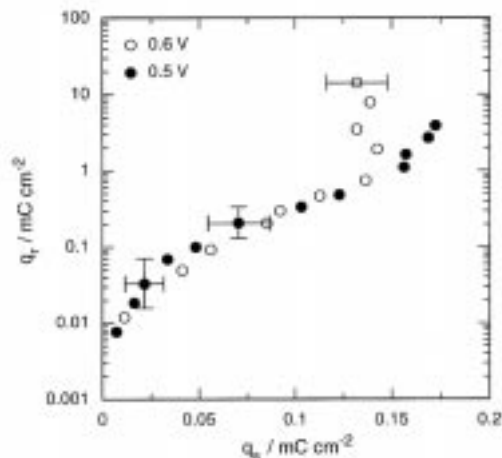


FIG. 2. Reaction charge q_r , as a function of the stripping charge q_s measured on Pt(111) at 0.6 V_{RHE} (○) and 0.5 V_{RHE} (●). The error bars are shown at twice the standard deviation. The electrolyte compositions are given in the caption in FIG. 1.

non-zero value of r_p confirms our previous results that the non-CO pathway is active at this potential. But for an identical q_s value of 0.14 mC cm^{-2} , we previously estimated r_p as 0.035 s^{-1} at 0.6 V¹¹. This shows that the surface reactions indeed occur at a slower rate at the lower potential.

Because the rates of the surface reactions are potential-dependent, the reaction time cannot be used to mark the progression of reaction while comparing the influence of adsorbed residue on the reaction at different potentials. Instead, residue accumulation must be used, or equivalently q_s , to mark the progression of the reaction. For example, $q_s = 0$ denotes a clean surface and increasing values of q_s mark the extent of reaction. Figure 2 shows a comparison of the q_r data for reaction at 0.5 V and 0.6 V as a function of q_s . This comparison is invalid when the surface reactions attain steady state (when $q_s = 0.14 \text{ mC cm}^{-2}$ at 0.6 V) because, q_s does not increase even though reaction continues to occur on the surface. Interestingly, for lower values of q_s , the data for reaction at 0.6 V and 0.5 V fall on the same curve (within experimental error). This suggests that residue accumulation influences the course of the surface reactions in the same manner at the two potentials.

In summary, the results presented show that CO_2 production by the non-CO pathway occurs at a faster rate at the higher electrode potential of 0.6 V. Although the surface reactions occur at slower rates at the lower potentials, the accumulated residue affects the surface reactions in the same manner at the two potentials. Furthermore, the above result validates the usually implicit assumption that the mechanism of methanol electrooxidation is independent of potential. ■

Acknowledgments

The author would like to acknowledge the invaluable guidance and support from his advisor Professor Eric M. Stuve and, financial assistance from The Electrochemical Society - Department of Energy through the summer research fellowship and the National Science Foundation.

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About the Author

Suresh Sriramulu is pursuing a PhD in Chemical Engineering at the University of Washington, Seattle, under the guidance of Professor Eric M. Stuve.

Chain-Length Dependence of Crystallinity of Alkylamine Monolayers on $\text{YBa}_2\text{Cu}_3\text{O}_7$

A Summary Report to the Electrochemical Society for a 1998 Department of Energy Summer Research Fellowship

by Jason E. Ritchie

The extreme interfacial reactivity of $\text{YBa}_2\text{Cu}_3\text{O}_7$ has slowed the industrial and commercial use of this technologically-important superconducting material. The development of methods aimed at optimizing both the surface properties and reproducible processing methods will have a profound influence on high- T_c superconductivity research.

Recently, the McDevitt and Kanis groups have described the mechanism of adsorption and infrared characterization of crystalline monolayers spontaneously adsorbed on $\text{YBa}_2\text{Cu}_3\text{O}_7$.^{1,2} Results are reported here from recent infrared studies which show the chain length on the observed crystallinity of the adsorbed monolayer. In addition, further evidence regarding the orientation of the terminal methyl group is provided by examining infrared spectra of even and odd carbon chained amine adsorbates.

The Reflection-Absorption Infrared (RAIR) spectra of several different carbon chain length alkylamines were compared. Figure 1 shows RAIR spectra of hexyl (C_6), decyl (C_{10}), dodecyl (C_{12}), and octadecylamine (C_{18}) adsorbed on $\text{YBa}_2\text{Cu}_3\text{O}_7$ (001) thin films. Previous publications have shown that the asymmetric methylene vibration ($\sim 2920\text{ cm}^{-1}$) is very sensitive to the chemical environment of the monolayer.³⁻⁵

The RAIR spectrum of octadecylamine shows the greatest degree of crystallinity, with an asymmetric methylene peak position of 2916 cm^{-1} (which is consistent with values obtained for crystalline octadecylthiol monolayers on gold) and a full width at half maximum (FWHM) of 12 cm^{-1} . Meanwhile, dodecylamine adsorbed on $\text{YBa}_2\text{Cu}_3\text{O}_7$ displays an asymmetric methylene peak position of 2924 cm^{-1} and a FWHM of 21 cm^{-1} indicating a somewhat disordered structure. The shortest amine examined, hexylamine, showed a very broad asymmetric methylene vibration ($>30\text{ cm}^{-1}$ FWHM) that is positioned at approximately 2930 cm^{-1} , indicating a very liquid-like monolayer.

From analysis of the infrared data, it is apparent that as the chain length of the monolayer is increased the peak position of the asymmetric methylene vibration mode shifted to lower

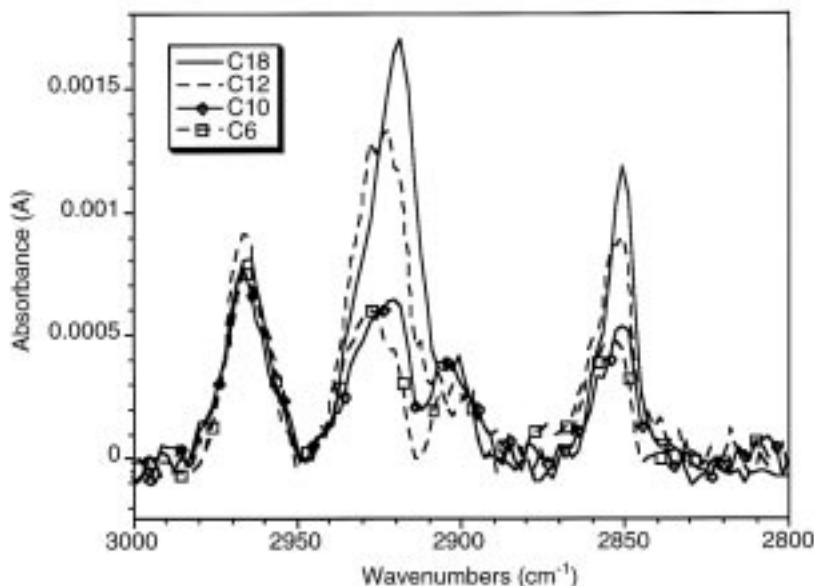


Fig. 1. Chain length dependence of the RAIR spectra of primary alkylamines adsorbed on $\text{YBa}_2\text{Cu}_3\text{O}_7$ (001) thin films.

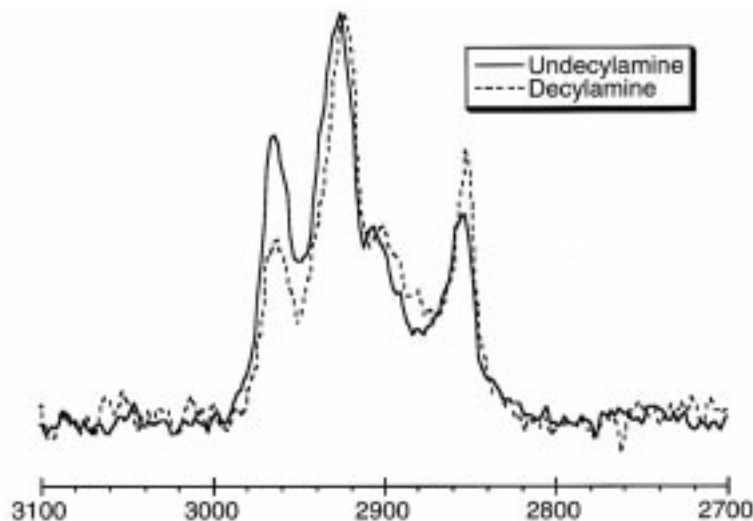


Fig. 2. Comparison of the RAIR spectra of undecylamine and decylamine monolayers on $\text{YBa}_2\text{Cu}_3\text{O}_7$. The y-axis of the undecylamine case has been scaled to make the peak intensities of the asymmetric methylene vibrations equal. This is due to sample to sample variations in factors such as surface area and roughness. Note the dramatic increase in intensity for the methyl vibration in the odd numbered alkylamine adsorbate relative to the asymmetric methylene vibration.

energy, indicating an increase in crystallinity. In addition the width of the vibration decreased, indicating an increase in the chemical homogeneity and overall order of the system.

In our previous work, we noted the lack of a methyl signal in our spectra that was attributed to a methyl vibrational dipole that lies nearly in the plane of the substrate.¹ Since the RAIR spectra use p-polarized light, a vibra-

tional dipole must have a component that is perpendicular to the plane of the substrate in order to couple to the incident radiation. Thus, a dipole parallel to the plane would be expected to be absent in the RAIR spectra, while a dipole that is perpendicular to the plane is expected to yield a large RAIR signal.

If the methyl dipole lies in the plane for an even numbered carbon chain, then that dipole would be expected to

lie nearly perpendicular to the plane for an odd carbon chained amine such as undecylamine (C_{11}). A comparison of RAIR spectra of decyl and undecylamine monolayers adsorbed on $YBa_2Cu_3O_7$ (001) is shown in Fig. 2. From these spectra it is clear that the undecylamine monolayer produces a much more pronounced methyl vibration than the decylamine monolayer indicating much better coupling between the dipole and the incident radiation. Note that the decylamine monolayer is slightly disordered and shows a small amount of methyl vibration due to this disorder.

In summary, the chain length dependence of amine monolayers adsorbed on $YBa_2Cu_3O_7$ has been explored. Like the prior work with alkylthiols on gold (111), it is found that the degree of order for these monolayer assemblies increases dramatically as the chain length is increased past C_{10} . In addition, an interesting odd-even effect on the methyl-vibration intensity is noted consistent with that predicted from molecular modeling studies. ■

Acknowledgments

This research was performed under the direction of Professor John T. McDevitt in the Department of Chemistry and Biochemistry at the University of Texas at Austin.

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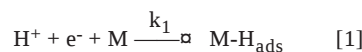
Jason Ritchie was awarded his PhD in August of 1998 and is pursuing a postdoctoral appointment in the Department of Chemistry at the University of North Carolina at Chapel Hill in the laboratory of Royce W. Murray.

Mechanistic Analysis of Hydrogen Evolution and Absorption Reactions on Iron

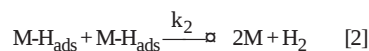
A Summary Report to the Electrochemical Society for a 1998 Department of Energy Summer Research Fellowship

by M. H. Abd Elhamid

Hydrogen embrittlement occurs to most ferrous alloys due to the absorption of hydrogen into the metal as a result of the hydrogen evolution reaction (HER).¹⁻⁴ The mechanism by which hydrogen absorption occurs relies on the mechanism of the HER.² The HER is a multistep reaction which starts with the discharge of the H^+ ions on the metal surface as follows:²



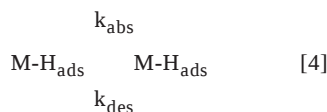
where $M-H_{ads}$ refers to an adsorbed hydrogen atom on the metal surface and k_1 is the discharge rate constant of the HER. The formation of molecular hydrogen occurs either via the chemical (Tafel) recombination:



where k_2 is the recombination rate constant of the HER or electrochemically as follows:



The hydrogen absorption reaction, (HAR), occurs as a side reaction of the hydrogen adsorption step of the HER, Eq. 1, as follows:



where $M-H_{abs}$ refers to the absorbed hydrogen atom inside the metal lattice and k_{abs} and k_{des} refer to the rate constants of the forward and backward directions of reaction 4, respectively. This absorbed hydrogen diffuses deeper into the metal lattice and eventually causes embrittlement.

The analysis of the hydrogen evolution and absorption reactions on metals has been extensively studied in the literature.³ Many methods have been used to help better understand the mechanism of both reactions. While some of the techniques used to study the kinetics of both reactions have some disadvantages, others have to be used with great caution. Iyer et al.⁴ developed the so called I-P-Z model that was unique in the sense that the model is an analytical one which avoids the use of non-linear fitting of

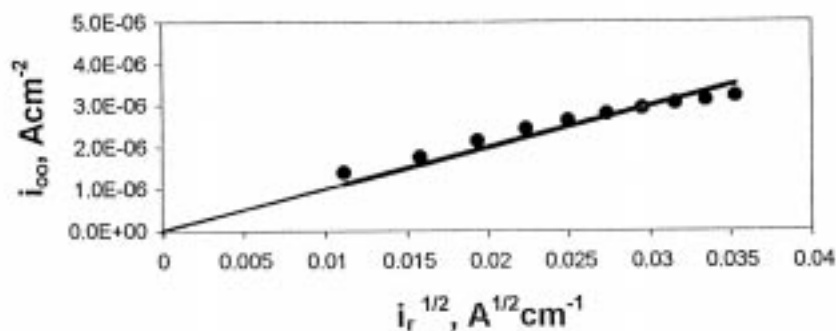


FIG. 1. The relation between the steady state permeation current and the square root of the recombination current obtained on an iron membrane of thickness 0.25mm in 0.1N H_2SO_4 + 0.9N Na_2SO_4 .

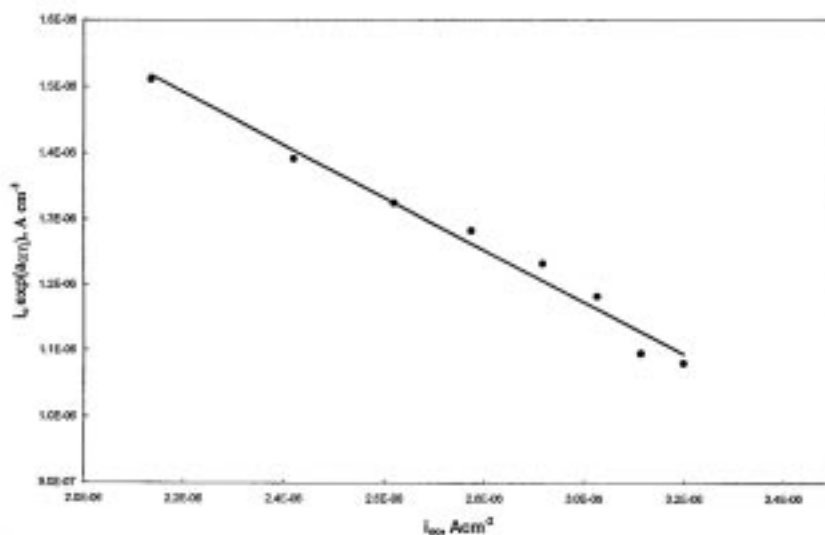


FIG. 2. The relation between the charging function, $i_{exp(\alpha \xi)}$, and the steady state permeation current, i_{oo} , obtained on an iron membrane of thickness 0.25mm in 0.1N H_2SO_4 + 0.9N Na_2SO_4 .

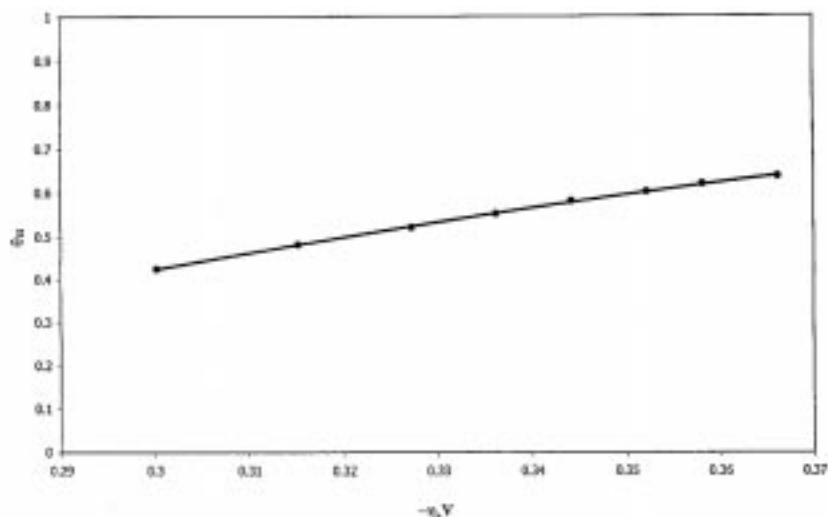


FIG. 3. The relation between the hydrogen surface coverage, θ , and the cathodic overpotential, η , obtained on an iron membrane of thickness 0.25mm in 0.1N H_2SO_4 + 0.9N Na_2SO_4 .

experimental data to extract kinetic parameters. Furthermore, it implements data from hydrogen evolution and absorption reactions to fully describe the kinetics of both reactions.⁴ The aim of this work is to analyze the kinetics of the HER and HAR, on iron in 0.1N H₂SO₄ + 0.9N Na₂SO₄ using the I-P-Z model.

The electrochemical hydrogen permeation cell developed by Devanathan and Stuchurski⁵ was used to collect data on both the HER and HAR on iron. The samples were 99.5% iron membranes of 0.25 mm thickness obtained from Goodfellow. Details about the experimental setup and solutions and samples preparation can be found elsewhere.⁶ The I-P-Z model describes the HER and HAR in terms of the following set of equations assuming a coupled discharge-Tafel recombination mechanism for the HER:

$$i_c = Fk_1 C_{H^+} (1 - \theta_H) \exp(-\alpha \eta) \quad [5]$$

$$i_r = Fk_2 \theta_H^2 \quad [6]$$

$$i_\infty = FDC_{H^+}/L \quad [7]$$

$$i_\infty = k'/b \quad [8]$$

$$i_\infty = (k'/[b\sqrt{(Fk_2)}])^{1/2} i_r \quad [9]$$

$$i_c \exp(\alpha \eta) = i_0' - (i_0' b/k') i_\infty \quad [10]$$

where i_c is the cathodic current density of the HER, k_1 is the discharge rate constant of the HER, C_{H^+} is the hydrogen ion concentration, θ_H is the hydrogen surface coverage, $a = RT/F$, α is the transfer coefficient of the HER, η is the hydrogen overpotential, k_2 is the recombination rate constant of the HER, $i_r = i_c - i_\infty$ and is defined as the recombination current density of the HER, where i_∞ is the steady state hydrogen permeation current density, k' refers as to the absorption-desorption constant of the HAR, $b = L/FD$, $i_0' = i_0 / (1 - \theta_H)$ where i_0 is the exchange current density of the HER, and θ_H is the equilibrium hydrogen surface coverage. Eq. 10 is a straight line relation between the charging function, $i_c \exp(\alpha \eta)$, and the steady state permeation current, i_∞ . The slope of which gives $1_0' b/k'$ and the intercept is i_0' . Consequently, values of k' and i_0' can be evaluated. The value of i_0' can be used to estimate i_0 , assuming $i_0 \approx i_0'$; while k' can be used to evaluate the hydrogen surface coverage, θ_H . The value of k' can also be used to evaluate the recombination rate constant, k_2 ,

from the slope of Eq. 9. Figure 1 shows the relation between the steady state permeation current and the square root of the recombination current. This figure shows a straight line relation passing by the origin which means that the HER follows the couple discharge-Tafel recombination mechanism and the requirement for the I-P-Z model is fulfilled.⁴ Figure 2 shows the relation between the charging function, $i_c \exp(\alpha \eta)$, and the steady state permeation current, i_∞ . This figure shows a reasonably straight line with a negative slope, which demonstrates the validity of the model. A value of 2×10^{-6} A-cm⁻² for i_0' was estimated from the intercept of the line in Fig. 2. This value matches with the values reported for the exchange current density obtained for iron in the literature.⁷ Table I shows values of k_1 , k_2 and k' as calculated from Figs. 1 and 2.

TABLE 1. Values of the rate constants of the HER and HAR calculated using the I-P-Z model on an iron membrane of thickness 0.25 mm in 0.1N H₂SO₄ + 0.9N Na₂SO₄.

k_1 , (cm/s)	1.25×10^{-7}
k_2 , (mol/cm ² s)	2.67×10^{-8}
k' , (mol/cm ³).....	1.04×10^7

The value of k' was used to estimate the hydrogen surface coverage, θ_H , at different values of the hydrogen overpotential, η . Figure 3 shows the variation of the hydrogen surface coverage, θ_H , with the hydrogen overpotential, η . This figure indicates that the coverage increases with the hydrogen overpotential, which is similar to other results in the literature.⁸

In conclusion, the I-P-Z model was applied to analyze both the hydrogen evolution and absorption reactions on iron. The model was able to fully describe the kinetics of both reactions as it gives values for: (1) the exchange current density of the HER, i_0 ; (2) the discharge rate constant of the HER, k_1 ; (3) the thickness dependent absorption-desorption constant, k' ; and (4) the recombination rate constant, k_2 .

Work is underway to extend the applicability of the I-P-Z model to analyze the kinetics of both reactions in presence of organic inhibitors such as benzotriazole, BTA. This work includes analysis of both reactions at one thickness of the iron membrane at different

BTA concentrations to quantify the effect of BTA on both reactions. This work will be extended to evaluate the kinetics of both reactions at different BTA concentrations and different membrane thicknesses. The latter will help in the evaluation of the k_{abs} and k_{des} rate constants of reaction 4. ■

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In-Situ Scanning Tunneling Microscopy of Ir(100) Electrodes with Adsorbed Nitric Oxide and Carbon Monoxide

A Summary Report to the Electrochemical Society for a 1998 Department of Energy Summer Research Fellowship

by Shouzhong Zou

Adsorbate-induced substrate phase transitions are often seen in interfacial studies, especially in ultra-high vacuum (UHV) environments.¹ While a variety of adsorbate-induced surface structural changes have been reported in both UHV and electrochemical systems,^{2,3} most commonly encountered is the removal of surface reconstruction upon molecular adsorption.¹ For example, clean Ir(100) undergoes hexagonal-type reconstruction and exhibits a (5x1) periodicity in UHV as revealed by low-energy electron diffraction (LEED). However, the adsorption of CO or NO removes the reconstruction as deduced from the attenuation of the 1/5th order spots in the LEED patterns when the adsorbate coverage reaches a critical value.^{4,5} Such structural transformations can in some cases exhibit characteristic

changes in the corresponding adsorbate vibrational spectra, therefore enabling these measurements to be utilized as an empirical assessment of substrate structure when direct spatial information is not available.

While such phase transitions are also of central importance at ordered electrochemical interfaces, the availability of direct in-situ information on spatial substrate structure remains sparse, especially at transition metal surfaces. As LEED is inapplicable, the advent of in-situ atomic resolution scanning tunneling microscopy (STM) provides an invaluable real-space probe of metal substrate as well as adlayer structure.⁶ This is especially the case when STM data are combined with adsorbate vibrational information obtained from in-situ infrared reflection-absorption spectroscopy (IRAS).⁷

The adsorption of CO and NO on Ir(100) in aqueous acidic solution has been studied in our laboratory utilizing in-situ IRAS.⁸ The CO and NO vibrational features obtained were essentially the same as those observed for adsorption on (1x1)-Ir(100) in UHV, suggesting the same substrate structure in the electrochemical environment.⁸ While significant, this conclusion is nonetheless suggestive rather than indicative. It is therefore of critical importance to directly probe the atomic spatial arrangement of such systems by means of in-situ STM. This report presents in-situ STM images for Ir(100) surface obtained in N₂-purged, NO-saturated, and CO-saturated 0.1 M HClO₄. The results show that Ir(100) retains the (1x1) structure in the electrochemical environments, even

(continued on next page)

without NO or CO adsorbed. However, Ir(100) apparently undergoes surface restructuring upon CO adsorption.

The flame-annealing procedure for the Ir(100) crystal followed is described elsewhere.⁸ After annealing, the surface was transferred to the STM cell while protected by a drop of ultrapure water. The sharp hydrogen adsorption/desorption characteristics obtained in the cyclic voltammograms⁸ were reproduced in the STM cell containing 0.1 M HClO₄, suggesting that the crystal is highly ordered, as indeed was confirmed by the STM images.

Figure 1 presents an atomic-resolution image obtained in 0.1 M HClO₄ at 0.25 V vs SCE. The distance between each bright dot (i.e., tunneling maximum) in the square planar array is about 2.8 Å, close to the atomic size of an Ir atom. The square arrangement of these dots clearly reveals that in the electrochemical environment, Ir(100) retains its *unreconstructed* structure. Such an observation is not unreasonable, given that in UHV (1×1)-Ir(100) also exists and is stable up to 800 K.⁹ In addition, a (1×1) LEED pattern has also been observed on a Ir(100) electrode pretreated by a similar annealing protocol, and transferred into UHV.¹⁰

Of central interest here is the influence of the adsorbates on the substrate structure. First, we exposed the unreconstructed Ir(100) surface to NO-saturated 0.1 M HClO₄ at 0.5 V. The NO undergoes dissociation upon adsorption, yielding a maximum NO coverage of only approximately 0.25.⁸ However, the characteristic IRAS fingerprints for molecular NO provide an empirical assessment of the substrate structure, also suggesting that the substrate is unreconstructed.⁸ Interestingly, the Ir(100) electrode retains its initial atomic arrangement upon NO adsorption as indicated by the similar images to those obtained in 0.1 M HClO₄. The low coverage of molecular NO, with its consequent high mobility, is likely responsible for not observing an ordered adlayer structure in the STM images. This result confirms the assertion of the unreconstructed Ir(100) in the electrochemical systems based on the in-situ IRAS results.⁸

Rather different images were obtained, however, when the clean surface was subjected to CO-saturated solutions. The adsorbed CO was obtained by purging the gas slowly into a STM chamber. Within about 15 minutes, the image developed nanoscale superstructural features, decorating the terrace in a random fashion. The shape and height

FIG. 1. Constant height STM image of Ir(100) in 0.1 M HClO₄ at 0.25 V vs SCE, with $E_{\text{bias}} = -297$ mV and $I_t = 8.2$ nA.

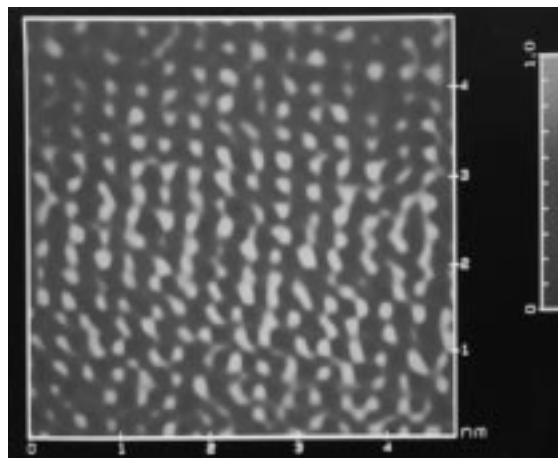
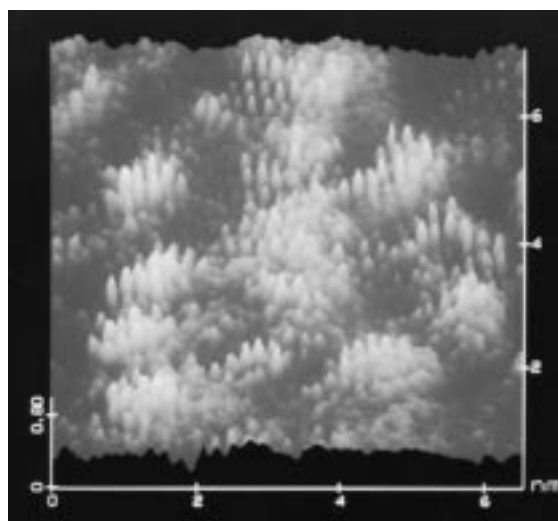


FIG. 2. Constant height STM image of Ir(100) in CO saturated 0.1 M HClO₄ at -0.1 V vs SCE, with $E_{\text{bias}} = 4.3$ mV and $I_t = 7.7$ nA.



of these clusters are rather irregular. Some of them are brighter than others, indicating they are at higher positions normal to the terrace plane. These clusters are probably not impurities on the surface since they do not exist when CO is absent and the images are reproducible. A typical atomic-resolution image of these clusters is shown in Fig. 2. The distance between the adjacent dots within each cluster is about 2.8 ± 0.1 Å, suggesting their identity as Ir atoms. The square unit cell observed in the clusters suggests that the surface is “roughened” by CO adsorption while remaining in a (1×1) atomic arrangement, although the uncertainty in the orientation of the unit cell with respect to that of the clean surface obscures this conclusion to some extent. Nevertheless, it is clearly evident that the adsorption of CO on originally large-scale (1×1) terraces induced the formation of small islands of Ir atoms.

A different kind of adsorbate-induced nanoscale substrate restructuring has also been seen on Pt(100) electrodes.¹¹ The adsorption of CO, CN⁻, sulfur, and submonolayer iodine triggered the for-

mation of flat “mesa-like” features of dimensions about 20 to 40 Å, which are composed of Pt “microterraces” retaining the original (1×1) structure.¹¹ The driving force for the formation of mesas was tentatively attributed to optimization of the number of energetically more favorable adsorbate-surface bonds.¹¹ Given the similar chemical nature of the substrates, it is possible that the formation of the present clusters also originates from a similar source, although the restructuring on Ir(100) is less clear cut than on Pt(100). Another plausible explanation could be the probable high dynamic pressure of CO in the present system, since similar CO-induced surface roughening at near-ambient gas pressures has also been seen in gas-phase STM studies on Pt(111).¹² Studies aimed at further clarifying the nature of such adsorbate-induced surface restructuring in electrochemical systems are planned to be undertaken by examining the influence of different adsorbates on the substrate structure.

In summary, in-situ STM images demonstrate that in electrochemical environments, Ir(100) is unrecon-

structed, even in the absence of strong adsorbates. A “surface roughening” characterized by the appearance of metal clusters nonetheless having a (1x1) unit cell is induced by the adsorption of CO. This study shows the value of in-situ STM in revealing interfacial spatial information. It also supports the validity in this case of utilizing adsorbate vibrational spectral fingerprints as empirical assessments of the substrate structure.^{3, 8} ■

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