An Experimental and Theoretical Study of Interactions between Unlike Surface Anions and Increases in the Rate of Electrochemical Reactions

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Received: October 12, 2005; In Final Form: January 24, 2006

Experimental and theoretical results are presented on increases in the rate of electrochemical reactions, which are achieved by replacing a small fraction of the original anions in solution with more inhibiting ones. The rate of the electrochemical oxidation of formic acid was substantially increased by replacing a small amount of the supporting electrolyte, perchloric acid, with either sulfuric acid or tetrafluoroboric acid. The largest increases were achieved by substituting mixtures of the last two acids. A theoretical analysis of an electrochemical reaction coupled to anion adsorption is presented. The analysis reveals that, if repulsive forces of appropriate strength form between unlike surface anions, replacing a fraction of the original anions in solution with one or two kinds of more inhibiting anions can increase the rate of reaction.

Introduction

Many studies have exposed the large extent to which anions affect electrochemical reactions.[1−16] In a study on the electrochemical oxidation of methanol,[1] it was found that the effects of anions are comparable to the effects of surface geometry. In another study on methanol oxidation,[2] the adsorption of anions decreased the current in a potential range where previously it was believed oxide formation was responsible for the inhibition. In other work,[3] it was determined that the oxidation of hydrogen, the oxidation of carbon monoxide, and the reduction of oxygen are all highly sensitive to anion adsorption.

Considerable research supports the theory that the effects of anions on electrochemical reactions originate from their adsorption and subsequent blocking of surface sites.[1−16] Surface anions inhibit reactions requiring vacant sites. A study of the oxidation of methanol at polycrystalline Pt is consistent with this picture.[4] The methanol current measured when perchloric acid was the electrolyte was larger than that measured when sulfuric acid was the electrolyte. The current obtained using the latter electrolyte was greater than the current that was measured when phosphoric acid was the electrolyte. The smallest currents were obtained using HCl solutions. The results were explained by considering anions to inhibit methanol oxidation by blocking surface sites. The trend in the oxidation currents follows the trend given by "anion adsorption strengths" which are ordered as[4]

$$ClO_4^- < HSO_4^- < H_2PO_4^- < Cl^-$$
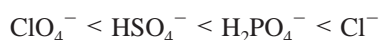
A large number of results in the literature follow the trends in anion adsorption strength and the competition for surface sites.[5−16] Because the inhibitory properties of anions are well established, it is easy to conclude that the dominant interactions of an adsorbed anion are with the atoms of the electrode surface. In this paper, an experimental and theoretical study is presented on the increase in the rate of electrochemical reactions that is seen when a fraction of the original supporting electrolyte is replaced by more inhibiting ones. The results present strong

evidence that adsorbed anions can have evident influences on a reaction through interactions that are different from those associated with adsorption and blocking surface sites. Other studies indicate reactions are affected by surface anions through interactions not related to blocking surface sites.[17−19] Two of these are closely related to the study presented here. They report unexpected increases in the rates of the electrochemical oxidations of formic acid at Pd[18] and methanol at Pt[19] in response to increases in the overall anion adsorption strength of the supporting electrolyte.

Experimental results are presented in this paper from the application of cyclic voltammetry to the electrochemical oxidation of formic acid[3,17,18,20−26] at polycrystalline Pt using perchloric acid as the supporting electrolyte. Measured currents are provided for the cases in which sulfuric acid, fluoroboric acid, and mixtures of these two acids replace a fraction of the perchloric acid. In all cases, replacing a fraction of perchloric acid with the more inhibiting acids can substantially increase the current. By comparing the effects of fluoroboric acid and sulfuric acid, it is seen that the mechanism by which the current is increased is independent of anion adsorption strengths. The experiments were conducted at zero degrees Celsius. The percent increases are greater than those obtained at room temperature. The experimental results, a theoretical analysis, and previous results provide strong evidence that the enhanced currents are not caused by chemical changes nor by changes in the electrode surface. It is argued that the existence of nonreactive interactions between unlike surface anions is the most consistent explanation of the increase in the rate of formic acid oxidation.

Following the experimental results, a theoretical analysis of an electrochemical process involving a surface intermediate and coupling to anion adsorption is presented. Steady-state current densities are calculated for different situations. When the experimental solution contains one type of anion and a fraction of its concentration is replaced with more inhibiting anions, calculations show that the current density decreases if the interactions between all surface anions are treated as the same. However, if the magnitude of interactions between unlike surface anions is greater than a threshold, which in turn is greater than the magnitude of interactions between like surface anions, a

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greater current density is realized. Anions in solution and surface anions are hydrated. Although hydration is important (e.g., it affects the anion's interaction strength), it is ignored in the model. The simplicity of the model facilitates the deduction of the main features involved in the enhancement of reactions. It is shown that, under some conditions, the simple model analyzed here produces results for steady-state currents that are identical to those obtained using more complicated models, models with several adsorbed intermediates and more than one reaction route.

Experimental Section

The working electrode was a polycrystalline Pt disk, 7.65 mm diameter, embedded in polytetrafluoroethylene. It possessed an actual or real area of 0.983 cm^2. The Pt disk was polished with alumina (Buehler, Lake Bluff, IL) mixed with high purity water on Microcloths (Buehler) glued to flat mirrors. A different Microcloth was used for each size of alumina. The final particle size was 0.05 μm. After the initial preparation, the electrode was only polished with the 0.05 μm particle size. In the initial preparation, the electrode was polished with the 0.05 μm particle size long after a good surface was determined so that the final surface would play the role of a limit. Before transferring the electrode to a solution or between solutions the disk was washed with high purity water and then it was covered with a layer of high purity water or with a layer of formic acid solution. A polytetrafluoroethylene cap was placed loosely over the disk in such a way it did not touch the liquid layer on the electrode surface.

After polishing, the electrode was transferred to an electrochemical cell that contained a solution of 0.50 M perchloric acid. The potential was cycled until a cyclic voltammogram corresponding to a clean surface was obtained, like the one in Figure 1(a) in ref 19. After each experiment, in which one cyclic voltammogram for a formic acid solution was measured, the electrode was washed and polished. The surface was always checked by measuring the cyclic voltammogram for a 0.50 M perchloric acid solution. If the shape and amplitude did not match the original cyclic voltammogram, the electrode was polished again. Matching the shape and amplitude ensures that the real area of the electrode surface is maintained with an error directly related to the width of the measured curve. It is of interest to refer to the cyclic voltammogram in Figure 1(b) of ref 19 that was measured for a solution containing 0.49 M perchloric acid and 0.01 M fluoroboric acid. The idea was to examine whether any effects of the relatively small amount of fluoroborate anions could be detected. No effects were detected but the results, Figures 1(a) and (b) in ref 19, demonstrate the reproducibility of the surface.

Cyclic voltammetry was applied to the oxidation of formic acid. The potential was cycled with a scan rate of 100 mV/s until a limiting cyclic voltammogram was achieved; i.e., the same current−potential curve is retraced on each subsequent potential cycle. Limiting cyclic voltammograms have been used to compare electrochemical phenomena by other groups[16] and in experiments involving instabilities (stable limiting voltammograms are not obtained at the points of instabilities).[27,28] There were no instabilities observed within the range of conditions examined here and once a limiting cyclic voltammogram was achieved, there was no measurable drift due to "poison formation." For a limiting cyclic voltammogram, the amount of poison (surface bonded CO) formed during the cycle equals the amount that is removed through reaction. Limiting cyclic voltammograms are easy to identify after a sufficient length of time: For a formic acid solution containing only one electrolyte,
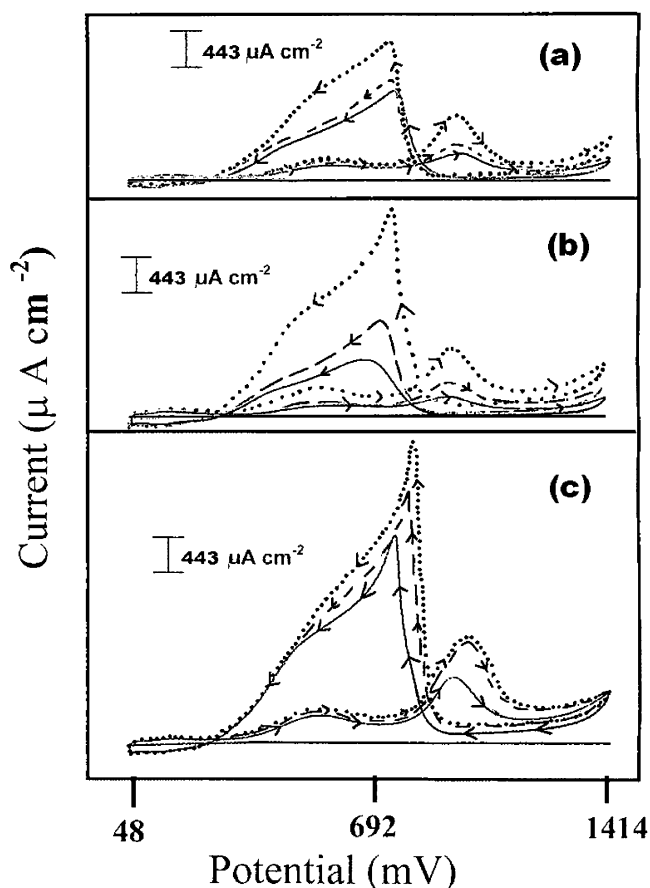

Figure 1. Cyclic voltammograms measured during the oxidation of 0.10 M formic acid in various supporting electrolytes. Current is plotted against potential (RHE). Scan rate = 100 mV/s. Temperature = 0.0 $\pm$ 0.2 °C. The horizontal "base" line corresponds to zero current. (**a**) Dashed curve: 0.500 M HClO$_4$. Solid curve: 0.500 M H$_2$SO$_4$. Dotted curve: 0.494 M HClO$_4$, 0.006M H$_2$SO$_4$. (**b**) Dashed curve: 0.500 M HClO$_4$. Solid curve: 0.500 M HBF$_4$. Dotted curve: 0.490 M HClO$_4$, 0.010 M HBF$_4$. (**c**) Solid curve: 0.490 M HClO$_4$, 0.010 M HBF$_4$. Dotted curve: 0.486 M HClO$_4$, 0.004 M H$_2$SO$_4$, 0.010 M HBF$_4$. Dashed curve: 0.488 M HClO$_4$, 0.006 M H$_2$SO$_4$, 0.006 M HBF$_4$.

a limiting cyclic voltammogram was achieved after about 60 potential cycles. It usually took longer to obtain a limiting voltammogram for solutions containing a small amount of a second electrolyte, about 80 cycles. Limiting voltammograms were monitored after they were stabilized and measured. They were found to remain stable for at least an additional hour.

All experimental solutions contained 0.10 M formic acid. Different solutions contained different amounts and different kinds of inorganic acids: only sulfuric acid, only perchloric acid, perchloric acid and small amounts of sulfuric acid, only fluoroboric acid, perchloric acid and small amounts of fluoroboric acid, and perchloric acid and small amounts of both sulfuric acid and fluoroboric acid. In most applications of cyclic voltammetry to the 0.10 M formic acid solutions, the inorganic acid mixtures were used in the order that they are listed. Experiments were repeated three times, and each time the inorganic mixtures were used in the stated order. The electrode surface was polished after measuring each limiting cyclic voltammogram. Standard deviations calculated from the measured data (presented in the next section) are consistent with good reproducibility for a disk electrode. According to the theory (also presented later) the results should be reproduced, at least qualitatively, with any noble metal electrode.

All other aspects of the experiments are published in detail elsewhere.[18,19] Every facet of the experimental details imple-

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mented in the experiments on formic acid oxidation are the same as those reported in ref 19 except that here the system was held at a temperature of 0.0 ± 0.2 °C. All reported potential values are with respect to the reversible hydrogen electrode (RHE).

Experimental Results on the Oxidation of Formic Acid. In this section, results from experiments on the electrochemical oxidation of formic acid are presented. Limiting cyclic voltammograms (CVs), measured during the oxidation of a 0.10 M formic acid solution, are displayed in Figure 1. The solid CV in Figure 1(a) was obtained using a supporting electrolyte consisting of 0.5 M H_2SO_4. The conditions are such that two peaks occur during the forward scan. The first peak corresponds to the oxidation of formic acid to carbon dioxide through a reaction path that has intermediates with relatively short lifetimes.[13] Another reaction path has the intermediate surface-bonded CO in it.[13] Surface CO blocks the other reaction path and causes the current to decrease in the first peak. The second peak occurs because of the onset of a relatively rapid oxidation of surface CO.

The dashed curve in Figure 1(a), which exhibits values of the current larger than those of the solid curve, was measured in an experiment using a supporting electrolyte consisting of 0.50 M $HClO_4$. Comparing the solid and dashed curves reveals the well-known result[4] that H_2SO_4 inhibits electrochemical processes more than $HClO_4$ does. Because of this latter result, the result represented by the dotted CV in Figure 1(a) is surprising. The dotted CV was measured using a solution containing 0.494 M $HClO_4$ and 0.006 M H_2SO_4. The dotted CV reveals that replacing a small fraction of the 0.5 M $HClO_4$ supporting electrolyte with the more inhibiting H_2SO_4 causes a substantial increase in the current. The current is increased above all peaks and over most of the potential range.

Results analogous to those in Figure 1(a) are depicted in Figure 1(b). The solid CV in Figure 1(b) was measured in an experiment in which the supporting electrolyte consisted of 0.5 M HBF_4. The dashed CV, which exhibits a current larger than that of the solid CV, again corresponds to a supporting electrolyte consisting of 0.50 M $HClO_4$. The dotted CV in Figure 1(b) was measured in an experiment in which the supporting electrolyte consisted of 0.49 M $HClO_4$ and 0.01 M HBF_4. Although HBF_4 is the more inhibiting electrolyte, the result revealed by the dotted CV shows that replacing 0.01 M $HClO_4$ with HBF_4 leads to a substantially enhanced current.

Some insight into the mechanism that causes the increase in current is seen by comparing the solid curve in Figure 1(a) (the supporting electrolyte consists of only sulfuric acid) with the solid curve in Figure 1(b) (the supporting electrolyte consists of only HBF_4). The comparison reveals that HBF_4 inhibits formic acid oxidation more than sulfuric acid does. However, replacing small amounts of perchloric acid with HBF_4 leads to increases in the current that are larger than any obtained by replacing any amount of perchloric acid with sulfuric acid.

The largest increase in current achieved by replacing a fraction of $HClO_4$ with another inorganic acid was obtained for $[HBF_4] = 10$ mM. The CV for this case is reproduced in Figure 1(c) (solid CV). Taking this solution and replacing another fraction of $HClO_4$ with H_2SO_4 can cause even greater increases in the current. An example is represented by the dotted curve in Figure 1(c), which was obtained using a supporting electrolyte consisting of 0.486 M $HClO_4$, 0.004 M H_2SO_4, and 0.010 M HBF_4. Using other mixtures of the three acids as the supporting electrolyte leads to current responses that are larger than the largest current achieved using a mixture of two acids. Another example is the dashed CV in Figure 1(c) for which the
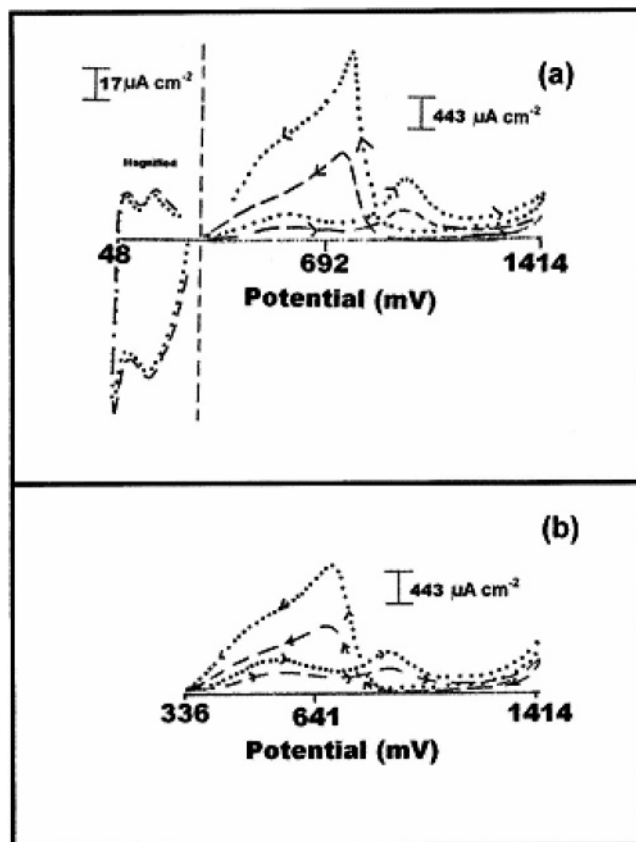

Figure 2. (**a**) Magnification of the hydrogen region. Cyclic voltammograms in Figure 1(b) [(0.500 M $HClO_4$) and (0.490 M $HClO_4$, 0.010 M HBF_4) measured while enlarging the low potential region. Dashed curve: 0.500 M $HClO_4$. Doted curve: 0.490 M $HClO_4$, 0.010 M HBF_4. (**b**) Cyclic voltammograms measured under the same conditions as in (a) except the lower potential limit is raised to a value that is just outside the hydrogen region. Dashed curve: 0.500 M $HClO_4$. Dotted curve: 0.490 M $HClO_4$, 0.010 M HBF_4.

supporting electrolyte consisted of 0.488 M $HClO_4$, 0.006 M H_2SO_4, and 0.006 M HBF_4.

The low potential part of the cyclic voltammograms extends into the hydrogen region. In Figure 2(a), results are presented that were obtained by repeating the experiments that provided the results in Figure 1(b). When measuring the cyclic voltammograms in Figure 2(a), the analogue signal was magnified by slowly decreasing the value of the current converter as the hydrogen region was approached. The part of Figure 2(a) that is magnified clearly shows reduction and oxidation reactions for the solution in which the supporting electrolyte contains only 0.5 M perchloric acid (dashed curve) and for the solution containing 0.49 M perchloric acid and 0.01 M fluoroboric acid (dotted curve). Although the analyses of the experimental results are deferred to the Conclusion section, it is worthwhile to point out here that peak currents and peak potentials are all affected by potential limits. However, they do not affect the main effect discussed in this paper: the increase in current caused by replacing a small amount of the original electrolyte with a second more inhibiting electrolyte. In Figure 2(b), cyclic voltammograms are recorded for the case in which the value of the lower potential limit is outside the hydrogen region. The solution with 0.49 M perchloric acid and 0.01 M fluoroboric acid still exhibits a current greater than that exhibited by the solution in which the supporting electrolyte consists of only 0.50 M perchloric acid.

In Figure 3(a), the solid rectangles represent peak currents (second peak in forward direction) plotted against $[HBF_4]$ for
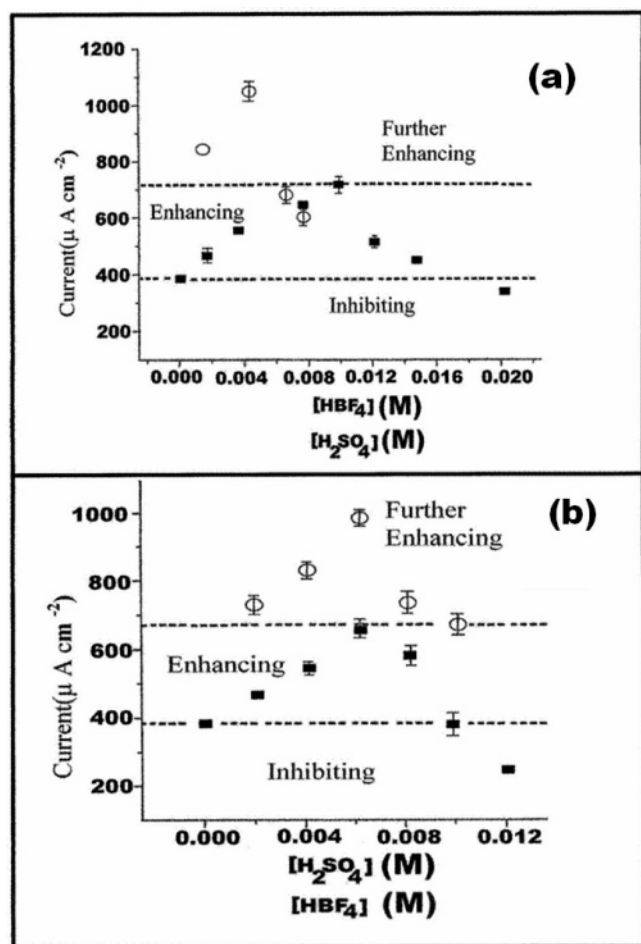
Figure 3. Peak current (second peak in forward direction) is plotted against the amount of perchloric acid replaced by a more inhibiting acid. The vertical bars = ± 1 standard deviation. (**a**) Solid rectangles: Peak current is plotted against [HBF$_4$]. [HClO$_4$] = 0.5 M − [HBF$_4$]. Open circles: Peak current is plotted against [H$_2$SO$_4$]. [HBF$_4$] = 0.010M, [HClO$_4$] = 0.49 M − [H$_2$SO$_4$]. (**b**) Solid rectangles: Peak current is plotted against [H$_2$SO$_4$]. [HClO$_4$] = 0.5 M − [H$_2$SO$_4$]. Open circles: Peak current is plotted against [HBF$_4$]. [H$_2$SO$_4$] = 0.006 M, [HClO$_4$] = 0.494 M − [HBF$_4$].

solutions in which the latter acid replaced small amounts of HClO$_4$. The largest current peak in this plot occurs at [HBF$_4$] = 0.01 M. Conditions under which the largest increases in current are achieved by using mixtures of three acids are revealed to a greater extent in Figure 3. The open circles in Figure 3(a) represent peak currents plotted against [H$_2$SO$_4$] for a system in which the amount of the latter acid was varied and the amount of HBF$_4$ was fixed, [HBF$_4$] = 0.01 M, [HClO$_4$] = 0.49 − [H$_2$SO$_4$]. The plot reveals larger peak currents are achieved in the mixtures of three inorganic acids at small concentrations of H$_2$SO$_4$. The region marked "enhancing" in Figure 3 is a region in which the current is larger than that obtained when the electrolyte consisted only of 0.50 M HClO$_4$. The region marked "further enhancing" contains current values that are larger than the largest current value obtained using an electrolyte consisting of a mixture of HClO$_4$ and one other acid. The vertical bars on the data points in Figure 3 represent ± one standard deviation. Each one was calculated from three separate experiments.

In Figure 3(b), the solid rectangles are peak currents plotted against [H$_2$SO$_4$] for the case in which the latter acid replaced small amounts of HClO$_4$. The largest peak current occurs at [H$_2$SO$_4$] = 6.0 mM. This value was maintained in solutions containing a supporting electrolyte consisting of a mixture of
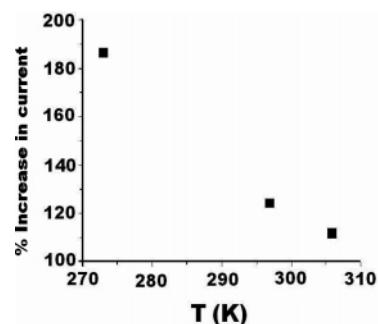

Figure 4. "Percent increase" in peak current (second peak in forward direction; percent increase is defined here as 100 times the larger peak current divided by the smaller peak current.) is plotted against temperature. [HCOOH] = 0.10 M. The larger peak current was obtained by using the solution containing 0.490 M HClO$_4$ and 0.010 M HBF$_4$. The smaller peak current was measured using a solution in which the supporting electrolyte contained only 0.500 M HClO$_4$.

the three acids. The peak currents measured in experiments using the latter solutions are plotted as a function of the amount of HBF$_4$ that replaced HClO$_4$, open circles. The results show that replacing a fraction of HClO$_4$ with a second acid can produce further enhancements in the current.

In Figure 4, the percent increase in the peak current (second peak in forward direction) that is obtained by changing the supporting electrolyte from 0.50 M perchloric acid to one that contains 0.49 M perchloric acid and 0.01 M fluoroboric acid is plotted as a function of temperature. For the system containing these two anions, the measured maximum current increase at the three temperatures occurred at this concentration of fluoroboric acid, 0.01 M, (See increments used in Figure 3.). It is seen that the increase in current decreases with temperature.

Theoretical Results

A theoretical analysis on the effects of anion adsorption on an electrochemical reaction is now presented. The reaction process consists of the electrochemical adsorption of a molecule followed by the reaction of the adsorbed molecule:

$$x + Pt \xrightarrow{k_a} Ptx_{ads} \xrightarrow{k_b} Pt + y + e^- \tag{1}$$
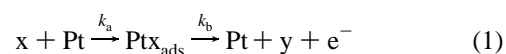
where Pt represents a vacant site. The rate of change with respect to time of the surface concentration of x, θ_x, obeys the following differential equation:

$$d(\theta_x)/dt = k_a S - k_b \theta_x \tag{2}$$

In eq 2, S is the concentration of vacant sites. All surface concentrations are scaled to range from 0 to 1. The primary anion in solution is called A$_1^-$. Situations will be considered in which a fraction, f_2, of A$_1^-$ is replaced with the anion A$_2^-$, and in which an additional fraction, f_3, of A$_1^-$ is replaced by the anion A$_3^-$. When three kinds of anions are in solutions the density of vacant sites is usually represented by

$$S = 1 - \theta_x - \theta_1 - \theta_2 - \theta_3 \tag{3}$$

where the θ_i's (numerical subscripts) are the anion surface concentrations. The equation of motion for each anion surface concentration is written as

$$d(\theta_i)/dt = k_i f_i cS - k_{-i} \theta_i \tag{4}$$

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where, $i = (1, 2, 3)$, c is the concentration of A_1^- in the bulk solution when it is the only anion present, and $f_1 = 1 - f_2 - f_3$.

The steady-state expression for θ_x can be obtained by setting both sides of eqs 2 and 4 equal to 0 and solving the resultant algebraic equations. Using the steady-state expression for θ_x and considering one kind of anion in solution ($f_1 = 1$), the steady-state current density can be expressed as

$$j_1 = Q_o k_b \theta_x = Q_o k_b K/(1 + K + K_1) \qquad (5)$$

In eq 5, Q_o represents the magnitude of charge transferred on depositing a monolayer of hydrogen atoms, $K = k_a/k_b$, and in general, $K_i = ck_i/k_{-i}$ [$i = 1$ in eq 5], which here is called the adsorption coefficient of the anion A_i. The current density, eq 5, decreases as K_1 increases which implies anion adsorption inhibits the reaction. If three kinds of anions are present in solution then the denominator in eq 5 is replaced by

$$\sigma = 1 + K + f_1 K_1 + f_2 K_2 + f_3 K_3 \qquad (6)$$

The anion A_3^- is more inhibiting than A_2^- which, in turn, is more inhibiting than A_1^-, i.e., $K_3 > K_2 > K_1$. For both the case $f_3 = 0$ and the case f_3 not equal to 0, the denominator represented by eq 6 is greater than the denominator in eq 5. Hence, in the description given so far, replacing A_1^- with more inhibiting anions causes the current to decrease.

Besides the large amount of electron density between a surface anion and atoms of the electrode surface, electron density exists around the remainder of the anion. This latter part of the electron density can cause repulsive interactions between unlike surface anions that are in addition to the interactions contained in the description given by eq 3.

It is now shown how the additional interactions between unlike surface anions can enhance the current when a fraction of the original anion A_1^- is replaced by more inhibiting anions. Additional interactions between unlike surface anions are accounted for by interaction parameters, α_{ij}. Insertion of the interaction parameters transforms eq 4 to the following equations of motion for the anion surface concentrations:

$$d(\theta_1)/dt = k_1 f_1 c[1 - \theta_x - \theta_1 - (1 + \alpha_{12})\theta_2 - (1 + \alpha_{13})\theta_3] - k_{-1}\theta_1 \qquad (7)$$

$$d(\theta_2)/dt = k_2 f_2 c[1 - \theta_x - (1 + \alpha_{12})\theta_1 - \theta_2 - (1 + \alpha_{23})\theta_3] - k_{-2}\theta_2 \qquad (8)$$

$$d(\theta_3)/dt = k_3 f_3 c[1 - \theta_x - (1 + \alpha_{13})\theta_1 - (1 + \alpha_{23})\theta_2 - \theta_3] - k_{-3}\theta_3 \qquad (9)$$

The interactions between surface anions and the electroactive species remain the same as that described above, i.e., S in eq 2 is given by eq 3.

For the description that includes interaction parameters, the steady-state current density can be deduced as before except that eqs 7 to 9 are used instead of eq 4. The expression for the current density is complex. It is convenient to define large terms in the expression before presenting it. Although only terms first order in the interaction parameters exist in eqs 7–9, higher order terms appear in the current density because of coupling between species. Two sums that appear in the current density that contain terms second and third order in the interaction parameters are given by

$$B = f_1 f_2 \alpha_{12}^2 K_1 K_2 + f_1 f_3 \alpha_{13}^2 K_1 K_3 + f_2 f_3 \alpha_{23}^2 K_2 K_3 - 2f_1 f_2 f_3 \alpha_{12}\alpha_{13}\alpha_{23} K_1 K_2 K_3 \qquad (10)$$

and

$$C = -f_1 f_2 f_3[(\alpha_{12} - \alpha_{13})^2 + \alpha_{23}(-2\alpha_{12} - 2\alpha_{13} + \alpha_{23})]K_1 K_2 K_3 \qquad (11)$$

A sum also appears containing first-order terms:

$$D = f_1 f_2 \alpha_{12} K_1 K_2 + f_1 f_3 \alpha_{13} K_1 K_3 + \alpha_{23} f_2 f_3 K_2 K_3 \qquad (12)$$

With the definitions in eqs 5 and 6, and in eqs 10–12, the current density can be written as

$$j = Q_o k_b K(1 - B)/[\sigma - 2D - (1 + K)B - C] \qquad (13)$$

For the case of three kinds of anions, expressions deduced from eq 13 that illustrate the role the interaction parameters play in enhancing the current are long and involved. Only numerical results are presented in the case of three kinds of anions. An expression revealing information about the interactions, which is analogous to the one in ref 19, is provided for the case of only two kinds of anions. Numerical results are also presented for situations involving the system with two kinds of anions.

All remaining analyses are conducted on differences in current densities. Equation 13 is used for all analytical and numerical calculations of current densities. First an analysis is conducted on the difference in current densities Δj_1 defined by

$$\Delta j_1 = j_{12} - j_1 \qquad (14)$$

where j_{12} is the current density given by eq 13 with $f_3 = 0$ (two different kinds of anions, A_1^- and A_2^-, in solution), and j_1 is the current density given by eq 13 with $f_2 = f_3 = 0$, (one kind of anion, A_1^-, in solution). The latter current density is equal to the current density given by eq 5. If eq 14 is positive, it means that replacing a fraction of the anion A_1^- with the more inhibiting anion A_2^- causes an increase in the current response. This possibility is examined in the limit of very small f_2. Expanding eq 14 in powers of f_2, it is found that the zero order term vanishes. To first order in f_2 the difference in current densities is given by

$$\Delta j_1 = -f_2 j_1 \alpha_{12}^2 K_1 K_2 + f_2 j_1\{\alpha_{12}K_1 K_2[2 + \alpha_{12}(1 + K)] - (K_2 - K_1)\}/(1 + K + K_1) + O(f_2^2) \qquad (15)$$

In eq 15, j_1 is given by eq 5. By specifying that eq 15 must be greater than 0, a criterion for an enhanced current is obtained that is satisfied by the interaction parameter α_{12}:

$$(K_2^{1/2} - K_1^{1/2})/(K_2^{1/2}K_1) < \alpha_{12} < (K_2^{1/2} + K_1^{1/2})/(K_2^{1/2}K_1) \qquad (16)$$

Equation 16 is a sufficient condition for the achievement of an enhanced current. An increased current is obtained if α_{12} obeys these inequalities.

Limiting forms of eq 16 reveal relations between inhibition and enhancement of the reaction by A_2^-. In the limit that $K_2 \rightarrow \infty$ (the direction of increasing inhibition), the term on the left side of eq 16 becomes equal to the term on right side; i.e., the interval of values for the interaction parameter α_{12} for which an enhanced current can be achieved goes to zero. It is also seen from eq 16 that the minimal value of α_{12} required to achieve an increased current becomes smaller and approaches
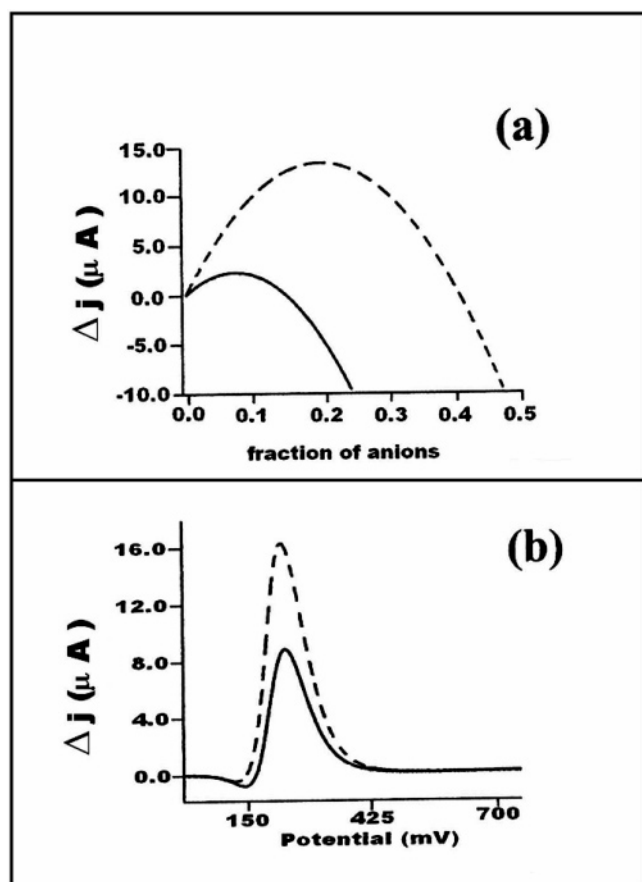
Figure 5. (**a**) Dashed curve corresponds to the difference in current density Δj_1 (the current for a system containing the anions, A_1^- and A_2^-, minus the current for a system that contains only the anion A_1^-) plotted as a function of f_2 (the fraction of A_2^-). Solid curve corresponds to the difference in current density Δj_2 (The current density for a system containing A_1^-, A_2^-, and A_3^-, minus the current density for a system containing A_1^- and A_2^-.) plotted as a function of f_3. Parameters for eq 13: $Q_o = 210\ \mu C$, $k_b = 46$ s^{-1}, $K = 23/14$, $K_1 = 0.95$, $K_2 = 1.15$, $\alpha_{12} = 0.17$, $K_3 = 1.25$, $\alpha_{13} = 0.21$, $\alpha_{23} = 0.17$. (**b**) Dashed curve corresponds to the difference in current density Δj_1 plotted as a function of potential. For the system containing two kinds of anions, $f_2 = 0.1$. Solid curve corresponds to the difference in current density Δj_2 plotted as a function of potential. For the system containing two kinds of anions $f_2 = 0.10$. For the system containing three kinds of anions the fractions are, $f_1 = 0.88$, $f_2 = 0.10$, $f_3 = 0.02$. Other parameters and functions for eq 13: $k_b = 10\ \exp[a\ (v - ub)]$, $a = 0.0213$ (mV)$^{-1}$, $ub = 240$ mV, $K = 52/k_b$. $K_1 = \exp[2a\ (v - u1)]/2$, $u1 = 230$ mV, $K_2 = \exp[2a\ (v - u2)]/2$, $u2 = 220$ mV, $\alpha_{12} = 1/(1 + 2\ K_2)$. $K_3 = \exp[2a\ (v - u3)]/2$, $u3 = 205$ mV. $\alpha_{13} = 1/(1 + K_3/2)$, $\alpha_{23} = 1/[1 + (K_2 + K_3)/4]$.

zero as the value of K_2 approaches the value of K_1. As K_2 approaches the value of K_1, the inhibiting strength of A_2^- approaches the inhibiting strength of A_1^-. When the inhibition strengths are equal, any arbitrarily small value for α_{12} will enhance the current.

That an increase in current can be achieved by replacing a fraction of the anion A_1^- with A_2^- is also supported by numerical solutions. The dashed curve in Figure 5 (a) is a plot of the difference in current densities, $\Delta j_1 = j_{12} - j_1$, vs f_2. The parameter values used in calculating the plot are given in the figure caption. All positive values of Δj_1 in Figure 5(a) correspond to the amount that the current increases.

To see effects of replacing additional amounts of the original anion A_1^- with a third anion A_3^- that is more inhibiting than A_2^-, another difference in current densities, Δj_2, is considered. It is expressed as

$$\Delta j_2 = j_{12\ 3} - j_{12} \tag{17}$$

where $j_{12\ 3}$ is the current density as defined by eq 13 for the case in which three kinds of anions, A_1^-, A_2^-, and A_3^- are present in solution, and j_{12} is the current density for the case in which only two different kinds of anions, A_1^- and A_2^-, are in solution. The fraction, f_2, is held fixed at the value 0.1 in both j_{123} and j_{12}. The difference in current density Δj_2 is plotted in Figure 5(a) as a function of f_3, the solid curve. Positive values of Δj_2 correspond to increases in current realized when a fraction, f_3, of A_1^- is replaced by A_3^-.

The results in Figure 5(a) are for a fixed value of the potential. They may be misleading. The interaction parameter is not a constant. The interaction parameter is a function of potential. A heuristic formulation for the potential dependence of the interaction parameter is provided. The rate of change of the interaction parameter with respect to time is assumed to contain a growth term, which, for a fixed value of the interaction parameter increases with respect to a decreasing potential. A second term represents the rate at which the interaction decreases which, for a fixed value of the interaction parameter, increases with respect to the potential. The maximum size of the interactions is restricted to be less than one. The stated temporal variation has a one-to-one correspondence with the differential equation describing the cathodic adsorption of a molecule and its anodic desorption. The steady-state solution for the interaction parameter is

$$\alpha_{12} = 1/(1 + 2K_2) \tag{18}$$

where the ratio of the rate coefficient for shrinkage to the rate coefficient for growth is set proportional to K_2. According to eq 18, as the potential grows larger, the interaction between unlike surface anions approaches the smallest magnitude, and also, the anion's interaction with the electrode approaches its greatest value. The potential dependence of the other interaction parameters is of a similar form.

In Figure 5(b), the difference in current densities, Δj_1, is plotted as a function of potential, dashed curve. Recall that the difference is equal to the current density for a system with two kinds of anions, j_{12}, minus the current density for a system containing only one kind of anion, j_1. The fractions of the anions A_1^- and A_2^- are fixed at $f_1 = 0.9$, $f_2 = 0.1$, respectively, in the current density j_{12}. The parameter values and the form of all potential dependent functions are given in the caption of Figure 5(b). The plot reveals a relatively sharp peak representing a large increase in the rate of reaction for a short potential range.

To see the effects of introducing the most inhibiting anion A_3^- into the system, the difference in current densities, Δj_2, is plotted as a function of potential in Figure 5(b), solid curve. The difference is equal to the current density for a system with three kinds of anions, j_{123}, minus the current density for a system with two kinds of anions, j_{12}. Positive values for Δj_2 correspond to increases in the current. The values for the fractions of A_1^-, A_2^-, and A_3^- in j_{123} sequentially by $f_1 = 0.88$, $f_2 = 0.10$, and $f_3 = 0.02$. The values for the fractions of A_1^- and A_2^- in j_{12} are $f_1 = 0.9$ and $f_2 = 0.1$, respectively. The increases in current represented by the solid curve are significant especially in view of the large increase in current already achieved by replacing a fraction of A_1^- with A_2^- (the dashed curve).

The model considered was simplified so that the cause of the increase in current could be isolated. However, the results for a constant potential value are identical to those that would be obtained using a model describing a reaction process that includes the formation of more than one surface intermediate,

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the existence of more than one reaction path, and production of side products. The oxidation of formic acid and the oxidation of methanol have mechanisms that contain these components. The results for the simple model will be shown to be equivalent to the results obtained using the model for methanol oxidation in ref 19. To demonstrate the equivalence, ref 19 must be consulted.

To show that the expression for the current density for methanol oxidation (only one anion present) in ref 19 [eqs 30–32 in ref 19] is the same as the expression in eq 5 (for a constant potential value), the symbols in ref 19 are changed as follows:

$$BK(1 - r_b) \rightarrow Q_o k_b K, \text{ (in the numerator only)} \quad (19)$$

$$K(1 + r_a) \rightarrow K, \text{ (in the denominator)} \quad (20)$$

$$K_a c_{ab} \rightarrow K_1 \quad (21)$$

The notation from the expression for the current density in ref 19 is on the left-hand side. Making these transformations, eq 19 to eq 21, causes the expression for the current density in ref 19 to be exactly the same as that in eq 5. The equations here and those in ref 19 for the more complicated expressions for current density can also be shown to be equivalent by applying eq 20 and transformations analogous to eq 21 for other anion adsorption coefficients.

That the model represented by eqs 2, 3, 7, 8, and 9 produces identical expressions for the current density as that obtained using a more detailed complex models is more than a mathematical quirk. It implies that the model presented here has the fundamental ingredients for the understanding of how replacing a fraction of the original anion in solution with more inhibiting ones can increase the current. The interaction between unlike anions creates reaction sites. In ref 19, it is discussed why a whole class of mechanisms leads to the results in eq 5 and eq 13 (the two-anion case). Exceptions are noted.

Conclusions

The current response exhibited by the electrochemical oxidation of formic acid can be increased substantially by replacing a small amount of the supporting electrolyte, perchloric acid, with either sulfuric acid or tetrafluoroboric acid. The largest current response is exhibited when a mixture of sulfuric acid and tetrafluoroboric acid replaces a small fraction of perchloric acid.

The design of the experiments and the results make it highly unlikely that the enhanced rate of formic acid oxidation is caused by changes in the reaction mechanism or any chemical change. Upon replacing some perchloric acid with tetrafluoroboric acid, ClO_4^- is joined by BF_4^- in the set of surface anions. Both ClO_4^- and BF_4^- have similar properties. Both anions are extremely weak bases and both possess symmetric electronic distributions. Both were used in catalyses because they are considered weakly binding and allow relatively easy access for the reactant to the catalyst.[29] It is highly doubtful that these two anions partake in an elementary reaction during formic acid oxidation.[16]

Replacing a fraction of perchloric acid by sulfuric acid also increased the current response. Surface HSO_4^- (a weak acid) and surface SO_4^{-2} (a weak base) are introduced as new species. These anions have properties different from those of ClO_4^- and BF_4^-. This makes it improbable that replacement of perchloric acid by sulfuric acid could induce the same qualitative change in behavior as that induced by tetrafluoroboric acid unless the

changes are caused by a phenomenon that is independent of chemical change.

The results of using mixtures of three acids as the supporting electrolyte diminish the idea that chemical change is a candidate for the reason behind an increase in the current response. Some of the responses in the current obtained using the mixtures were larger than any achieved when the supporting electrolyte consisted of two inorganic acids. Additional reactions would have to be proposed to account for the further increase in current for the cases involving mixtures of the three acids.

Changes in locations (potential values) of peak currents might indicate the introduction of a new chemical process. The second peak in the forward direction undergoes a distinct shift to a higher potential in the case of three acids, Figure 1(c). However, this shift is consistent with previously observed changes in peaks at which surface CO reacts. Increases in the current, which are not induced by changes in the chemistry, can shift the peak to higher potentials. Increasing the current by increasing the concentration of the reactant can shift the peak to higher potential values. Such potential shifts are discussed in ref 19; other references are also cited. At potential values where the peak current occurs for other mixtures, the current is larger in the voltammograms for the mixtures containing three inorganic acids; see Figure 1(c). This is consistent with the idea that the same reactions occur. Due to an increased rate of production of surface CO, more CO reacts for a longer time. Current-producing reactions lasting a longer time will persist to larger potentials. Data that supports these ideas is now given. The current peak (*ip*) (second peak in forward direction) in the voltammogram for the solution in which the supporting electrolyte consisted of only 0.50 M perchloric acid is equal to 380 $\mu A/cm^2$. The corresponding value of the peak potential (*pp*) is 966 mV. The largest second peak in Figure 1(c), which is for a solution in which three inorganic acids were mixed, has the values $ip = 988$ $\mu A/cm^2$ and $pp = 1017$ mV. A shift can also be achieved in the solution containing only 0.50 M perchloric acid as the supporting electrolyte by increasing the concentration of formic acid from 0.10 M to 0.13M. For this latter solution the values associated with the second peak are $ip = 610$ $\mu A/cm^2$ and $pp = 1006$ mV.

The experimental results displayed in Figure 3 provide evidence that chemical changes induced by the (hydrogen) sulfate anion or BF_4^- are not responsible for enhancing the current. These results show that the rate of formic acid oxidation increased and then decreased in a range involving only small amounts of sulfuric acid and tetrafluoroboric acid. If a very small concentration of an anion causes a chemical change, then increasing the concentration of the anion is expected to increases the effect or cause a saturation point to be reached.

The observation that current increases, which are caused by replacing a fraction of the original anions with more inhibiting ones, occur over most of the potential range, Figure 1, with noticeable increases at each peak, is consistent with the idea that the source of the increases is not a localized chemical reaction. Otherwise, an increase at just one peak would be observed. It is noted that an increase does not occur in the hydrogen region (Figure 2).

The results that reveal that the increase in reactivity, which is induced by replacing a fraction of the original electrolyte with a more inhibiting one, deceases with increasing temperature, Figure 4, suggests that the mechanism for the increase may not include an activation barrier. This, in turn, would not only make chemical reactions unlikely candidates for the increase in

reactivity, but kinetic processes in general. The cause of the increases may be static forces.

Previously published data supports the claim surface rearrangement does not cause the enhancement of the current displayed by the oxidation of formic acid. One study found that anions caused no measurable distortions to the surface of single crystals.[30] Changes in reactivity caused by surface rearrangement would be sensitive to the potential range in cyclic voltammograms. In previous work an enhanced rate was achieved for the oxidation of formic acid at Pd using both an upper potential limit located well into the oxide region and an upper limit at a value close to where the oxide region begins.[18] Finally, for a Pt electrode, the measured CV for a solution containing only 0.50 perchloric acid, and the CV for a solution containing 0.49 M perchloric acid and 10 mM tetrafluoroboric acid look identical.[19]

When the supporting electrolyte consists of only tetrafluoroboric acid, formic acid oxidation is inhibited more than when the supporting electrolyte consists of only sulfuric acid. See Figure 1. However, the current achieved by replacing a specific fraction of perchloric acid by tetrafluoroboric acid is larger than any current achieved by replacing perchloric acid with sulfuric acid (Figure 3). These results reveal that the mechanism that increases the rate of reaction is independent of adsorption strength.

The simplest approach for deducing the cause of the enhanced rate of formic acid oxidation is to examine the differences in the systems in which the enhanced current occurs. The main difference in the systems for which an enhanced current occurs is that a mixture of acids is contained in the electrolyte. The mixture of acids causes a different composition of surface anions to exist: a relatively large surface concentration of ClO_4^-, and small surface concentrations of BF_4^-, and/or HSO_4^- and SO_4^-. Varying the "concentrations" of the acids varies the concentrations and composition of surface anions, which are responsible for the variations in the current.

The electron density between an adsorbed anion and the atoms of the electrode surface is substantial, but electron density also surrounds the "nonbinding" part of the surface anion. Electron densities can interact among surface species. Interactions of neighboring electron densities should inhibit or enhance reactivity by affecting the amount of space available for reactive sites and the possible routes to the sites. It is reasonable to believe that the anions introduced have repulsive interactions on the surface with the original anions. These interactions are stronger than the interactions between the original surface anions. This causes an increase in reaction sites and the observed increase in current.

A mathematical description was presented of an electrochemical reaction involving a surface intermediate and coupling to anion adsorption. The current density was calculated for the case of only one kind of anion in solution. The result shows that anion adsorption inhibits the reaction. Another calculation revealed that replacing a fraction of the original anions with anions that are more inhibiting further decreases the current density if all the interactions between surface anions are treated the same. In additional calculations, the effects of the extra interactions between unlike surface anions were considered. Several situations were considered. The results show that these interactions caused a greater rate of formic acid oxidation, if the strength of the interactions between unlike surface anions is greater than a threshold, which, in turn, is greater than the strength of interactions between like surface anions.

Summary

The current response exhibited by the electrochemical oxidation of formic acid is increased substantially when a fraction of the supporting electrolyte, perchloric acid, is replaced with either sulfuric acid or tetrafluoroboric acid. These results are somewhat surprising because when the supporting electrolyte consists of only either sulfuric acid or tetrafluoroboric acid the current is less than that achieved when only perchloric acid is the supporting electrolyte. Even larger increases are obtained if a fraction of perchloric acid is replaced with mixtures of sulfuric acid and tetrafluoroboric acid.

The idea of chemical reactions being responsible for the enhanced current is inconsistent with many experimental results and theoretical arguments. Also, the increases in current are independent of "anion adsorption strength." The experimental and theoretical results are consistent with the explanation that interactions between unlike surface anions, which are different from those between like interactions, cause the enhanced current.

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