Determination of Ion Populations and Solvent Content as Functions of Redox State and pH in Polyaniline

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Abstract: The piezoelectric quartz crystal microbalance (QCM) is used to investigate the ion populations and solvent content of thin films of polyaniline (PA) on electrode surfaces as functions of redox state and pH. The data are shown to be consistent with a model for PA in which the initial oxidation at a potential of ca. 0.2 V vs. SCE to give the conductive form of the polymer creates charged sites by oxidation of amine moieties along the polymer chains. Higher potentials cause further (pH dependent) oxidation with cumulative removal of exactly one electron per ring to produce a polymer containing imine groups which can hydrolyze to form quinone and quinone/imine types of structures. The initial oxidation process is accompanied by proton expulsion at low pH values, indicating partial protonation of the PA amine nitrogens in the reduced form with loss of these protons on oxidation. In addition to the proton expulsion, anion insertion also takes place during oxidation under all conditions that were studied. Data from such measurements as a function of pH allow estimation of the pK_a values of the reduced (insulating) and oxidized (conducting) forms of PA, which are given as ca. −0.3 and 3, respectively. Experiments in strong (10 M) acid solutions reveal changes in solvent content during oxidation which are observed to influence the electrochemical response of PA. The ability to measure both electrochemical and gravimetric data simultaneously is shown to greatly constrain possible models for systems such as PA, leading to less ambiguity in their description.

The study of the properties of organic electronic conductors is driven both by considerable curiosity as to the nature of these unusual materials and by the wide variety of possible applications for them. Polyaniline (PA) is a particularly attractive substance from this perspective because it has a high conductivity,[1-3] is easily synthesized,[3-5] has well-behaved electrochemistry,[5] and is stable under ambient conditions.[3] This is in contrast to most other conducting polymers which are often adversely affected by oxygen or impurities.[6] In their conducting states PA and other conducting polymers exhibit phenomena which appear to be related to double layer charging,[7,8] a characteristic of which is the large apparent capacitance seen for potentials at which they are conductors. Ion migration into or out of the polymer film has been assumed to accompany this charging process,[3,4,6-8] and there have been several ex situ measurements of ionic content following charging.[3,9] In situ measurements are obviously preferable because of questions regarding the integrity of the film after removal from solution; however, very few such studies have been made.

We have been investigating how ion and solvent transport processes influence the electrochemical behavior of PA and other polymers using a new technique for making in situ mass measurements of thin films present at electrode surfaces. The technique is based on the quartz crystal microbalance (QCM),[10] a piezoelectric device capable of monolayer mass sensitivity which is widely used by the vacuum community for thin film thickness measurements. In the present method the quartz crystal is sandwiched with two electrodes, one of which is used as the working electrode in an electrochemical cell. These electrodes are used to impose a radio frequency electric field across the crystal at a resonant frequency that is determined by the dimensions and total mass loading of the crystal. A change in the mass of the working electrode causes a change in the resonant frequency of the device, which can be used to determine the quantity of added mass. A great advantage of the QCM when used in conjunction with electrochemistry is that it allows simultaneous, in situ determination of electrode mass and electrochemical parameters. Thus, one can electrochemically induce mass changes of thin films at electrode surfaces (such as might be caused by ion or solvent transport during redox events) and monitor these mass changes concurrently with the electrochemical measurements. Some electrochemical studies using this technique have already appeared in the literature.[11-14] It is particularly worthwhile to study ion transport in thin films on electrodes since this process has previously been identified as a potentially rate limiting step for the propagation of charge through such films.[15-17] However, to date very little has been discovered regarding the identities of the migrating ions and how these relate to charge propagation rates. In this work we report on the in situ, quantitative determination of ion transport in thin films of PA. We also give quantitative information on solvent content of such films. It will be seen that the combination of information provided by the QCM and electrochemical measurements verifies the model for PA redox processes put forth by MacDiarmid and co-workers[18] and allows for further elaboration of some of the more subtle features of PA electrochemistry.

Experimental Section

Reagent grade acids were used as received. Reagent grade aniline was distilled under reduced pressure to give a colorless liquid prior to use. Solutions were made with deionized water from a Millipore purification

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system. One inch diameter, overtone polished, 5 MHz AT-cut quartz crystals were obtained from Valpey-Fisher. These crystals oscillate in the shear mode (i.e., displacement during the oscillation is parallel to the electrode surface). Gold electrodes were evaporated onto these with an Edwards E306A coating system, using either Cr or Si as an adhesion layer. The keyhole electrode design used is similar to that described in ref 19, with the piezoelectrically and electrochemically active areas being 0.28 and 0.34 cm^2, respectively. As noted in previous studies, it is essential to keep one side of the crystal out of the solution to avoid capacitive shunting of the crystal by the solution.[19] Thus, mounting of the crystal was accomplished with a number 9 O-ring joint with PTFE O-rings on both sides. One end of the O-ring joint was blown onto a standard H cell. Locally built electrochemical instrumentation was used along with a Kipp and Zonen XYY′ recorder which allowed simultaneous recording of both current and QCM frequency as functions of applied potential. All potentials are quoted vs. SCE.

The QCM instrument uses a Motorola MC1733 video amplifier-based feedback circuit as the oscillator to drive the crystal near its minimum impedance frequency. The output signal from this circuit was sent to a Philips PM6654 frequency counter equipped with a digital to analog converter which provided the output to the recorder. With this instrumentation the detection limit for frequency changes is 0.3–0.5 Hz. In some cases the entire frequency (or conductance) spectrum of the resonator was obtained with a Hewlett-Packard 4192A impedance analyzer.

Cyclic voltammetry was used as diagnostic tool to assess the quality of the films grown with use of the various conditions. Electrochemical/QCM measurements were made with use of both potential step and potential sweep methods. Solutions were routinely purged of oxygen with a stream of Ar, although this was found to have virtually no effect of the electrochemical response to PA.

Results and Discussion

Use of the QCM in Solution. The Sauerbrey equation[20] can be used to calculate the mass change at the electrode surface from the change in the resonant frequency of the quartz crystal (subject to some assumptions to be discussed below)

$$\Delta f = -f_0^2 m/NA\rho \qquad (1)$$

where Δf is the observed frequency change, f_0 is the fundamental frequency of the crystal (5 MHz), m is the mass change at the electrode surface, N is the frequency constant for quartz (0.167 MHz cm^{-1} for AT crystals), A is the surface area of the deposit, and ρ is the density of quartz (2.648 g/cm^3). The negative sign denotes that the resonant frequency decreases with increasing mass. Using this equation one can calculate a mass sensitivity for a 5-MHz crystal of 56 Hz/μg/cm^2. This mass sensitivity has been previously verified by measuring the deposition of various metals from solutions in which the current efficiency for deposition is 100%.[12,13,19,21] To give a point of reference, a close-packed monolayer of Pb atoms on polycrystalline gold weighs 0.28 μg/cm^2 and gives a frequency change of 15 Hz, in agreement with eq 1.[13] This equation has been found to give an accurate description of the QCM response for cases in which the added mass amounts to less than a few percent of the total mass of the resonator.[22] The essential criterion for application of this equation is that the film behave as a rigid layer, i.e., that the film should be perfectly elastic (with viscosity equal to 0) and thin enough so that the frequency change is negligible with respect to the resonant frequency. In this case the viscoelastic properties of the film do not influence the measurement, giving the so-called rigid layer approximation.[23a] It will be shown below that this is indeed the case for PA films on the QCM.

The resonant frequency of the QCM is known to be influenced by experimental variables other than mass at the surface. Immersion of the surface of the crystal into a solution causes large frequency changes which are caused by viscous loading of the crystal.[23b] When making measurements of relative frequency changes caused by redox processes in a given solution this does not cause problems because the solution contribution gives only a constant offset to the frequency. However, experiments which entail transfer to different solutions require special attention to this source of frequency change. Stress in the deposit and temperature fluctuations can be causes of frequency changes.[19,24,25] The influence of stress has been investigated by several groups.[24,25] When the deposited films are metals, metal oxides, or other solid, high lattice energy materials there can be a pronounced effect of stress on the frequency response to mass changes. However, it has been shown that the integral response across the crystal face is invariant to stress.[24] Also, the stresses in polymer films (especially those electropolymerized in the solution in which they will be examined) are not generally expected to be of sufficient magnitude to influence the frequency response. Temperature affects the crystal by changing the density and viscoelastic properties of the solution and by changing the elastic constants of the quartz. However, we have found that the use of crystals cut to give a near zero temperature coefficient at room temperature obviates the need for temperature control for short-term experiments.

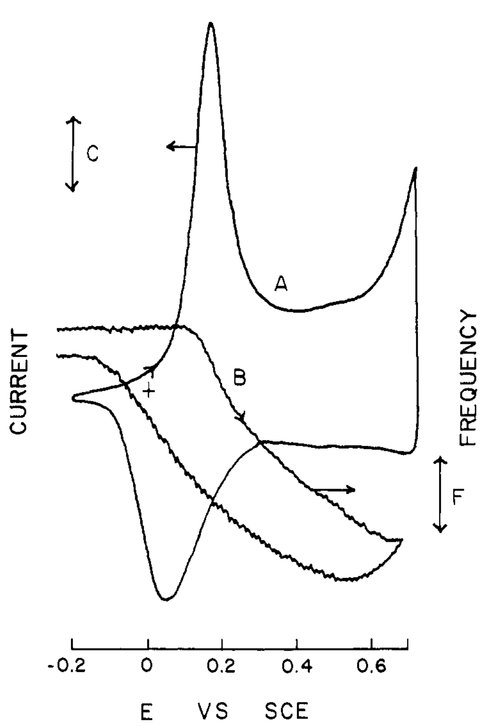

Figure 1. CV/QCM steady state scan from −0.2 to 0.75 V in 0.1 M aniline, 1.0 M H_2SO_4. Scan rate, 100 mV/s. C = 100 μA, F = 20 Hz. (A) Cyclic voltammetric response. (B) QCM frequency response. Curve B is offset 40 mV to the left with respect to curve A.

Film Growth. Several groups have reported on the electrochemical behavior of PA.[1–5,8,26,27] The film may be deposited on the electrode surface by either potentiostatic or galvanostatic oxidation of the aniline monomer in acid solutions at potentials above ca. 0.7 V. The cyclic voltammogram (CV) of PA shows a redox process at about 0.2 V, with a relatively sharp peak for the oxidation and a broad peak for the reduction. These peaks result from the redox process which is responsible for the dramatic change in the conductivity of PA,[1–3] i.e., oxidation produces a conducting film and reduction produces an insulating film. Negative of the redox process one observes a small charging current while positive of it one observes a large charging current, behavior which is consistent with the transition from an insulator

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to a conductor. These features are apparent in curve A of Figure 1 which shows a typical cycle during the growth of the film. The films were routinely electrodeposited by potential cycling from −0.2 to 0.75 V at a scan rate of 200 mV/s in a solution 0.1 M in aniline and 1.0 M in H_2SO_4. The large currents seen at the end of the positive scan result from the superposition of two distinct redox processes. One is the oxidation of the film, which has been noted by others.[2,3,5,26,28] A loss of conductivity is observed to result from this process.[2] The product of the oxidation is hydrolytically unstable, and oxidation at potentials greater than 0.8 V in the absence of aniline monomer leads to degradation of the electrochemical response of the film. More will be said about this oxidation in a later section. The second redox process is oxidation of the aniline monomer to produce precursors to the PA film.

Curve B shows the QCM response which was recorded concurrently with the CV. A stable frequency is seen for potentials below −0.1 V in the region where little current is flowing. As the film is oxidized the frequency begins to drop, indicating a mass increase of the film on the electrode surface. This frequency drop is seen to continue during the double layer charging region. Immediately after the reversal of the scan direction a larger drop in frequency is seen, followed by a gradual increase. The frequency finally levels off at a value 10 Hz lower than that initially observed. The net decrease in frequency is a result of growth of the film during the cycle and corresponds to deposition of 0.18 $\mu g/cm^2$ or about 10^{-9} mol/cm^2 of the polymer. Assuming a film density of 1.2 g/cm^3 (vide infra), this amount of deposition corresponds to an increase in the film thickness of 1.5 nm. The other features of the QCM response will be discussed below.

In order to apply eq 1 to deposition of PA one must first verify that the film behaves as a rigid layer. This was done in two ways. The width at half-height of the conductance maximum (which corresponds to the resonant point) of the quartz crystal was measured before and after deposition of the PA film both in and out of solution. Had the viscoelastic properties of the film been influencing the resonant frequency, then broadening of the resonant well would have been observed.[29] No detectable broadening from this source was seen under any conditions. However, significant broadening was observed on immersion of the film (or bare crystal) in solution. This is expected and results from viscous loss in the solution.[29] (It is important to realize that under normal conditions the frequency change and broadening of the impedance well caused by immersion of the QCM into solution do not change the mass sensitivity.) A further test of rigid layer behavior entailed plotting the total frequency change (f_T) upon deposition of the film (measured at −0.2 where the film is in its reduced form) vs. the charge consumed in oxidation of the film from −0.2 to 0.5 V. Assuming that f_T is a measure of the mass of deposited film (including any solvent or ions which might be contained within it) and that Q_{ox} also measures the total amount of deposited film (i.e., that the percent of electroactivity does not depend on film thickness in the range studied here), then this plot should give a straight line with a zero intercept. Linearity indicates that the same incremental frequency change is observed for an incremental increase in film thickness regardless of the total amount deposited. If the film were acting as a viscous medium, then the plot would exhibit concave curvature indicating loss of mass sensitivity as thickness increased due to damping of the shear wave as it travelled through the film. Figure 2 shows the linear plot obtained for these data which verifies that the film behaves as a rigid layer at 5 MHz. Previous ellipsometric work by Bard and co-workers[30] indicated a transition from one growth morphology to another at a thickness of ca. 150 nm. Again, assuming a density of 1.2 g/cm^3, the data in Figure 2 indicate that our films behave rigidly up to a thickness of ca. 300 nm. Thus, since the growth procedures were the same in this work and ref 30, it seems that for these thin films the QCM is relatively insensitive to such changes in morphology, although a slight increase in solvent content is indicated with increasing film thickness (vide infra) and may be related to a morphological change.

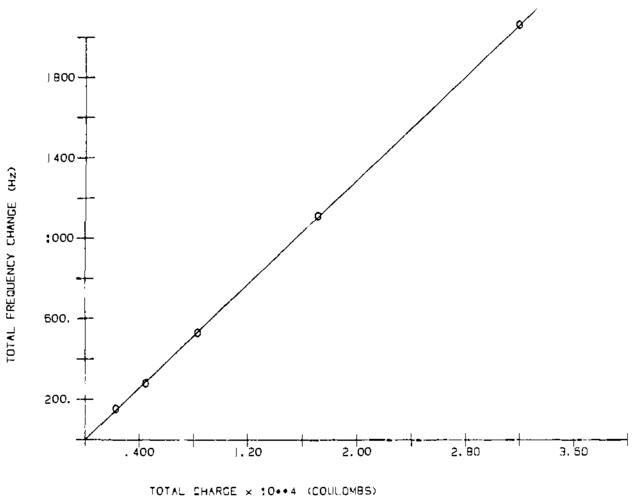

Figure 2. Plot of the total observed frequency change vs. the oxidative charge from −0.2 to 0.5 V (see text) for a polyaniline film grown under the conditions of Figure 1.

Another extremely useful piece of information which can be obtained from the QCM is the mass of polymer deposited, exclusive of any ions or solvent contained within it. This is essentially the number of mol/cm^2 of aniline units in the film (Γ_{PA}). The following procedure was used to obtain this quantity. Prior to film growth the crystal was washed thoroughly with aqueous acid, water, and methanol, and its resonant frequency was measured with the impedance analyzer. Following growth, the film was washed with pH 7 phosphate buffer which contained $NaHSO_3$ to ensure that the film was maintained in its reduced form (exposure to air leads to slow oxidation of the film). This was followed immediately by water and methanol rinses and rapid drying in a vacuum oven at 70 °C. The electrochemical cell was sealed with desiccant inside, and the resonant frequency was again determined with the impedance analyzer. The frequency decrease relative to the bare crystal was used in eq 1 to calculate the mass of the deposited film. The molecular weight of the aniline unit (calculated assuming a head-to-tail structure) then gives Γ_{PA}. Dry conditions are essential to this measurement because the dry film is very hygroscopic, as evidenced by the rapid frequency decrease seen on exposure to room air (typically 10–30% relative humidity). This key experiment was repeated several times with films of various thicknesses. In all cases the "dry" frequency change scaled with and was less than f_T. In a typical experiment, for a total frequency change of 274 Hz in solution, the value corresponding to Γ_{PA} was 109 Hz or 2×10^{-8} mol/cm^2 of aniline units in the film. Thus, one infers from these data that the ions and solvent account for 165 Hz of the total frequency change of 274 Hz. It will be shown below that the individual solvent and ionic contributions to this value can be discerned.

With the value of Γ_{PA} and the total charge required to deposit the film, it is a simple matter to calculate the current efficiency for deposition. It is important to make this measurement at a potential at which the film is reduced because of ambiguity as to the charge consumption in the double layer charging region. Thus, we recorded the charge consumed during film growth with cycling from −0.2 to 0.75 V, with the final reading of total coulombs passed made at −0.2 V. A similar experiment was made in which the film was grown at a constant potential of 0.75 V, with reduction at −0.2 V prior to the charge measurement. In both cases the total charge passed was about 10 mC cm^{-2}. A current efficiency of 40% was found for the potential cycling method, and a value of 15% was found for the potentiostatic method. A current efficiency of 100% would imply that 1 electron is removed for the deposition of one aniline ring. We hesitate to

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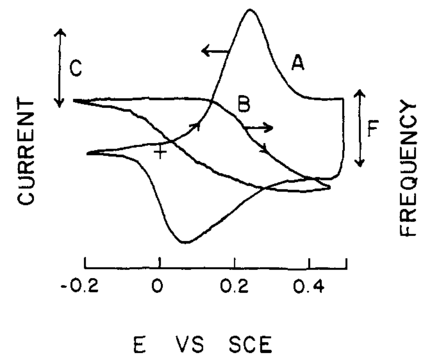

Figure 3. CV/QCM steady state scan from −0.2 to 0.5 V in 1.0 M H_2SO_4. Scan rate, 100 mV/s. C = 200 μA, F = 40 Hz. (A) Cyclic voltammetric response. (B) QCM frequency response. Curve B is offset 40 mV to the left with respect to curve A.

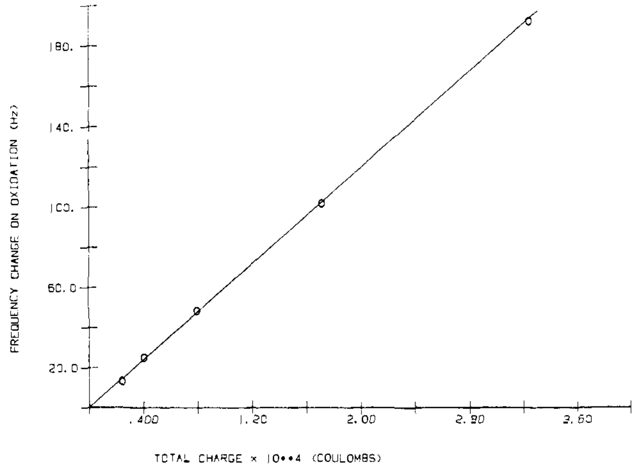

Figure 4. Plot of the frequency change observed for oxidation from −0.2 to 0.5 V vs. the oxidative charge for the same scan (see text) for a polyaniline film grown as in Figure 1.

attribute too much significance to the absolute values until the completion of more detailed studies which are currently in progress. However, that the cycling method gives higher values is consistent with the QCM data in Figure 1 which show that a significant fraction of the deposition occurs after the reversal of the scan direction. We interpret this to mean that the conductive form of the film is less soluble than that obtained on further oxidation (i.e., above 0.75 V), so that the cycling method captures more of the oxidized precursors to PA before they can escape into solution. This would be in accord with observations made by many workers[31] that the conductive forms of these types of polymers generally have very low solubility. Since the tremendous gain in configurational entropy which generally results from dissolution of normal polymers is probably not available to conductive polymers due to their rigidity, it is perhaps not surprising that they have such limited solubilities.

Mass Changes during Cycling. Curve A in Figure 3 shows the result of a steady state[32] CV scan from −0.2 to 0.5 V in a solution 1.0 M in H_2SO_4. Curve B shows the corresponding QCM response. The frequency decreases on oxidation and increases on reduction. We shall denote the frequency change on oxidation to 0.5 V as Δf_{ox}. Figure 4 shows a plot of Δf_{ox} vs. Q_{ox} which demonstrates that the frequency decrease is linearly related to the film thickness. As before, the frequency continues to decrease during oxidation in the double layer charging region. The hysteresis (i.e., displacement of the anodic and cathodic peaks along the potential axis) observed in the CV is duplicated in the QCM response, and the original frequency is attained at the end of the scan. Furthermore, both the frequency change and anodic charge are independent of scan rate from 0 mV/s[33] to 400 mV/s. These observations indicate that the mass change which accompanies the oxidation tracks the charge consumption and is reversible. We propose that this frequency decrease is caused by a net mass increase resulting primarily from the insertion of anions which serve to charge the electrical double layer of the film and to neutralize any net charge on the polymer chains which might arise from protonation of the PA film in its oxidized form. Careful examination of the CV and QCM curves reveals that significant amounts of charge are passed during the oxidation prior to the beginning of the frequency decrease. It will be seen that this feature of the data can be explained with the model presented below.

Table I

anion	Δf (Hz)	MW of anion (g/mol)	Δf/MW
Cl^-	46	35.5	1.30
Br^-	72	79.9	0.90
HSO_4^-	89	97.1	0.92
ClO_4^-	88	99.5	0.88
$CF_3CO_2^-$	102	113.0	0.90

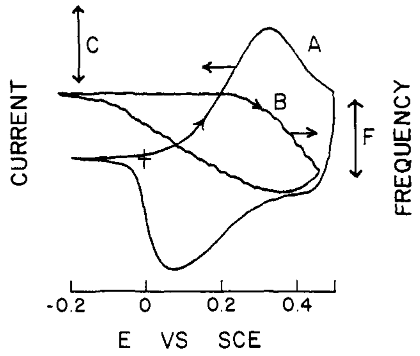

Figure 5. CV/QCM steady state scan from −0.2 to 0.5 V in 0.1 M H_2SO_4. Scan rate, 200 mV/s. C = 400 μA, F = 40 Hz. (A) Cyclic voltammetric response. (B) QCM frequency response. Curve B is offset 40 mV to the left with respect to curve A.

In order to verify the above proposal, the frequency changes for oxidation of PA in 1.0 M solutions of various acids were measured. For HCl, HBr, H_2SO_4, $HClO_4$, and CF_3CO_2H the frequency changes scale with the masses of the anions. These data for a typical film are shown in Table I. Such excellent agreement could only occur if the QCM were measuring the masses of inserted anions. Similar experiments were done in a solution 1 M in HCl and 4 M in NaCl. The observed frequency change was the same as that seen in a 1 M HCl solution, indicating a response in 1 M acid which is independent of the presence of an excess of cations (except for the proton which has a profound effect on PA electrochemistry). Kobayashi et al.[8] have also observed the insensitivity of PA electrochemistry to addition of a variety of mono- and divalent cations in 1 M HCl. It is interesting to note that the relative mass change seen for Cl^- insertion is a bit too large. It is possible that water of hydration accompanies the anion into the film, thereby accounting for the increased mass. This would be in accord with the notion that Cl^- is fairly strongly hydrated due to its high charge to radius ratio.[34] The other anions are known to be only very weakly hydrated.[34]

pH Dependence. Experiments similar to those shown in Figure 3 were done in 0.1, 0.5, 1.0, 2.5, 5.0, and 10.0 M H_2SO_4 to observe the influence of pH on the ion migration process. Figure 5 shows

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(31) Frommer, J. E., preprint.

(32) The CV response of PA depends somewhat on whether the film has been resting in its reduced form for several minutes prior to the scan or has been continuously cycled prior to the scan. Our use of the term "steady state scan" implies that the film was continuously cycled prior to the scan. The cause of the above-mentioned effect will be discussed below.

(33) Charge and frequency were measured at effectively 0 mV/s by varying the potential in 10-mV increments and holding the film at each potential for several minutes to allow equilibration prior to the charge and frequency measurements.

(34) Amis, E. S.; Hinton, J. F. *Solvent Effects on Chemical Phenomena*; Academic Press: New York, 1973; Vol. 1, Chapter 3.

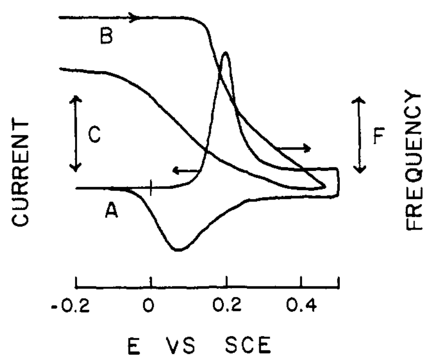


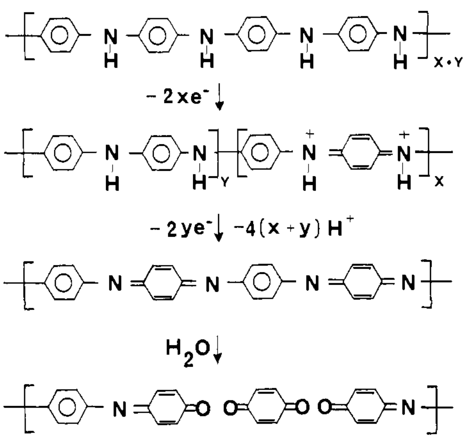
Figure 6. CV/QCM scan from −0.2 to 0.5 V in 10 M H_2SO_4 after holding the potential at −0.2 for 5 min following the previous scan. Scan rate, 50 mV/s. C = 400 μA, F = 40 Hz. (A) Cyclic voltammetric response. (B) QCM frequency response. Curve B is offset 40 mV to the left with respect to curve A.

the steady state CV and corresponding QCM data for the 0.1 M solution. While the electrochemical response in 10 M acid is quite sharp (see Figure 6), that of the film in 0.1 M acid is quite broad and misshapen. This is probably due to increased resistance of the film which is a consequence of decreased conductivity at this pH. MacDiarmid and co-workers have shown that the conductivity of the film is dependent on pH in this region,[3] with conductivity decreasing as pH is raised. The curvature seen in the CV immediately after reversal of the scan direction (i.e., the charging transient) is indicative of a system with large resistance and/or large capacitance, whereas small values are implied by the absence of such features for acid concentrations larger than 0.5 M. Another feature of the data in Figure 5 is that the capacitive current in the double layer charging region is significantly larger for the lower acid concentration. Also, the relative amounts of charge under the peak and in the capacitive region are different for the different acid concentrations.

When the experiments are not carried out under steady state conditions (i.e., when the PA film is allowed to stand in its reduced state for several minutes before the next oxidative scan) effects are observed which we feel can be attributed to solvent transport. Figure 6 shows a particularly dramatic example of these effects. Curves A and B show the CV and QCM responses, respectively, of a PA film in 10 M H_2SO_4 which was allowed to stand for 5 min in its reduced form before the oxidative scan. The frequency change is much larger than it would be for the steady state experiment, and the initial frequency is not regained at the end of the scan. However, if the film is held in its reduced state for 2–3 min, the frequency slowly increases back to its original value. If the potential is continuously cycled, the size of the QCM frequency response on the second scan changes to that observed during the negative scan in Figure 6. Also, on the first scan the anodic peak is considerably sharper and shifted 110 mV to positive potentials relative to the steady state scans. Such effects have been observed for other polymer films[15] and have been attributed to low solvent levels in the reduced films. Such an interpretation for our data would be in agreement with the well-known dehydrating properties of concentrated H_2SO_4 solutions. These effects are not observed for acid concentrations of 1 M or less, so we conclude that solvent transport during cycling is minimal under these conditions. We are currently conducting experiments with D_2O to attempt to verify that these effects are related to solvent transport.

Quantitative Aspects. There have been indications from previous work that anions are inserted into PA films during oxidation,[3,8] and the results here verify those findings. Furthermore, we have shown that the number of inserted anions (relative to the charge which is passed during the oxidation) is related to the acid concentration. MacDiarmid and co-workers[18] have proposed a model for PA in which both the oxidized and reduced forms can exist in protonated and deprotonated states. They have also shown conductivity vs. pH data which indicate that the pK_a of the oxidized form is above pH 2. As will be seen below, our results are in agreement with these findings and also place the apparent pK_a of the reduced form between 0 and −1. Reference to Scheme I reveals the reasoning behind these assertions.

Scheme I



In Scheme I the reduced form is shown in its deprotonated state and the oxidized form in its protonated state. To simplify the discussion, let us assume that a pH can be found at which these two forms of PA are in these states of protonation. Consider the case in which the oxidation is carried out at such a pH, so that no protons are gained or lost in the film. The reduced form is uncharged, so it should contain only solvent and whatever level of sorbed electrolyte required by the partition coefficient of the electrolyte and its solution concentration. According to the model proposed by MacDiarmid and co-workers,[18] oxidation can be viewed as a continuous process with x (the fraction of oxidized sites) varying from 0 to 1. The creation of cationic sites leads to a requirement for charge compensating anions, which presumably come from the external supporting electrolyte. This anion insertion occurs both during the beginning of the oxidation process (corresponding to the peak at 0.2 V in the CV) and during the double layer charging region. One anion should be inserted for each "double layer" electron which is removed. Thus, at a pH at which the degrees of protonation are as shown in Scheme I, the model requires quantitative agreement between the number of moles of anions inserted and electrons removed. This assumes that the level of sorbed electrolyte is small so that cation expulsion does not contribute significantly to the generation of anionic charge within the film. In fact, it will be shown that even at a pH of 1 the film is partially protonated in its reduced form so that Donnan exclusion should prevent sorption of the supporting electrolyte, thereby eliminating the possibility of cation expulsion.

Consider now the case in which the acid concentration is 1.0 M. According to our estimate of the pK_a of the reduced form it should be partially protonated at this pH. The protonated sites will be neutralized by anions. On oxidation these sites will deprotonate, so that the polymer can reach the resonance stabilized structure shown in Scheme I. At this point the pH within the film will be out of equilibrium with the solution, so one expects the protons to exit, leaving behind the anions which now can serve to neutralize the protonated sites of the oxidized form. Assuming a Grotthus mechanism for proton transport followed by solvation at the film/solution interface, only a very small mass change (given by the mass of unsolvated rather than solvated protons) should be observed for this fraction of the overall charge which is passed during the oxidation. The remainder of the mass change will be caused by insertion of additional anions which provide the balance of negative charge required by the film. Thus, as the acidity is increased and the reduced form of PA becomes more fully protonated, one expects the ratio of the number of anions inserted to the number of electrons extracted to decrease. Again, it is unlikely that cation expulsion could account for a significant fraction of the anionic charge needed for the oxidation process because the concentration of cations within the film should be low due to Donnan exclusion caused by the protonation of PA.

The above discussion can be cast in a more quantitative form by recognizing that the frequency change on oxidation, Δf_{ox},[35] is

Table II[a]

$[H_2SO_4]$ (mol/L)	Q_{ox} (C/cm^2)	PA_r	PA_0
0.1	2.5×10^{-3}	0.32	0.52
0.5	2.8×10^{-3}	0.37	0.58
1.0	3.0×10^{-3}	0.41	0.61
2.5	3.6×10^{-3}	0.53	0.73
5.0	3.8×10^{-3}	0.58	0.78

[a] $f_T = 672$ Hz, $\Gamma_{PA} = 5.1 \times 10^{-8}$ mol/cm^2.

related to the difference in anion content of the reduced and oxidized forms and to the total number of aniline units in the film by the following equation

$$\Delta f_{ox} = (PA_0 - PA_r)\Gamma_{PA}MW_a(-f_0^2/N\rho) \qquad (2)$$

where PA_0 and PA_r represent the fractions of aniline units with accompanying anions in the oxidized and reduced forms, respectively, Γ_{PA} gives the number of mol/cm^2 of aniline units in the film, MW_a is the molar mass of the inserted anion, and the last factor converts from mass per unit area to frequency. An assumption that no solvent transport occurs during the oxidation is required to write this equation. It is clear from eq 2 that PA_r represents the fractional degree of protonation in the reduced form. Thus, the pK_a of the reduced form of PA can be calculated given an experimental determination of this variable as a function of pH.

Equation 3 gives the relationship between the oxidative charge and the anion content of the oxidized film

$$Q_{ox} = F PA_0 \Gamma_{PA} \qquad (3)$$

where Q_{ox} is the charge/cm^2 passed on oxidation to some arbitrary potential within the double layer region, and F is the Faraday constant. This equation represents the electroneutrality requirement that the number of electrons removed from the system must equal the final number of anions within the film. Thus, once Q_{ox} and Γ_{PA} are known (both of which are experimentally determined parameters), one can calculate PA_0. The use of this value with Δf_{ox} in eq 2 then gives PA_r.

Equation 4 gives the total frequency change on film growth measured in solution (f_T) as the sum of its components

$$f_T = \{(MW_{PA}\Gamma_{PA}) + (PA_r MW_a \Gamma_{PA}) + (MW_s \Gamma_s)\}(-f_0^2/N\rho) \qquad (4)$$

where MW_{PA} is the molar mass of the aniline unit in the polymer (91 g/mol for the head-to-tail structure), and MW_s and Γ_s are the molar mass and number of mol/cm^2 of any solvent which might be in the film in its reduced form in the growth solution. Thus, the three components which contribute to the total frequency change observed on growth of the film are the mass of the aniline units, the mass of anions which are present in the film due to partial protonation in the reduced form in 1.0 M H_2SO_4, and the mass of solvent. Use of f_T with the previously determined parameters in eq 4 gives the mass of solvent in the film.

Table II shows values of Q_{ox}, PA_r, and PA_0 obtained at various acidities for a film which contained 5.1×10^{-8} mol/cm^2 of aniline units. These values were calculated from eq 1–4 for a CV scan which started at −0.2 V and ended at 0.5 V. An important feature in Table II is the dependence of PA_r and PA_0 on the pH. PA_r is seen to increase from 0.32 in 0.1 M acid to 0.58 in 5.0 M acid. This indicates that the film in its reduced form in 0.1 and 5.0 M acid has 32% and 58% of its nitrogens protonated, respectively. The pH at which 50% of the nitrogens are protonated is the apparent pK_a, and this appears to correspond to an acid concentration of between 2.0 and 2.5 M or a pH between −0.3 and −0.4. Thus, the reduced form of PA is quite a strong acid. Comparison can be made to diphenylamine which has a pK_a of 0.79. If the nitrogens in PA behaved as monomeric acids (i.e., had ideal pH titration curves), then the degree of protonation calculated from the apparent pK_a would be only about 10% at a pH of 0.3 and less than 5% at a pH of 1. However, this is not the case. The film is still 32% protonated at a pH of 1. This broadening of the titration curve is typical of polymeric acids (or bases) in ion exchange resins,[37] resulting primarily from repulsive electrostatic interactions between the protonated sites along the chain, although the change in ionic strength with pH also contributes to the broadening. Thus, the intrinsic pK_a[37] for PA is undoubtedly somewhat higher than the apparent value of between −0.3 and −0.4.

Table III

Δf_{ox} (Hz)	f_T (Hz)	$\Gamma_{PA} \times 10^8$ (mol/cm^2)	$Q_{ox} \times 10^3$ (C/cm^2)	PA_r	PA_0	$\Gamma_s \times 10^8$ (mol/cm^2)
22	274	2.1	1.1	0.44	0.52	11
50	637	4.7	2.4	0.45	0.53	28
60	843	5.7	3.0	0.45	0.52	40

The values for PA_0 increase from 0.52 at an acid concentration of 0.1 M to 0.78 at 5.0 M. The value decreases with decreasing acid concentration due to deprotonation of the oxidized, conducting form of PA, and a consequent decrease in the number of charge compensating anions required to maintain electroneutrality. This would explain the dramatic degradation in the electrochemical response observed on going from pH 0 to 1 and would also be in agreement with the data of MacDiarmid and co-workers[3,18] which indicate that the conductivity of PA begins to decrease just as the pH is raised above 0.

Table III shows data obtained for several film thicknesses at a constant acid concentration of 1 M. It is clear that the values of PA_r and PA_0 are reproduced quite well for different films and for different thicknesses. Also, Γ_s is given in the table. The ratio of Γ_s to Γ_{PA} gives the number of water molecules per aniline unit in the film in the 1.0 M H_2SO_4 growth solution as varying between 5 for a thin film and 7 for a thicker film. Thus, the amount of solvent within the reduced film is not large, so the porosity must be quite small. Attempts to determine gross porosity by electrochemically reducing various species (such as ferricyanide and uranyl ion) at negative potentials where the polymer is an insulator revealed that even extremely thin films block these reductions and can be assumed to be relatively nonporous, except to oxygen and protons.

Second Oxidation Process. PA is known to undergo a second oxidation process at more positive potentials which leads to film degradation.[28] The structure of the polymer produced by this oxidation is thought to be that shown in Scheme I.[18,37] The polymer in this more highly oxidized (imine) form is a very poor base due to the nature of the imine nitrogens. Thus, even oxidation is relatively concentrated aqueous acid solutions should lead to deprotonation of nearly all of the nitrogens. The instability is thought to result from the known sensitivity of imines to hydrolysis. To further verify the model put forth above, we have studied this oxidation process in detail. Figure 7 shows a CV/QCM scan from −0.2 to 0.9 V. The second wave is seen at about 0.6 V. Positive of this wave the charging current drops to normal levels, indicating loss of conductivity. We have measured the pH dependence of the formal potential for this wave and have obtained a linear E vs. pH plot with a slope of −116 mV/pH unit and a correlation coefficient of 0.9994. This indicates that there are two protons lost per electron which is removed, in agreement with the proposed structures. Integration of the current in the figure including both the charge under the peaks and the charge in the double layer charging region and comparison with Γ_{PA} reveals that exactly one electron per ring is removed during a scan from −0.2 to 0.9 V, in accord with the model. This key comparison has been made

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(35) Recall that we define Δf_{ox} as the frequency charge which occurs for potential scans between −0.2 and 0.5 V, the upper limit being an arbitrarily chosen value within the so-called double layer charging region.

(36) Helfferich, F. *Ion Exchange*, McGraw-Hill: New York, 1962; Chapter 4.

(37) Chance, R. R.; Boudreaux, D. S.; Bredas, J. L.; Silbey, R. *Abstracts of Papers* 192nd National Meeting of the American Chemical Society, Anaheim, CA; American Chemical Society: Washington, DC, 1986; Abstract 117.

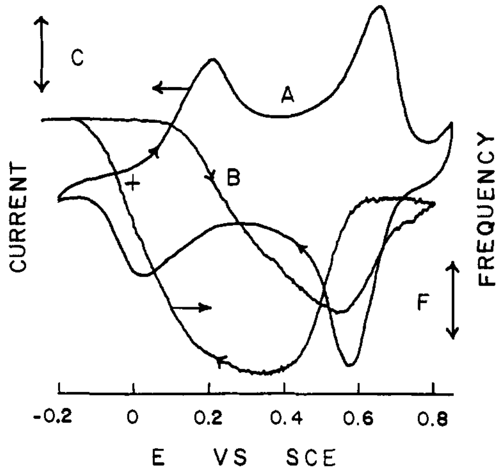

Figure 7. CV/QCM steady state scan from −0.2 to 0.9 V in 1.0 M H_2SO_4 adjusted to a pH of 1.75 with 50% NaOH. Scan rate, 50 mV/s. $C = 40\ \mu A$, $F = 20$ Hz. (A) Cyclic voltammetric response. (B) QCM frequency response. Curve B is offset 40 mV to the left with respect to curve A.

on several films of different thicknesses and always gives one electron per ring.

The QCM response in Figure 7 shows that there is a pronounced mass loss on oxidation over the wave at 0.6 V. As a possible explanation, we propose this to result indirectly from the deprotonation of the PA nitrogens which accompanies oxidation to the imine form. This deprotonation lifts the requirement for charge compensating anions. Thus, the oxidation produces a film which contains excess anions as well as the protons which are produced by deprotonation. At this point the film is far from equilibrium with respect to the sorption of supporting electrolyte from solution. Since Donnan exclusion is not a factor in the neutral, oxidized film, any excess charge within the film can be compensated by insertion or expulsion of the appropriate species. In such a situation the kinetics of the candidate processes will probably determine which is dominant. A qualitiative determination can be made by examining the data in the figure. The frequency attained at the end of the positive scan is lower than the initial frequency, indicating that the film contains more mass than it did in its reduced form. Keeping in mind that under the conditions in the figure the reduced film is ca. 10% protonated, it is clear that the oxidized product actually contains more ionic species than does the reduced film (assuming, as before, that the solvent content of the film does not change appreciably during oxidation). Thus, it appears that while some of the anions are expelled during the second oxidation process, a significant number of them remain behind in the film, their charge being compensated by protons. The presence of this excess, sorbed electrolyte could then account for the increased film mass relative to the reduced form. We are somewhat puzzled by the consistent observation that the frequency on the negative scan attains a level lower than that on the positive scan. It is possible that some of the sorbed electrolyte remains in the film during the reduction back to the conductive form, but that equilibrium is reattained on further reduction to the amine form. However, this explanation is quite speculative and must remain so pending a more detailed understanding of the coupling between protonation, sorption equilibria, and electromigration.

It has been reported that repeated scanning over the wave at 0.6 V leads to an irreversible loss of the electrochemical response of the film.[28] We find the same phenomenon. During repeated scans over this oxidation wave one observes the appearance of two new, closely spaced, reversible redox processes at 0.43 and 0.50 V. Continued cycling causes increases in these responses at the expense of the waves at 0.2 and 0.6 V. Also, the two waves merge and become virtually indistinguishable. A previous interpretation has been offered[28] that oxidation above 0.6 V leads to hydrolysis of the imine to form benzoquinone. This was supported[28] by spectral and electrochemical observation of a product with the same characteristics as benzoquinone. We agree with this interpretation and further speculate that the two closely spaced waves initially observed are probably quinone and quinone/imine (the precursor to the quinone) which results from initial hydrolysis at only one ring position as shown in Scheme I. The loss of electrochemical response is accompanied by large frequency increases which we interpret as indicating that the hydrolysis products of the oxidized film are soluble and leave the surface. We are currently investigating the rate of this degradation reaction as a function of pH. Preliminary results clearly indicate that it is an acid-catalyzed reaction, in agreement with the hypothesis of an imine hydrolysis.

Because of the pH dependence of the second oxidation process the maximum potential which can be attained without film degradation is also pH dependent. For example, at a pH of 3, cycling a PA film from −0.2 to 0.5 will lead to eventual degradation due to partial oxidation to the imine form, whereas at a pH of 0 it has been reported that the film may be cycled more than a million times between these limits with no evidence of degradation.[28] We have further found that the rate of degradation is pH dependent, with the loss of electrochemical response occurring much more rapidly at lower pH values. In concentrated acid solutions the degradation is very fast, so that only a few scans over the wave need be made before nearly complete loss of response is observed. This finding has significance for battery applications of PA. Stringent control of the potential is required at all pH values because of the faster rate of degradation of the imine form at low pH and the small separation of the waves at higher pH. In this connection we also report that prolonged exposure of the film to solutions of pH greater than ca. 11 in the presence of air leads to total oxidation to the imine form and the subsequent decomposition of the film.

Conclusions

Concurrent electrochemical and microgravimetric measurements on PA have allowed for a relatively clear picture of the insulator-to-conductor transition at 0.2 V to be formulated. The experimental data indicate that anion insertion occurs during this transition, that little, if any, solvent transport occurs (with the possible exception of chloride-containing media), and that proton expulsion can occur at lower pH values. The continuous nature of the anion insertion in the double layer region is in agreement with the description of PA put forth recently by MacDiarmid and co-workers.[18] Recent ESR data reported by Glarum and Marshall[38] along with an interpretation of the electrochemical response based on a one-dimensional density of states function are also in agreement with this model. Furthermore, correlation of the QCM and electrochemical data shows conclusively that the pH dependent conductor to insulator transition (to the imine form) at more positive potentials is caused by the cumulative removal of one electron per ring inclusive of the double layer charge, again in agreement with previous work.[18,38] The body of experimental evidence thus points to formation of energy bands on polymerization of aniline, with the band edges appearing at ca. 0.15 and 0.7 V (the second value depends on pH), the values given as the averages of the anodic and cathodic peaks in the CV. The peaks in the voltammogram result from the traversal of the electrode potential across the band edge,[38] while the so-called double layer current results from the continuous removal of electrons from the partially occupied band.[38]

The stoichiometry for the oxidation of PA and the forms chosen to represent the various oxidation states given here and supported by previous workers[18,38] are not in agreement with those put forth by Genies and Tsintavis.[26] For example, they favor a description of the product of the second oxidation process (at 0.8 V) as a nitrenium derivative. The reasons for these discrepancies are unclear at the present time. However, it should be pointed out that quite different experimental conditions were used for the coulometric experiments here and in ref 26 (most of the work in ref 26 was done in a molten fluoride electrolyte), and these are the key experiments on which the models are based. It has recently

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J. Am. Chem. Soc. **1987**, *109*, 3581–3585

been proposed[18b,37] that a better description of the conductive form of PA is as an open shell cation radical species, rather than as a protonated imine (see Scheme I). Our work does not speak to the proper description of the conductive form of PA, but rather it addresses the stoichiometry of the electron and proton transfers associated with the various oxidation and reduction steps. We show the conductive form as consisting of a mixed amine/protonated imine structure simply as a way to indicate partial oxidation, not to imply support for one structure over another.

Further quantitative comparisons of our data with those of others are possible from the work of Gottesfeld et al.,[39] who recently studied the ellipsometric behavior of PA films. Among other things they were able to measure the film thickness and determine a correlation between the anodic charge consumption (our Q_{ox}) and the thickness. Assuming a film density of 1.2 g/cm^3 to calculate the thickness from Γ_{PA}, our results agree quantitatively (to within 5%) with theirs. Thus, measurements probing widely different properties using completely different techniques give excellent agreement, lending strong support to the quantitative aspects of both techniques.

Wrighton and co-workers have published a detailed study of the dependence of the resistance of PA on electrode potential.[2] They show that the resistance begins to drop at the very initial stages of the first oxidation process, when less than 10% of the oxidative charge has been passed. Our results show that significant charge is passed before the insertion of anions during the first oxidation process in 1 M acid which can be interpreted as meaning that deprotonation of the film to reach the conductive form shown in Scheme I, followed by proton loss to the external solution, occurs immediately on initiation of this oxidation process. These two results taken together argue that in acid solutions in which the reduced form is significantly protonated, formation of the resonance stabilized conductive form by deprotonation is a prerequisite for conductivity and that a small amount of oxidation induces deprotonation which can lead to large changes in conductivity.

The finding that protons can have a significant role in the charge compensation process for PA is germane to its possible use as a battery material. To the extent that protons take part in this process, the energy density of the battery will be improved. In addition, it is not unreasonable to suppose that proton transport should be faster than anion transport, so that larger power densities could be achieved. We are currently examining the rates of the switching process in various media in which the charge compensating ions are known to be predominantly anions or protons so as to probe these questions further.

A major result of this work is the demonstration that by providing additional constraints on models for experimental systems, the QCM can provide a wealth of information on electrochemical processes that involve mass changes of the electrode surface. This is especially true for thin films on electrode surfaces in which solvent and ion transport processes are very difficult to quantify by other methods. We are currently examining several other thin film systems such as polythiophene, polypyrrole, and polyvinylferrocene to determine the importance of these processes to the kinetics and thermodynamics of their electrochemical reactions. As the technique develops and its sensitivity is improved, we expect that even monolayer adsorption of organic species will be measurable. In fact, it has already proved possible to monitor monolayer adsorption/desorption of surfactants derivatized with redox groups.[40] We feel that because of its relative ease of use and low cost the QCM should become a widely used technique for probing electrochemical surface processes.

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Registry No. PA, 25233-30-1; HCl, 7647-01-0; HBr, 10035-10-6; H_2SO_4, 7664-93-9; $HClO_4$, 7601-90-3; CF_3CO_2H, 76-05-1.

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Photoassisted Catalytic Dissociation of H_2O To Produce Hydrogen on Partially Reduced α-Fe_2O_3

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Abstract: The photodissociation of H_2O on partially reduced Fe_2O_3 powders and pellets is shown to be a catalytic process if the semiconductor is illuminated by visible light of energy greater than 2.2 eV. Activation of the Fe_2O_3 catalysts involved reduction in a mixture of H_2 and H_2O followed by oxidation. Up to 380 μmol of H_2 were produced with 190 μmol of Fe_2O_3 powder. The rate was 40 μmol h^{-1} g^{-1} for the first 200 h and started to decay thereafter. O_2 was also produced as shown by using $H_2{}^{18}O$ in amounts of up to 40 $\pm$ 15% of the amount of H_2 detected in the same experiment. In photoelectrochemical experiments with use of a three compartment cell the active pellets produced photocurrents of approximately 4 μA cm^{-2} mW^{-1} at +0.5 V bias (SCE, pH 13). Simultaneously, H_2 was produced at a rate of 0.06 μmol h^{-1} mW^{-1}. A lower limit to the conversion efficiency of approximately 10^{-3} H_2 molecules per photon is obtained.

Iron oxide has been investigated extensively in recent years to probe its ability to dissociate water either by photoassisted electrolysis[1-11] or by a photocatalytic reaction.[12] It has also been recently reported as an active catalyst in producing NH_3 from N_2 and H_2O.[13,14] The material is an n-type semiconductor with an indirect band gap of 2.2 eV.[15] The excitation of photoelectrons from the valence band to the conduction band requires visible light,

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