

Oxidation of Ammonium on Platinum in Acidic Solutions

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Oxidation of ammonium on polycrystalline Pt has been studied in perchloric and sulfuric acid solutions at room temperature. Ammonium was electrochemically active, and N₂ and NO were detected using differential electrochemical mass spectroscopy. Cyclic voltammetry and electrochemical quartz crystal microbalance data showed that ammonium affects the formation and reduction of Pt oxides, probably due to formation of very stable adsorbed nitrogen or nitrogen-oxygen species stable down to the H_{ads} region. An oxidation peak occurred at 0.8 V_{RHE} in positively going scans, decreasing strongly with increasing sweep rate. A corresponding reduction shoulder at about 0.66 V_{RHE} was seen, probably caused by formation and reduction of NH_{x,ads} or N_{ads} species. Formation of Pt oxides was shifted to slightly higher potentials in the presence of ammonium, and the reduction charge of the Pt oxide reduction peak at 0.80 V_{RHE} was independent of sweep rate, indicating that the amount of Pt oxides formed was limited by other adsorbates. In particular, the most strongly adsorbed hydrogen was shifted to lower potentials by adsorbed species formed at high potentials as well as adsorption of bisulfate mutually stabilized by ammonia. The voltammetric response in the hydrogen desorption region was not affected, showing that all adsorbed species were desorbed at low potentials in the negatively going scan.

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Background for the study.— Our interest in oxidation of ammonium in acidic solutions stems from the observation that ammonia affects the performance of polymer electrolyte membrane fuel cells (PEMFCs).¹⁻³ Both partial and full recovery has been reported when operating the PEMFC on neat hydrogen after exposure to ammonia, and it is of interest to determine if the recovery mechanism may be related to electrochemical oxidation of ammonium. Further, adsorbed species on the Pt surfaces in the fuel cell (FC) catalyst layer may impede the rate and selectivity of the desired FC reactions, the hydrogen oxidation reaction (HOR), and the oxygen reduction reaction (ORR). However, this study will not address ammonia poisoning of fuel cells directly, but the data reported in this paper are useful to better understand the poisoning and recovery mechanism of ammonium in PEMFC as we have reported elsewhere.³

Objectives of this study.— The aim of the present study is to better understand oxidation of ammonium in acidic solutions which has not been studied in any detail before, but has been reported to be extremely slow.⁴ However, this was stated in the context of bulk oxidation of ammonia in direct ammonia fuel cells (DAFC), where very high oxidation currents are desirable. In this study volatile oxidation products, and at which potentials these form, were assessed using differential electrochemical mass spectrometry (DEMS). Classical electrochemical methods like cyclic voltammetry (CV) and rotating disk electrode (RDE) were also used. Formation of adsorbed products was detected using electrochemical quartz crystal microbalance (EQCM). An overview of the available literature on ammonia oxidation in alkaline solutions is given next.

Oxidation of ammonia in alkaline solutions.— Different reaction mechanisms for oxidation of ammonia in alkaline solutions have been suggested.^{4,5} Oswin and Salomon⁴ proposed a reaction mechanism where ammonia is electrochemically dehydrogenated in steps to form N_{ads} , which then combine to form N_2 . Gerischer and Mauerer⁵ have suggested a different reaction mechanism that is better supported by available experimental data. The mechanism is rather complex partly because the nature of the intermediate species is not known

$$OH^- \rightleftharpoons OH_{ads}^{(1-\delta)-} + \delta e^-$$
 [1]

$$NH_{3,aq} \rightleftharpoons NH_{3,ads}$$
 [2]

$$NH_{3,ads} + OH_{ads}^{(1-\delta)-} \rightarrow NH_{2,ads} + H_2O + (1-\delta)e^{-}$$
 [3]

$$H_{2ads} + OH_{ads}^{(1-\delta)-} \rightarrow NH_{ads} + H_2O + (1-\delta)e^{-}$$
 [4]

$$NH_{rads} + NH_{vads} \rightarrow N_2H_{nads}$$
 [5]

$$N_2H_{n,ads} + nOH_{ads}^{(1-\delta)-} \rightarrow N_{2,ads} + nH_2O + n(1-\delta)e^{-}$$
[6]

$$N_{2,ads} \rightarrow N_{2,g}$$
 [7]

$$NH_{ads} + OH_{ads}^{(1-\delta)-} \rightarrow N_{ads} + H_2O + (1-\delta)e^-$$
 [8]

where x and y is 1 or 2 and n = x + y.

Although the reaction mechanism is complex, one should note the key role played by adsorbed NH₂ or NH in forming the N-N bond before further oxidation takes place; see Eq. 5. Gerischer and Mauerer⁵ found that the electrode deactivated quickly initially, probably due to partial blocking by OH_{ads}. This initial deactivation was easily reversed. If the electrode was polarized for longer periods, a more persistent deactivation was found, ascribed to formation of Nads considered to be a self-poisoning reaction in the Gerischer-Mauerer mechanism. de Vooys et al.⁶ found that there was a very distinct onset of this latter deactivation process above 0.57 $V_{\rm RHE}$. Gootzen et al.⁷ found, using DEMS, that the rate of nitrogen evolution was stable for at least 10 min at an electrode potential of 0.65 $V_{\rm RHE}$, but the total current fell quickly. Two species were thus formed during oxidation of ammonia: nitrogen and an adsorbed species which gradually saturated the electrode surface, which can be explained by self-poisoning of the surface by Nads; see Eq. 8. Wasmus et al.8 found that the adsorption process of species originating from NH₃ at 0.40 V_{RHE} was complete in about 5 min. The adsorp-

tion was associated with an oxidative current. Both Gootzen et al.⁷ and Wasmus et al.⁸ report experimental evidence for the Gerischer-Mauerer mechanism based on adsorbate experiments. Wasmus et al.⁸ reported that when a positively going sweep was applied after adsorption at 0.40 $V_{\rm RHE}$, nitrogen evolution was detected by DEMS, and was associated with an oxidative current. This showed that the source of nitrogen evolution was a species with oxidation number less than 0, e.g., NH_{2,ads} or NH_{ads}. If the adsorbed intermediate species leading to nitrogen evolution had

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been N_{ads} , nitrogen evolution would occur with no net faradaic current. Gootzen et al.⁷ found that the current changed from reductive to oxidative with time when negatively going sweeps were halted at 0.55 V_{RHE} , which can be explained assuming that two reactions take place at the same time. The first reaction is the reductive formation of $NH_{x,ads}$ from N_{ads} (see Eq. 8); the second reaction is the oxidative formation of nitrogen from $NH_{x,ads}$ via $N_2H_{n,ads}$; see Eq. 5-7.

Strongly adsorbed nitrogen species can be reduced by operating the electrode at potentials in or close to the hydrogen adsorption region.^{7,8} In negatively going sweeps, Wasmus et al.⁸ reported significant formation of NH₃, detected as the fragment m/e = 15 at potentials below 0.50 $V_{\rm RHE}$. The exact nature of the adsorbate, which was the source of this NH₃ formation, was not reported. They also observed an m/e = 30 (NO) signal at potentials below 0.15 $V_{\rm RHE}$ when the upper reversal limit in the CV was at least 1.20 $V_{\rm RHE}$, and the NO signal was much stronger when scanning to 1.60 $V_{\rm RHE}$. de Vooys et al. concluded that adsorbates formed from NO dissolved in acidic electrolyte were reduced to ammonia at low potentials.⁹

Formation of NO and N_2O by oxidation of ammonium has been reported by Wasmus et al.,⁸ and commenced at approximately 0.80 V_{RHE} with a plateau of maximum rate at potentials above 1.00 V_{RHE} . However, the intensities of the NO_x mass signals were much smaller than those seen for nitrogen at the same potential. Formation of nitrous oxides only at high electrode potentials suggests that the presence of adsorbed oxygen species on the electrode is a prerequisite for these reactions.

Experimental

All glassware used was thoroughly washed and then placed in a hot solution of 5–10 wt % H_2O_2 in 0.5 M sulfuric acid. The equipment was then rinsed with purified water (Barnstead NANOpure II system followed by a MilliPore Milli-Q UV Plus system). The RDE cell was cleaned in concentrated KOH overnight before it was boiled in high-purity water and rinsed. The reference electrode (RE) used in all experiments, except in the RDE experiments, was a reversible hydrogen electrode (RHE) consisting of a platinized Pt gauze in a glass tube sealed on one end, filled with the same electrolyte as the cell, and electrochemically charged with H_2 . A saturated calomel electrode was used as RE in the RDE experiments, but the potentials are quoted against the RHE. The counter electrode (CE) was a Pt wire in all experiments.

TraceMetal grade acids and NH₄OH (Fisher) as well as NaOH·H₂O (Alfa Aesar, 99.996% pure on metal basis) were used. EQCM data for perchloric acid were measured using Trace-Select chemicals (Fluka), and for the RDE and adsorbate experiments SupraPur chemicals (Merck) were used. Continuous nitrogen purge was used to remove oxygen from the solutions [Ultrahigh-purity (UHP) grade from Praxair and AGA]. Ar (MTI Gase, N 6.0) was used for purging in the RDE and adsorbate experiments. UHP helium from Praxair was used in the DEMS experiments because N₂ was one of the species of interest.

DEMS.— A comprehensive description of the DEMS system used is given by Wasmus et al.¹⁰ The major difference in our work was how the working electrode (WE) was prepared. A solution of 2.2 wt % BN-18 (*polyvinyl* butyral resin) in 97.8 wt % diacetone alcohol was thoroughly mixed 2:1 by weight with Pt black (HiSPEC 1000, Alfa Aesar) and then painted by hand onto a microporous PTFE substrate to form a thin, even layer. The ink was allowed to dry for at least 1 day. The electrode was cleaned by repeatedly stepping the potential between 0.03 and 1.60 V_{RHE}. The cleanliness of the WE was checked by monitoring the *m/e* = 28 (CO) and 44 (CO₂) signals.⁸ In a separate experiment CO₂ was bubbled through the solution, and the adsorbed species formed by CO₂ reduction at 0.20 V_{RHE} on the WE were stripped off in a 5 mV/s positively going scan after the electrolyte had been bubbled with He. The mass signal *m/e* = 44 closely followed the oxidation current, verifying that the applied sweep rate was low enough.

EQCM.— An experimental setup from Elchema (EQCN-701 and PS-305 potentiostat) was used in the EQCM measurements. Ohmic compensation was used at sweep rates higher than 50 mV/s. The cell resistance was measured using a Solartron 1280B. An EG&G 175 sweep generator was used, and the data were logged by an oscilloscope (Tektronix TDS 420A) or an AD card (DaqBoard, IOtech).

The crystals used were Pt sputtered, AT-cut, unpolished 10 MHz crystals (International Crystal Manufacturing) with no adhesion layer between the quartz and the Pt layer. The mass sensitive area was 5–8% smaller than the electrochemically active area.¹¹ After the WE had been platinized, see below, 20–30 cyclic sweeps were allowed prior to any measurements to stabilize the Pt surface. The WE was regularly cleaned by sweeping the potential between 0.025 and 1.25 $V_{\rm RHE}$ at 50 mV/s. The standard sweep rate used was 50 mV/s, with potential sweep limits 0.025 and 1.25 $V_{\rm RHE}$. The roughness factor was typically 15–25 as determined from the hydrogen underpotential deposited (UPD) charge assuming that 210 μ C/cm² corresponds to a full monolayer coverage.

A complication of the EQCM method is that the mass response may change dramatically if the crystal is cycled for a long time, even though the recorded CVs show very small changes.¹²⁻¹⁴ The change is believed to be caused by roughening of the electrode surface on a mesoscopic scale,¹⁴ i.e., not the same roughness as measured by electrochemical techniques like hydrogen UPD observed with CV. To avoid this the crystals were regularly platinized by pulse deposition in a solution of platinic acid in hydrochloric acid depositing a total of 5 μ g Pt each time to restore the electrode. The Pt black deposit was rinsed well with purified water followed by exposure to a 50/50 mixture of concentrated nitric and sulfuric acid for about 30 s,¹⁵ and then thoroughly rinsed with purified water.

The frequency response of the quartz crystal is proportional to the mass change of the active area of the crystal according to the Sauerbrey equation,¹⁶ which is applicable to small changes in mass,¹⁴ but other factors than mass changes may also influence the frequency response.¹⁴ The theoretical sensitivity of the crystal used in this work, which has a fundamental resonance frequency of 10 MHz, is -0.8673 ng/Hz. The mass sensitivity was calibrated by bulk deposition of Cu from a 5 mM solution of cupric sulfate in 0.5 M H₂SO₄ at 0.06 V_{RHE}. The Sauerbrey coefficient was found to be -1.24 ± 0.10 ng/Hz. The absolute calibrated value is significantly higher than the theoretical value. The reason for the deviation is most likely that the theoretical Sauerbrey coefficient is calculated assuming infinite dimension of the crystal.¹⁷ Less than 100% current efficiency for copper deposition may also contribute to the deviation.

RDE and flow cell experiments.— An RDE rotator from Pine Instruments (AFASRE) combined with a Pine AFRDE5 bipotentiostat was used, and the analog data were logged with an AD card (6036E from National Instruments) controlled by LabVIEW (National Instruments). Measurements were performed in a standard electrochemical cell with three separate compartments for the RE, CE, and WE. The WE substrate was a glassy carbon disk (Sigradur G from Hochtemperatur Werkstoffe GmbH) mounted in a PFTE holder, and had a geometric area of 0.164 cm². The active part of the WE was prepared by pipetting a 20 μ L aliquot aqueous suspension (2 mg catalyst per mL being constantly sonicated to prevent settling) of carbon-supported Pt (20 wt % Pt on C, E-TEK) onto the glassy carbon substrate. The droplet was dried in a N₂ stream and then another 20 μ L aliquot of dilute, aqueous Nafion solution was added on top to mechanically stabilize the catalyst.¹⁸

The flow cell has been described in more detail elsewhere.¹⁹ The WE, a 9 mm diameter polycrystalline Pt cylinder (MaTecK, 99.95% purity), was mounted into the thin-layer flow cell pressing against an approximately 50 μ m thick spacer exposing 0.283 cm² Pt surface to the thin-layer electrolyte volume. The same potentiostat and data aquisition as for the RDE was used. The electrolyte entered the center of the WE compartment and flowed in a radial pattern over



Figure 1. (Color online) (a) CVs at 5 mV/s in neat 0.1 M H_2SO_4 (– –) as well as in 0.1 M H_2SO_4 + 0.1 M NH₄OH (—) and DEMS data for (b) m/e = 28, (c) 30, and (d) 44, measured using the electrolyte containing ammonium. Thick lines in (b)–(d) are used for positively going sweep, thin lines for negatively going sweep.

the WE towards the edge at a flow rate of approximately 5 μ L/s. The design allows easy electrolyte exchange and flushing while maintaining potential control, enabling adsorbate experiments.

Results

Volatile species formed by oxidation of ammonium.— Potentiodynamic measurements with simultaneous measurements of mass spectra in both sulfuric and perchloric acid solutions were performed. The results are shown in Fig. 1 and 2. Substantial background levels in the DEMS system were present for some of the species of interest, in particular m/e = 14, 28, and 44. The signalto-noise ratio was enhanced using the MS software to average 8 to 16 individual data points. The DEMS data were corrected for background drift, and data from 5–8 different sweeps were averaged to further minimize the noise.

As seen from Fig. 1 and 2, there was a stronger m/e = 28 signal (N₂) in the positively going sweep in the perchloric than in the sulfuric acid solution. The maximum of the m/e = 28 signal appeared at about 0.79 $V_{\rm RHE}$ in both solutions. An N₂ signal of similar magnitude was measured in both solutions at about 0.68 $V_{\rm RHE}$ in negatively going sweeps. The m/e = 14 signal (N) was also monitored in the perchloric solution (see Fig. 2d), and followed the m/e = 28 signal closely. The m/e = 28 signal is thus due to nitrogen evolution.

We also detected an m/e = 30 signal in both solutions, but somewhat stronger in the sulfuric than in the perchloric solution. This signal is attributed to formation of NO at the WE at potentials higher than 1.25 $V_{\rm RHE}$. In alkaline solutions it has been found that nitric oxides (NO and N₂O) were formed at potentials higher than 0.80



Figure 2. (Color online) (a) CVs at 5 mV/s in neat 0.1 M HClO₄ (– –) as well as in 0.1 M HClO₄ + 0.05 M NH₄OH (—) and DEMS data (b) m/e = 28, (c) 30, and (d) 14, measured using the electrolyte containing ammonium. Thick lines in (b)–(d) are used for positively going sweep, thin lines for negatively going sweep.

 V_{RHE} .⁸ The highest NO and N₂O signals were detected at potentials higher than 1.20 V_{RHE} in alkaline solutions compared to about 1.4 V_{RHE} in the acidic solutions studied here.⁸ No m/e = 44 (N₂O) signals were detected in this study, probably due to the high background level.

Coulometry.-- The total charge passed as a function of potential was determined. The net oxidation charge passed during one complete CV cycle was calculated both for the neat 0.5 M sulfuric acid, $Q_{\rm ox}^{\rm acid}$, and for the acid containing 0.5 M ammonium, $Q_{\rm ox}^{\rm NH_4^+}$, for different sweep rates between the potential limits 0.05 and 1.25 $V_{\rm RHE}$. The net oxidation of ammonium in one complete cycle $\Delta Q_{\rm ox}$ is found by $\Delta Q_{\text{ox}} = Q_{\text{ox}}^{\text{NH}_4^+} - Q_{\text{ox}}^{\text{acid}}$, and is shown in Fig. 3a. The influence of the upper reversal potential on the net oxidation charge was also investigated at 50 mV/s as shown in Fig. 3b. The net charge passed in electrolytes containing ammonium was positive, i.e., a net oxidation process was taking place, for upper reversal potentials above 1.0 V_{RHE} . The net oxidation increased with decreasing sweep rate, i.e., longer times at high potentials. This is consistent with the observation of NO evolution in the DEMS experiments. No significant net oxidation current due to N2 evolution at intermediate potentials was seen. The variation in upper reversal limit was performed at a higher sweep rate than in the DEMS experiments (50 vs 5 mV/s). From Fig. 3a we would expect a higher net oxidation charge, consistent with the DEMS data also in the range of N₂ evolution, if a lower sweep rate had been used.

Effect of ammonium concentration.— DEMS measurements were also performed with lower concentrations (data not given here, see Ref. 11). The N₂ signal (m/e = 28) could also be detected in a



Figure 3. (Color online) (a) Difference in net oxidation charge, ΔQ_{ox} , between acid with addition of NH₄OH and neat sulfuric acid during one complete CV cycle at different sweep rates ν reversed at 1.25 V_{RHE} (b) ΔQ_{ox} as in (a), but here with varying upper reversal limits with a fixed sweep rate of 50 mV/s.

0.1 M HClO₄ solution containing 0.025 M NH₄OH. The NO signal (m/e = 30) was detectable in the solution containing 0.01 M NH₄OH but not with 0.05 M NH₄OH. The observed CVs and corresponding EQCM responses for different concentrations of ammonium in 0.5 M H₂SO₄ are shown in Fig. 4a and b, respectively. The mass responses of the electrodes in neat acidic solution seen in our study were similar to data reported by other authors.^{12,13} However, some researchers have reported larger mass changes,^{20,21} mainly in the hydrogen adsorption region, whereas the mass gain in the oxide region was similar in all literature sources; see Ref. 11 for further details.

A shoulder appeared at approximately $0.80 V_{RHE}$ in the CV in the positively going scan; see Fig. 4a. The Pt oxide formation region



Figure 4. (Color online) (a) CV and (b) corresponding EQCM response measured on platinized Pt at 50 mV/s in electrolyte containing 0.5 M H_2SO_4 base electrolyte. The mass response for neat acidic solution is also shown with an offset of 20 ng/cm² for clarity. The legend applies to both plots. Arrows indicate the effect of increasing ammonium concentration. Arrows in the upper part of (b) indicate the path followed by the mass response through one CV cycle.



Figure 5. (Color online) CV recorded at 50 mV/s on platinized Pt in electrolytes with different ammonium and acid concentration to assess the combined effect of pH and ammonium concentration.

was affected so that the onset of oxide formation was less sharp when ammonium was present. There was also a slightly higher oxidation current at potentials above 1.0 $V_{\rm RHE}$ with ammonium present in the solution. The Pt oxide reduction peak at 0.80 $V_{\rm RHE}$ in the negatively going scan decreased with increasing concentration of ammonium, but there was a broad reduction wave following from 0.70 down to 0.50 $V_{\rm RHE}$. The reduction peak for adsorption of strongly bound hydrogen at 0.25 $V_{\rm RHE}$ was affected, and a shoulder appeared at about 0.18 $V_{\rm RHE}$. There was also a slightly higher reductive current at potentials below 0.10 $V_{\rm RHE}$. The hydrogen desorption peaks were not affected by the presence of ammonium.

There was an increasing hysteresis in the EQCM response with increasing ammonium concentration which was particularly noticeable at potentials below 0.90 $V_{\rm RHE}$; see Fig. 4b. A crossover was seen at approximately 0.92 $V_{\rm RHE}$ in the positively going sweep where the adsorbed mass in electrolytes containing ammonium became larger than in the neat acidic solution. The adsorbed mass at high potentials was higher the higher the ammonium concentration was. Also, the adsorbed mass on the electrode was higher in the negatively going sweep, showing that a stable adsorbate was formed at high potentials. This is consistent with the findings in the CV in the same potential range where a higher reductive current was observed. Higher reductive currents have also been seen in the presence of ammonia in alkaline solutions.⁶

Effect of pH on oxidation of ammonium.— Obviously the pH, the ionic strength, as well as the concentration of anions will change upon addition of ammonium hydroxide to the neat acidic solutions which also can affect the behavior of Pt. It is for example likely that ammonium adsorbs as ammonia on Pt through the lone electron pair so that a proton must be released upon adsorption. This means that the pH of the solution will affect the surface coverage of $NH_{3,ads}$ and thus the ammonium oxidation rate; see Eq. 2 in the Gerischer-Maurer mechanism. Two sets of experiments were made to evaluate this. First, NaOH was added to neat sulfuric acid instead of NH_4OH . The CV and corresponding EQCM response, which are not shown here, were very similar to those seen in neat acidic solution. This indicates that the effect of pH, ionic strength, and increased concentration of (bi)sulfate alone on the observable CVs and EQCM data is small.

In the second measurement 0.5 M NH₄OH was added to the neat 0.5 M sulfuric acid electrolyte. Then, an additional amount of sulfuric acid equivalent to 0.5 M was added; see Fig. 5. The effect of ammonium was partially reversed by addition of more acid to the 0.5 M H₂SO₄ + 0.5 M NH₄OH solution. However, there was still a significant influence of ammonium compared to the neat acidic so-



Figure 6. (Color online) (a) CVs of Pt in 0.5 M HClO₄ + 0.25 M NH₄OH at 50 mV/s with different upper reversal potentials. Refer to the text for explanation of arrows and numbers. (b) Detail of the CVs in the hydrogen adsorption region; the arrows indicate the effect of increasing reversal potential. Upper reversal potentials from 0.6–1.1 $V_{\rm RHE}$ are shown. Similar behavior was also seen in sulfuric acid solution (Ref. 11), but is not included here.

lution, suggesting that there is a combined effect of ammonium concentration and pH. The change in pH and ammonium concentration was accompanied by changes in ionic strength and concentration of (bi)sulfate as well, so that the three factors cannot be separated by these experiments.

Effect of the upper reversal potential.— The upper reversal potential was also an important parameter; see Fig. 6. The CV in the positively going scan was not affected by the reversal potential, i.e., the electrode surface was fully restored in the negatively going scan, also independently on the applied scan rate as discussed later; see Fig. 9. There was no effect of reversal potential on the hydrogen adsorption features in neat acidic solutions.¹¹

The peak potential for peak "1" occurred at a slightly higher potential in the sulfuric acid system (0.81 V_{RHE}) compared to perchloric acid (0.76–0.80 V_{RHE}). The peak potential was slightly dependent on sweep rate, especially in the perchloric acid system (+30 mV shift in the positive direction when increasing the sweep rate one decade).¹¹ Note that this peak occurred at the same potential as where nitrogen evolution was observed by DEMS; see Fig. 2.

Two reduction peaks were visible in the reverse scan in perchloric solutions at high potentials ("2" and "3" in Fig. 6a). Peak 3 was associated with the reduction of Pt oxides, occurring at 0.80–0.81 $V_{\rm RHE}$ consistent with our observations in neat perchloric acid.¹¹ The Pt oxide reduction peak was more rounded and also smaller in the presence of ammonium. We propose that peak 2 is associated with peak 1 forming an adsorbed surface redox couple in the system as further discussed below. Peak 2 occurred at 0.66–0.67 $V_{\rm RHE}$, at the same potential where N₂ formation was found by DEMS in negatively going sweeps; see Fig. 2.

Different reversal potentials were also applied in sulfuric acid containing ammonium as shown in Fig. 7. Peaks 1 and 2 were not observable in sulfuric acid solutions at 50 mV/s sweep rate. There was a clear effect of ammonium on the hydrogen adsorption region as shown in Fig. 7b. More reduction charge was passed at potentials below 0.2 $V_{\rm RHE}$ as the reversal potential increased. This was also seen in the perchloric acid system. However, increasing the reversal potentials in the hydrogen adsorption region. The influence of the reversal potential indicates that at least some of the effects in the hydrogen adsorption region generate the hydrogen adsorption peaks are all identically independent upon the upper reversal potential because the species causing the changes in the hydrogen adsorption region are reduced and removed at low potentials.



Figure 7. (Color online) (a) CVs of platinized Pt in $0.5 \text{ M H}_2\text{SO}_4$ + 0.5 M NH₄OH at 50 mV/s. (b) Details of the CVs in the hydrogen adsorption region; the arrows indicate the effect of increasing reversal potential. Upper reversal potentials from 0.6–1.5 V_{RHE} are shown.

EQCM data were also recorded with different upper reversal potentials in sulfuric solutions as shown in Fig. 8. The mass changes seen in the low potential region were not directly due to adsorption of hydrogen because the mass change due to this process is only about 2.3 ng/cm²,¹⁴ and also we find a decrease in mass detected by EQCM upon hydrogen adsorption. Most likely the mass changes in this region are due to desorption of water or specifically adsorbed anions like (bi)sulfate.¹⁴ Further, there was a more noticeable hysteresis between the positively and negatively going sweeps in the double-layer region when ammonium was present commencing at 0.30 $V_{\rm RHE}$; see also Fig. 4b. These species were not formed electrochemically because there was no differences in current in the positively going CVs compared to neat acidic solutions. The mass data measured by EQCM in neat acidic solution are shown for comparison in Fig. 8, and do not show any hysteresis for reversal potentials below 0.60 $V_{\rm RHE}$. The adsorbed mass in positively going sweeps was not dependent on the upper reversal potential used, which is consistent with our observation that the CV in the positively going scan is not affected either.

Effect of sweep rate.— The effect of sweep rate on the CVs both in sulfuric and perchloric acid was assessed, and the data for the sulfuric acid are shown in Fig. 9. In neat acid the only difference is in the oxide region where the amount of Pt oxides formed and reduced decreases with increasing sweep rate. In electrolytes containing ammonium, formation of Pt oxides at high potentials also de-



Figure 8. (Color online) EQCM data for Pt in 0.5 M H_2SO_4 + 0.5 M NH_4OH at 50 mV/s at different upper reversal potentials. The EQCM data measured with neat 0.5 M H_2SO_4 are also shown for comparison with an offset of 5 ng/cm² for clarity.



Figure 9. (Color online) The effect of the applied sweep rate on the differential capacitance (i.e., current divided by the sweep rate) in (a) neat 0.5 M H_2SO_4 and in (b) 0.5 M $H_2SO_4 + 0.5$ M NH_4OH . The arrows indicate the effect of increasing sweep rate. The sweep rates used were 500, 200, 100, 50, 20, 10, and 5 mV/s.

creases with increasing sweep rate, but the Pt oxide reduction peak is independent of sweep rate. The peak in front of the Pt oxide formation decreases with increasing sweep rate, as does the reduction shoulder in the double-layer region in the negatively going scans. The peak related to formation of H_{UPD} at about 0.25 V_{RHE} is less suppressed at slower sweep rates, indicating that the removal of adsorbates formed at higher potentials suppressing H_{UPD} is a slow process. Formation of the adsorbed species related to peak 1 is also slow as the peak is not seen at high sweep rates, see Fig. 9.

Time derivative of the mass response.— The time derivative of the mass changes for neat 0.5 M H_2SO_4 and acid with 0.5 M NH_4OH added is shown in Fig. 10. The curves shown are the average of five different measurements to lower the noise. The mass gain rate in the double-layer region in the positively going sweep was slightly lower for the electrolyte containing ammonium. Notice that there was a slightly higher rate of mass increase in the region 0.8–1.0 V_{RHE} in the positively going sweep in the electrolyte containing ammonium. Also, there was a slightly lower rate of mass loss in the oxide reduction peak in the negatively going scan. Further, the mass loss rate associated with the adsorption of the most strongly adsorbed hydrogen was lower in the electrolyte containing ammonium. However, there was a significantly higher mass loss rate in the region between the two hydrogen adsorption peaks. The rate of mass



Figure 10. (Color online) Time derivative of the EQCM data for neat 0.5 M H_2SO_4 and with additions of 0.5 M NH_4OH recorded at 50 mV/s. The data shown are the average of five data sets for each solution followed by a numeric 9-point Savitzky-Golay filter (Ref. 22).



Figure 11. (Color online) CV performed at 5 mV/s on an RDE with carbonsupported Pt (20 wt % Pt/C, E-TEK) in 0.50 M HClO₄ + 0.25 M NH₄OH at room temperature with no rotation (solid line) and with 1000 rpm (dotted line).

loss in electrolyte containing ammonium was also higher in the range 0.12–0.08 V_{RHE} in the negatively going scan.

RDE and flow cell experiments.— RDE experiments were performed to clarify if adsorbed or solution species were responsible for features 1 and 2 observed in CVs measured in ammonium containing electrolyte. If the species in question is a solution species, peak 2 in the negatively going scan should be strongly minimized when applying rotation. As is evident from Fig. 11 this is not the case, and the species responsible for peaks 1 and 2 in Fig. 6 is thus an adsorbed species.

A flow cell was used to study peaks 1 and 2 shown in Fig. 6. The WE was held at 0.60 $V_{\rm RHE}$ for 4 min while 0.5 M HClO₄ + 0.25 M NH₄OH flowed through the cell at a rate of 5 μ L/s. After this adsorption period, neat 0.5 M HClO₄ was flushed through the cell to rinse out ammonium, and a positively going scan was then initiated. The scan limits were 0.55–0.82 $V_{\rm RHE}$ in the first four sweeps, thereafter sweeping up to 1.15 $V_{\rm RHE}$ and down to 0.06 $V_{\rm RHE}$. This is compared to the same adsorption experiment, but where the four intermediate cycles were not performed. From the



Figure 12. (Color online) Adsorption in 0.5 M HClO₄ + 0.25 M NH₄OH at 0.60 V_{RHE} for 4 min followed by a positively going scan. The dotted line is the CV in neat 0.5 M HClO₄ electrolyte, the thin, black solid line is the first scan between the intermediate scan limits (0.55–0.82 V_{RHE}), the thick black line is measured after the four intermediate scans shown in the insert. The gray solid line was measured when not performing the intermediate scans. The flow rate of both electrolytes was 5 μ L/s and a polycrystalline Pt electrode was used.

insert in Fig. 12 it is clearly seen that the peaks 1 and 2 decrease rapidly with each scan in the narrow range. Further, note that the scans between the intermediate scan limits only affect peaks 1 and 2 in the following complete stripping scan as compared to the stripping scan where no intermediate scans were performed.

Discussion

Effects on hydrogen desorption and the double-layer region in positively going sweeps.— The hydrogen desorption peaks are not affected by the presence of ammonium. This shows that all adsorbed species are removed in the negatively going scan so that the effect of ammonium in the positively going scan is not initially noticeable. This was also reported by de Vooys et al.⁶ in alkaline solution. Further, there is no difference between CVs measured in neat acidic solutions and acids containing ammonium in the double-layer region in the positively going scan. Thus, electrochemical formation of adsorbed species does not take place at potentials below 0.65 $V_{\rm RHE}$, and oxidation of ammonium commences only at about 0.65 $V_{\rm RHE}$. A significant oxidation current was observed at potentials as low as 0.45 $V_{\rm RHE}$ in alkaline solutions.^{7,8}

EQCM data show that an adsorbed species is formed at potentials above 0.25 V_{RHE} because the hysteresis of the mass response increased upon addition of ammonium; see Fig. 8. We propose that this is adsorption of bisulfate stabilized by ammonia as also reported for Pt(111) by Shingaya et al.²³

Presence of a redox couple.— Peaks 1 and 2 in Fig. 6 coincide with the N₂ peaks seen in the DEMS measurements in positively and negatively going scans, respectively; see Fig. 1b and 2b. It is therefore likely that these peaks are associated with nitrogen evolution. The ratio between the MS signal and the faradaic current was calibrated from measurements of ammonia oxidation in alkaline solution (data not shown here). This calibration accounts for collection efficiency, ionization probability in the MS, as well as other factors influencing the signal strength in the DEMS. We estimate that the N₂ signal in the positively going scan accounts for less than 10% of the current. This shows that the charge associated with peak 1 is mainly due to a different reaction than N2 evolution, i.e., formation of an adsorbed intermediate species in the ammonium oxidation process as further discussed below. Further, it is likely that peak 2 represents reduction of the species formed in peak 1 in the positively going sweep. A closer inspection of the EQCM mass response in Fig. 4b and 10 reveals that the mass of the WE increases faster in ammonium containing solution than in neat acid solution in the positively going sweep in the range 0.75–0.95 $V_{\rm RHE}$, possibly caused by adsorption of the species involved in peak 1. Further, CVs recorded with and without rotation shown in Fig. 11 in an RDE cell were identical, showing that the species is adsorbed.

The results in Fig. 12 show that the adsorbate formed at 0.60 $V_{\rm RHE}$ is actively taking part in the process related to peaks 1 and 2. The peaks decreased when sweeping back and forth with the narrower potential limits. This reduction can partly be due to evolution of N₂ thus consuming the adsorbate, or due to other processes where other volatile or soluble species are formed. We see it as unlikely that the peaks are due to formation-reduction of Pt oxides, as the Pt oxide formation and reduction at higher potentials is not affected by the species responsible for peaks 1 and 2. This is concluded from the fact that the CVs are identical at higher potentials independent of if the sweeps between the narrow potential limits are performed or not. Peak 1 is more noticeable in perchloric than in sulfuric acid (see Fig. 6 and 7) probably also because (bi)sulfate adsorbes more efficiently on Pt, thus partially blocking the surface for adsorption of other species which in turn is reflected in the lower N₂ yield in sulfuric compared to perchloric acid.

The nature of the species has not been identified, nor the chemical reactions that yield the species responsible for peaks 1 and 2. The observation of N_2 evolution at the same potentials as peaks 1 and 2, however, indicates that the species is related to the mechanism leading to N_2 evolution. Based on the Gerischer and Mauerer mechanism, it seems natural to assume that the adsorbed species could be N_{ads} formed from $NH_{x,ads}$ in the positively going sweep. Future studies, including techniques such as Fourier transform infrared, may be helpful to resolve this matter.

Formation of N_{ads} was also reported by de Vooys et al.⁶ for alkaline solutions but then in the potential range 0.4–0.6 $V_{\rm RHE}$. It is not clear if N_{ads} would be further oxidized at high potentials. In the reverse sweep, N_{ads} may be reduced, forming either nitrogen via NH_{x,ads} with no net faradaic current, or reductively formed ammonium as reported by Gootzen et al.⁷ in alkaline solution. Adsorbates resulting from NO exposure is only reduced at potentials below 0.25 $V_{\rm RHE}$.⁹

The N_2 signal in the DEMS in the negatively going sweep is very similar both in perchloric and sulfuric acid electrolytes; see Fig. 1 and 2. This indicates that the source of N_2 formation in the negatively going sweep is an adsorbed species with similar surface coverage in both sulfuric and perchloric acid containing ammonium.

Effects on platinum oxides.— The Pt oxide formation and reduction is significantly affected by the presence of ammonium. The onset of Pt oxide formation is less sharp compared to neat acidic solution; see Fig. 4a. There is a significantly higher oxidation current at potentials above 1.0 $V_{\rm RHE}$ in the presence of ammonium. Formation of NO was seen by DEMS only at potentials above 1.2 $V_{\rm RHE}$; see Fig. 1c and 2c.

The Pt oxide reduction peak appearing at about 0.8 V_{RHE} is shifted negatively in the presence of ammonium; see Fig. 4a. However, the most noticeable effect of ammonium is that the charge associated with the Pt oxide reduction peak is almost independent of sweep rate, in contrast to what is found in neat acid where the peak decreases with increasing sweep rate, Fig. 9. The charge associated with the Pt oxide reduction peak is also much smaller than in the neat acidic solution. Similar observations were made by Wasmus et al.⁸ and Gootzen et al.⁷ in alkaline electrolytes. This indicates that the amount of "normal" Pt oxides formed is limited by another adsorbed surface species. Figure 12 shows that the adsorbed species responsible for peaks 1 and 2 is not responsible for the changes observed in the oxide region.

Adsorbed N-O species could also be present. Detection of NO by DEMS at high potentials (see Fig. 1 and 2) suggests the presence of adsorbed N-O species at high potentials. de Vooys et al.⁶ proposed that metal oxynitrides are present on the Pt surface in alkaline solutions containing ammonia at high potentials, and further proposed that the oxynitride species were very stable and inactive in the formation of NO and N₂O observed. Wasmus et al.⁸ found, when sweeping from high to low potentials, that nitric oxides were evolved at low potentials and explained this by reduction of highly oxidized nitrogen species formed at high potentials.

Effects in the double-layer region in negatively going scans.— A substantially higher reduction current was found in the doublelayer region in negatively going sweeps in the presence of ammonium than in neat acidic solutions. The reductive current increases with ammonium concentration (Fig. 4a) and upper reversal potential (Fig. 6 and 7), whereas it decreases with increasing sweep rate; see Fig. 9. We propose that less adsorbed species are formed in the positive scan at high sweep rate, whereas more adsorbed species are formed at high ammonium concentration and also with higher reversal potentials. The reduction charge in the double-layer region is also much higher in alkaline solutions containing ammonia than in neat alkaline solutions,^{7,8} suggesting that the same species are formed in alkaline solutions.

Effects on hydrogen adsorption.— There is a significant effect on the hydrogen adsorption peaks when ammonium is present in the solution. The most marked effect is that the peak at 0.25 V_{RHE} associated with the most strongly bound hydrogen is shifted to lower potentials. This effect is more pronounced with increasing ammonium concentration (see Fig. 4a), increasing upper reversal potential

for the CVs in the (bi)sulfate system (see Fig. 7), and higher sweep rates (see Fig. 9). The effect on the most strongly adsorbed hydrogen in the perchloric system is small; see Fig. 6. Shingaya et al.²³ found that ammonia and bisulfate coadsorbes

on Pt(111), i.e., ammonia and bisulfate mutually stabilize each other so that they desorb at lower potentials than in neat acidic solution, thus shifting formation of strongly adsorbed hydrogen to lower potentials. It is also known that the peak associated with the most strongly adsorbed hydrogen is strongly affected by adsorption of bisulfate.²⁴ The findings of Shingaya et al.²³ are very similar to our findings; the effect on the most strongly bound hydrogen peak is noticeable even at quite low upper reversal potentials (0.80 $V_{\rm RHE}$; see Fig. 7), and the effect is more pronounced at higher sweep rates; see Fig. 9b. For 0.1 M HF containing 0.01 M ammonium, Shingaya et al. reported very small effects on the hydrogen adsorption features. 23 This is in line with our observations in perchloric acid where the effect of ammonium on strongly adsorbed hydrogen is much smaller than in sulfuric acid.

At potentials below 0.15 $V_{\rm RHE}$ the reduction current increases with increasing reversal potential both in sulfuric and perchloric acid solutions containing ammonium; see Fig. 6 and 7. The EQCM data show that there is a mass loss on the EQCM which is not seen in neat acidic solution in the potential region $0.12-0.08 V_{\text{RHE}}$ in the negatively going scan; see Fig. 10. Wasmus et al.8 reported formation of N₂, NO, and N₂O at these low potentials in their alkaline electrolyte. We suggest that a similar desorption reaction occurs in our acidic system where a highly oxidized, very stable adsorbed nitrogen species is reduced to form either nitrous oxides, N2, or ammonium, or possibly all these species. Removal of these species is relatively slow, as seen by the fact that the effect on formation of strongly bound $\mathrm{H}_{\mathrm{ads}}$ at about 0.25 V_{RHE} is less pronounced when applying lower sweep rates; Fig. 9b.

Conclusions

We have found that ammonium is electrochemically active in acidic solutions at room temperature, but the oxidation is slow. CV and EQCM data show that presence of ammonium affects the formation and reduction of Pt oxide at high potentials involving the formation of very stable nitrogen or nitrogen-oxygen species. Some of these species are removed from the electrode only at very low potentials in the hydrogen adsorption region, and removal of these species is slow. An oxidation peak occurs in positively going scans at about 0.8 $V_{\rm RHE}$, which decreased strongly with increasing sweep rate, and a corresponding reduction shoulder at about 0.66 $V_{\rm RHE}$ is seen which could be due to formation of $NH_{x,ads}$ species on the surface. Formation of Pt oxides is shifted to slightly higher potentials in the presence of ammonium, and the charge of the normal Pt oxide reduction peak observed at about 0.80 $V_{\rm RHE}$ is independent on sweep rate, indicating the amount of normal Pt oxides formed is limited by other adsorbates.

The hydrogen adsorption region is strongly affected by ammonium, in particular the most strongly adsorbed hydrogen, the formation of which is shifted to lower potentials. Both species formed at very high potentials as well as coadsorption of ammonia and bisulfate on Pt are responsible for the shift of hydrogen adsorption to lower potentials. The observation that the most strongly adsorbed hydrogen is less negatively shifted in perchloric acid also shows that there is an anion effect in the sulfuric acid system due to coadsorption of ammonia and (bi)sulfate. The hydrogen desorption region is not affected by ammonium in either acidic solution, showing that the electrode surface is fully restored in the reductive scan.

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