

# THE EFFECT OF PREADSORBED SULFUR ON NITRIC OXIDE REDUCTION ON POROUS PLATINUM BLACK ELECTRODES

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**Abstract**—Sulfur can be deposited on porous platinum black gas diffusion cathodes to influence the course of the electrogenerative reduction of nitric oxide. Polarization (performance) curves and reactor selectivity data are compared for untreated cathodes and those treated with reduced SO<sub>2</sub>. Pure and dilute nitric oxide cathode feeds were used. With pure nitric oxide, the limiting current corresponding to nitrous oxide production was reduced 65% by preadsorbed sulfur. With dilute nitric oxide the two limiting currents observed were only slightly decreased by sulfur deposition. With both feeds adsorbed sulfur affects product distribution at low cell potentials so that hydroxylamine production is favored. The surface of the platinum black electrodes was characterized by hydrogen adsorption, and sulfur coverages on treated electrodes were determined by cyclic voltammetry in a separate three-electrode cell. The results from electrogenerative reduction are discussed in terms of steric and mechanistic consequences of sulfur coverages.

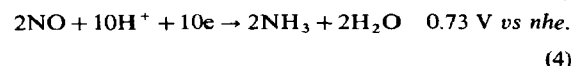
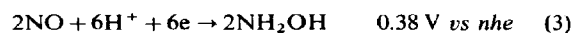
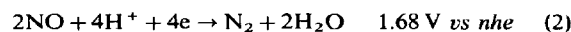
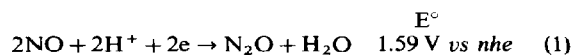
## INTRODUCTION

This work is part of an effort directed toward ascertaining and understanding the effects of surface addends on the electrochemical reduction of nitric oxide at porous platinum black-Teflon gas diffusion electrodes in connection with studies of electrogenerative processes. It is well known that various surface adsorbates, including sulfur, can act as catalyst modifiers, affecting a number of surface reactions [1-6]. The efficacy of electrogenerative (i.e. galvanic) nitric oxide reduction at unmodified electrodes has been demonstrated [7-9] and advantages of this mode of operation with respect to various applications have been discussed [8, 10, 11]. The effect of adsorbed sulfur on this system has been chosen for initial study here because of earlier promising results [8, 9] in which sulfur dioxide introduced into the nitric oxide feed and reduced onto the electrode appeared to favorably alter the selectivity of the reactor, but have a limited effect on overall nitric oxide conversion. Moreover, sulfur adlayers can be readily and reproducibly deposited and are resistant to chemical dissolution [eg 12].

Sulfur deposition in this study was performed through the reduction of adsorbed sulfur dioxide; electrogenerative cells were operated with both untreated and sulfur-treated platinum black-Teflon gas diffusion cathodes under controlled conditions to determine the effect of this preadsorbed sulfur on the cell performance and product distribution. Both pure and dilute nitric oxide (2.7% in nitrogen) were used as cathode feeds while hydrogen was employed at the anode. Sulfur coverages on the pretreated platinum black electrodes were determined by electrochemical methods in a separate three-electrode voltammetry cell.

## PREVIOUS WORK

The electroreduction of nitric oxide at a platinum surface in acid media has been extensively studied [13 and references therein]. Generally, four products can be observed corresponding to the following cathodic half-cell reactions:



The selectivity of the reduction is dependent on electrode potential, with N<sub>2</sub>O formation predominating at high cell potentials ( $E_{\text{cell}} > 0.6 \text{ V}$ ) and nitrogen, hydroxylamine and ammonia formation occurring below about 0.4 V [7]. The electrode surface state (i.e. oxide, bare metal or hydrogen-covered) also appears to be a significant factor [13, 14].

While the reaction of nitric oxide on clean metal surfaces has received attention, relatively little effort has been devoted to determining the effects of surface adsorbates on nitric oxide reactivity. In 1978 Fischer and Kelemen [15] studied the effect of adsorbed sulfur on NO and CO adsorption, and NO + CO reaction on Pt(100) single crystals. They found that a C(2 × 2) saturation sulfur coverage blocked NO adsorption. Lower coverages permitted NO adsorption on the free surface sites while inhibiting NO dissociation. Interpretation of these and related results involved both steric and electronic effects.

Matsumoto *et al.* [16] studied the effect of adsorbed sulfur on NO adsorption and dissociation on a polycrystalline Pd foil. In agreement with Fischer and

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Kelemen they observed facile NO adsorption on free sites at submonolayer sulfur coverages, with NO dissociation occurring only at low sulfur coverages ( $\theta_S < 0.3$ ). Similar results were obtained recently by Jorgensen *et al.*[17] for NO adsorption on Pd(100) in the presence of adsorbed sulfur.

In addition to the high-vacuum gas phase studies above, Pate and Langer reported on the effects of SO<sub>2</sub> and CO on the electrogenerative reduction of nitric oxide on Pt black electrocatalysts[9]. They found that while these catalyst inhibitors decreased nitric oxide reduction to some extent, reactor operation was still feasible[7]. They also noted that the presence of SO<sub>2</sub> or CO in the reactor feed altered selectivity to favor hydroxylamine production rather than ammonia. Hydroxylamine current efficiencies (that fraction of the total generated current which can be attributed to hydroxylamine production) were as high as 74% with a 45:55 CO:NO reactor feed, though in this extreme case NO conversions were relatively low (*ca* 20%). This compares to NH<sub>2</sub>OH efficiencies of 2–5% from pure NO feeds[7, 18]. These results were interpreted in terms of competitive CO adsorption and its effects on proposed N<sub>2</sub>O<sub>2</sub> surface dimers.

### EXPERIMENTAL EQUIPMENT AND PROCEDURES

Cell experiments reported here utilize high surface area platinum black electrodes in an electrogenerative (*ie* galvanic) configuration[7, 8, 10]. The cell consists of two platinum black electrodes (American Cyanamid type LAA-2, 5.07 cm<sup>2</sup> geometric area) separated by a barrier electrolyte phase (3M H<sub>2</sub>SO<sub>4</sub> prepared from Fisher concentrated H<sub>2</sub>SO<sub>4</sub> and deionized water). Cell components and supporting electrical equipment are shown in Fig. 1. The same hydrogen anode was used with all cathodes. The cell components were machined from Kel-F. During operation, the cathode feed was introduced to the cathode gas chamber, and hydrogen at one atmosphere was fed to the anode. Pure nitric oxide (Matheson CP grade) and 2.7% NO in N<sub>2</sub> (Matheson Certified Standard) served as cathode feeds in these experiments. Higher nitrogen oxides were removed from the feed stream by passage through a column of solid NaOH immersed in an acetone/dry ice bath.

Gas feed and product analyses to determine the reactor selectivities at various cell potentials were carried out with a six-foot Porapak Q gas chromatographic column at room temperature. This provided sufficient resolution of N<sub>2</sub>, NO and N<sub>2</sub>O. Ammonia and hydroxylamine levels in the electrolyte were determined by a standard colorimetric method[19, 20], and a recently developed gas chromatographic method[21], respectively.

Sulfur treatment of the platinum black cathode consisted of soaking a clean electrode in SO<sub>2</sub>-saturated 1M H<sub>2</sub>SO<sub>4</sub> overnight, followed by careful washing and one-half hour at a constant potential of 0.0 V *vs* rhe in the cell with clean (SO<sub>2</sub>-free) electrolyte. This pre-reduction step was part of the typical activation procedure carried out with every electrode (treated and untreated) before polarization curves were obtained. Some experiments were performed using a two-stage

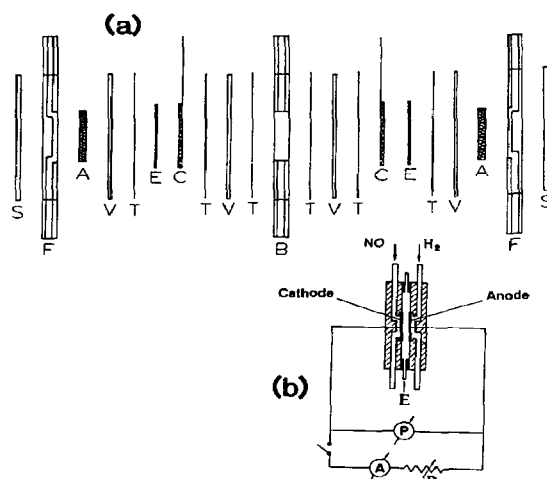


Fig. 1. (a) Exploded view of electrogenerative cell with components. S = 1/16" stainless steel support plate; F = Kel-F face plate; A = polypropylene spacer; V = Viton gasket, 0.19 mm thick; T = Teflon gasket, 2 mil thick; E = American Cyanamid LAA-2 platinum black-Teflon gas diffusion electrode, 1.125" diameter; C = 45 mesh platinum screen current collector; B = Kel-F electrolyte chamber, 3/16" thick. Assembly is held together with four stainless steel bolts. (b) Assembled electrogenerative cell in working configuration. E = electrolyte (3M H<sub>2</sub>SO<sub>4</sub>); P = voltmeter; A = ammeter; R = variable resistor. NO designates cathode feed inlet; either pure NO or dilute NO (2.7% in balance N<sub>2</sub>—see text).

pretreatment procedure. After the SO<sub>2</sub> soak (first stage), the electrode was soaked in freshly prepared 1M H<sub>2</sub>SO<sub>4</sub> for 18 h (second stage) before reduction. This second stage presumably removed any weakly-bound or trapped SO<sub>2</sub> from the highly porous electrode, and assured that only specifically-adsorbed SO<sub>2</sub> remained during the reduction step.

Sulfur layers were characterized using cyclic voltammetry[12, 22, 23] in a 250 ml standard high purity 3-electrode glass cell which was specially modified to hold a 1 inch diameter gas diffusion electrode. A Princeton Applied Research (PAR) model 175 Universal Programmer and a PAR 173 potentiostat were used in the generation and control of the electrode potential program, respectively. The electrolyte was 0.5M H<sub>2</sub>SO<sub>4</sub> prepared from Baker Ultrex ultrapure H<sub>2</sub>SO<sub>4</sub> and quadruply-distilled water and was deaerated with purified nitrogen. A platinum spiral served as the counter electrode and the reference electrode was a saturated calomel electrode (*sce*) filled with aqueous saturated NaCl exhibiting a constant potential of 0.264 V *vs* a reversible hydrogen electrode in the same electrolyte. The sulfur pretreated electrode was cycled repeatedly between 1.0 and -0.2 V *vs sce* at 0.5 V min<sup>-1</sup> and the voltammetric currents were digitally integrated using a Bascom-Turner model 4110 digital recorder. The overall sulfur oxidation charge was obtained using methodology commonly employed[12, 22–24] and explained below.

Table 1. Sulfur oxidation data for Pt LAA-2 gas diffusion electrode pretreated with reduced SO<sub>2</sub>

Cycle #	Q <sub>S,ox,i</sub>	Σ <sub>i</sub> Q <sub>S,ox,i</sub>	Q <sub>H,ox</sub>	θ <sub>S,i</sub>
0	—	—	—	0.996
1	2.867	2.867	0.010	0.705
2	2.233	5.100	0.110	0.478
3	1.696	6.796	0.540	0.306
4	1.068	7.864	0.900	0.197
—	—	—	—	—
—	—	—	—	—
13	0.011	9.803	1.604	0.001
14	0.002	9.805	1.611	0.000
15	0	9.805	1.640	0
16	0	9.805	1.640	0

Q<sub>S,ox,i</sub> = Sulfur oxidation charge for single cycle, coulombs

Σ<sub>i</sub>Q<sub>S,ox,i</sub> = Summation of sulfur oxidation charges through cycle *i*, coulombs

Q<sub>H,ox</sub> = Hydrogen oxidation charge for each cycle, coulombs

θ<sub>S,i</sub> = Sulfur coverage at end of indicated cycle *i*; θ<sub>S,i</sub> = 0.996 (1 - Σ<sub>i</sub>Q<sub>S,ox,i</sub>/9.805), where 0.996 is the initial sulfur coverage from equation (6).

## RESULTS

### Electrogenerative cell experiments

The effect of sulfur treatment on electrogenerative cell performance using both pure and dilute nitric oxide (2.7% in nitrogen) was investigated. The effect of sulfur on polarization (performance) curves of the pure nitric oxide cell can be seen in Fig. 2, where the curves obtained both with and without sulfur treatment of the electrode are shown. The open circuit voltage of the untreated cell is *ca* 0.94 V. Both curves exhibit limiting current behavior between 0.6 and 0.4 V, which is characteristic of these types of cells[7, 18]. This limiting current corresponds to the one-electron reduction of NO to N<sub>2</sub>O[7, 13] taking place in the platinum double layer region. These curves demonstrate that, while preadsorbed sulfur does diminish the rate of NO

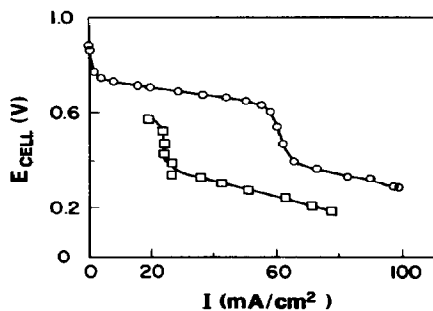


Fig. 2. Effect of reduced SO<sub>2</sub> on polarization curve for electrogenerative cell; cathode feed 100% NO at 5.1 cc/min. o is untreated cathode, □ is reduced SO<sub>2</sub>-treated cathode (see text). Anode and cathode are American Cyanamid Pt LAA-2 platinum black-Teflon gas diffusion electrodes. Electrolyte is 3 M H<sub>2</sub>SO<sub>4</sub>.

reduction (*ie* the cell current), significant reaction still occurs, the limiting current being reduced by about 65%.

The effect of sulfur on the product distribution from the pure NO cell is pronounced. Current efficiency (C.E.) plots for the untreated and sulfur-treated cells are shown in Figs 3 and 4, respectively. Here, current efficiency is defined as that fraction of the total cell current which is utilized for production of a designated product. The most striking effect of sulfur treatment is observed at low cell potentials. For an untreated cell the primary products in this potential range are ammonia and dinitrogen (C.E.<sub>NH<sub>2</sub>OH</sub> ≈ 3%), whereas with sulfur deposited on the cathode hydroxylamine predominates (C.E.<sub>NH<sub>2</sub>OH</sub> ≈ 80%) and dinitrogen is not produced. At potentials above 0.6 V all cells produced N<sub>2</sub>O, consistent with earlier findings[7]. Current accountabilities and nitrogen balance closures were consistently within 10%.

The effect of sulfur treatment on the performance of cells with dilute NO (2.7% in balance N<sub>2</sub>) cathode feeds is illustrated in Fig. 5. Two limiting currents, one at low and one at high current, are observed. This type

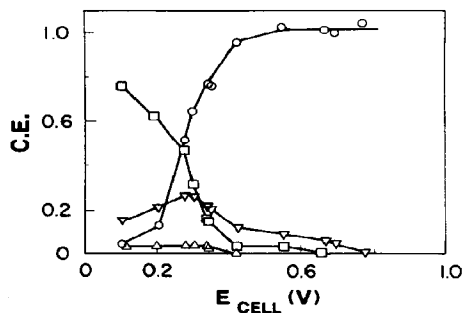


Fig. 3. Current efficiency (C.E.) as a function of cell potential for untreated platinum black cathode with pure NO feed at 5.1 cc/min. Anode feed is excess hydrogen. o = N<sub>2</sub>O; ∇ = N<sub>2</sub>; Δ = NH<sub>2</sub>OH; □ = NH<sub>3</sub> formation. Electrolyte is 3 M H<sub>2</sub>SO<sub>4</sub>. Cell potential was controlled by decreasing the cell load stepwise. Cell internal resistance 0.34 ohms.

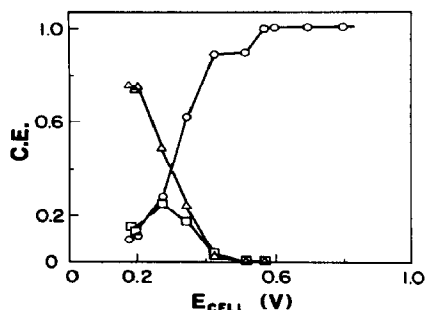


Fig. 4. Current efficiency as a function of cell potential for SO<sub>2</sub>-treated platinum black cathode; pure NO feed at 5.1 cc/min. O = N<sub>2</sub>O; Δ = NH<sub>2</sub>OH; □ = NH<sub>3</sub>. No dinitrogen formation was detected. Electrolyte was 3 M H<sub>2</sub>SO<sub>4</sub>. Cell internal resistance 0.26 ohms.

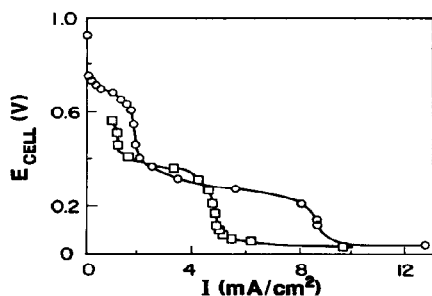


Fig. 5. Effect of reduced  $\text{SO}_2$  on polarization curve for electrogenerative cell; cathode feed 2.7%  $\text{NO}$  in  $\text{N}_2$ . Total feed flow is 5.2 cc/min.  $\circ$  = untreated cathode,  $\square$  =  $\text{SO}_2$ -treated cathode. Anode and cathode are American Cyanamid Pt LAA-2 porous platinum black-Teflon gas diffusion electrodes. Electrolyte is 3 M  $\text{H}_2\text{SO}_4$ .

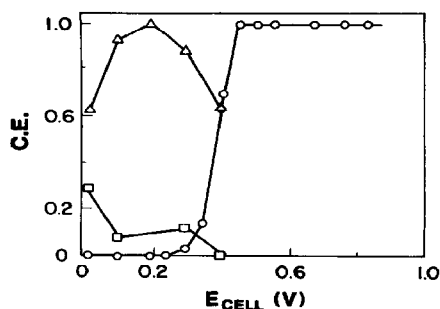


Fig. 7. Current efficiency as a function of cell potential for reduced  $\text{SO}_2$ -treated platinum black cathode; feed is 2.7%  $\text{NO}$  in  $\text{N}_2$  (5.2 cc/min).  $\circ$  =  $\text{N}_2\text{O}$ ;  $\Delta$  =  $\text{NH}_2\text{OH}$ ;  $\square$  =  $\text{NH}_3$ . Electrolyte is 3 M  $\text{H}_2\text{SO}_4$ . Cell internal resistance is 0.26 ohms.

of behavior, though common for electrolytic nitric oxide reduction experiments[13, 25–28], has not been previously reported for electrogenerative (galvanic) cells; it appears to be due to limiting production of a second, more reduced nitrogen compound. The sulfur treatment has the effect of decreasing both limiting currents slightly and accentuating the second (higher) one. The ratio of the high limiting current to the low limiting current is 5.0 for the untreated cell and 4.2 for the sulfur-treated cell. Since the first limiting current is due to the one-electron reduction to  $\text{N}_2\text{O}$ [7, 13], this result suggests that the untreated cell produces mostly ammonia (equation 4) and that the treated cell produces more hydroxylamine (equation 3).

The hypotheses above are confirmed by the product analyses, the results of which are shown in Figs 6 and 7 for the untreated and sulfur-treated cathodes, respectively. These results resemble those found with pure nitric oxide cathode feeds: sulfur deposition results in an increase in  $\text{NH}_2\text{OH}$  selectivity at the expense of ammonia and nitrogen production. In Fig. 6 dinitrogen efficiency was calculated by difference, assuming 100% current accountability, since the nitrogen diluent made actual  $\text{N}_2$  determinations difficult. The

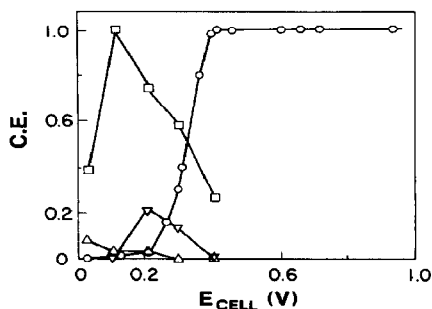


Fig. 6. Current efficiency as a function of cell potential for untreated platinum black cathode; feed is 2.7%  $\text{NO}$  in  $\text{N}_2$  (5.2 cc/min).  $\circ$  =  $\text{N}_2\text{O}$ ;  $\nabla$  =  $\text{N}_2$  (calculated by difference);  $\Delta$  =  $\text{NH}_2\text{OH}$ ;  $\square$  =  $\text{NH}_3$ . Significant  $\text{H}_2$  production at cathode observed below 0.1 V. Electrolyte is 3 M  $\text{H}_2\text{SO}_4$ . Cell internal resistance is 0.21 ohms.

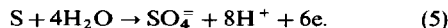
validity of this approximation was verified by calculating the resulting nitrogen atom balance at each potential; these consistently closed to within 2%.

#### Electrode characterization by hydrogen adsorption

The roughness factor and surface area of the Pt LAA-2 platinum black electrodes used in this work were determined in the conventional manner by measuring the charge consumed in the voltammetric oxidation of adsorbed hydrogen atoms. Untreated (sulfur-free) electrodes were cycled repeatedly ( $0.5 \text{ V min}^{-1}$ ) in the voltammetric cell between 0.2 and  $-0.25 \text{ V vs sce}$  and the hydrogen oxidation currents on the anodic scan were digitally integrated with respect to time to yield the hydrogen oxidation charge ( $Q_{\text{H,ox}}$ ). Over a series of seven experiments one hydrogen oxidation charge was  $Q_{\text{H,ox}} = 1.657 \pm 0.037$  coulombs. Assuming a unit charge of  $210 \mu\text{C}/\text{true cm}^2$ [29] for polycrystalline platinum a roughness factor of  $R = 1550$  based on  $5.07 \text{ cm}^2$  geometric area is calculated, corresponding to a hydrogen adsorption site density of  $2.04 \times 10^{18}$  H atoms/geometric  $\text{cm}^2$ . Sulfur coverage determinations described below are based on this hydrogen adsorption site density.

#### Sulfur coverage determination:

Slow scan ( $0.5 \text{ V min}^{-1}$ ) cyclic voltammetry was employed to determine the extent of sulfur coverage on the porous electrodes after the pretreatment and reduction steps. Reported coverages were based on oxidation of the adsorbed sulfur, assuming a 6-electron oxidation to  $\text{SO}_4^-$



Current integration methodology similar to that of Loucka[22] and others[12] was employed. It consisted of subjecting the electrode to single repetitive voltage cycles starting and ending at  $0.2 \text{ V vs sce}$  with upper and lower limits of 1.0 and  $-0.2 \text{ V}$ . An illustrative voltammetric response to repeated sulfur oxidation cycles on a pretreated porous platinum black-Teflon electrode in  $\text{N}_2$ -saturated  $0.5 \text{ M H}_2\text{SO}_4$  electrolyte is presented in Fig. 8. Approximately 15 cycles between

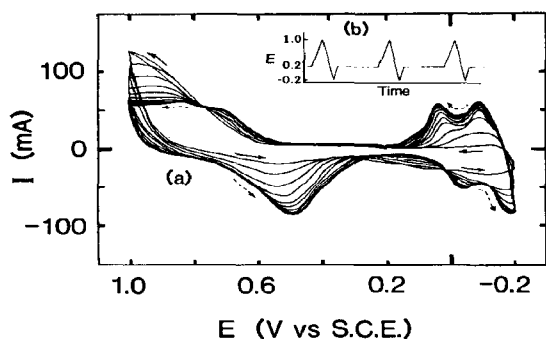


Fig. 8. (a) Voltammetric oxidation of sulfurous products of  $\text{SO}_2$  reduction on American Cyanamid platinum black LAA-2 gas diffusion electrode subjected to single-stage pretreatment (see text). Electrode repeatedly cycled at 0.5 V/min between 1.0 and  $-0.2$  V vs sce. Sulfur deposit is completely oxidized in about 15 cycles, and the voltammetric traces approach a reproducible steady-state trace. Solid arrows indicate first sulfur oxidation cycle; dashed arrows indicate steady state platinum residual trace. Electrolyte is deaerated 0.5M  $\text{H}_2\text{SO}_4$ . (b) Input waveform for sulfur oxidation scans. Scan rate is 0.5 V  $\text{min}^{-1}$ . Time between cycles is about 2 min.

1.0 and  $-0.2$  V vs sce were required to completely oxidize the sulfur layer and obtain a constant, reproducible platinum residual current trace. The net charge passed during each cycle was determined by integration of the voltammetric currents on both the anodic and cathodic legs of the cycle. Since platinum oxidation/reduction, hydrogen deposition/oxidation and the formation/removal of S-O intermediates[23] or "difficultly removable oxides"[22] are all self-cancelling within the chosen cycle, the net charge for each cycle ( $Q_{\text{S,ox},i}$ ) arises solely from the oxidation of sulfur to  $\text{SO}_4^-$  [reaction (5)]. The summation of  $Q_{\text{S,ox},i}$  over all cycles ( $Q_{\text{S,ox,tot}}$ ) was obtained and the total sulfur coverage ( $\theta_{\text{S,o}}$ ) related to the hydrogen coverage by[22]

$$\theta_{\text{S,o}} = Q_{\text{S,ox,tot}}/6Q_{\text{H,ox}} \quad (6)$$

where  $Q_{\text{H,ox}}$  is defined above as the charge for oxidation of a monolayer of adsorbed hydrogen on an untreated (sulfur-free) electrode. The sulfur coverage ( $\theta_{\text{S,o}}$ ) values reported here are thus related to the total number of available surface sites as determined by hydrogen adsorption.

Pretreating the electrodes by soaking for 18 h in  $\text{SO}_2$ -saturated 1M  $\text{H}_2\text{SO}_4$  (the one-stage pretreatment) followed by electrochemical reduction at  $-0.2$  V vs sce resulted in sulfur coverages of  $\theta_{\text{S,o}} = 1.00 \pm 0.06$ . These are significantly larger than surface saturated coverages from adsorbed gaseous  $\text{H}_2\text{S}$  determined on single crystals in high vacuum[2] and electrochemical[30] studies, and may result from significant amounts of non-adsorbed or weakly adsorbed  $\text{SO}_2$  present in the pores of the electrode and reduced together with the more specifically (strongly) adsorbed  $\text{SO}_2$ .

To study this further, experiments were performed using electrodes which were subjected to a two-stage pretreatment procedure; a second 18 h soak in neat aqueous 1 M  $\text{H}_2\text{SO}_4$  followed the  $\text{SO}_2$ -saturated soak.

This second treatment stage presumably would allow any weakly adsorbed or associated  $\text{SO}_2$  to be displaced or escape the electrode before the reduction step; apparently it does not result in removal of the more strongly bound specifically-adsorbed  $\text{SO}_2$ . Sulfur coverages on electrodes subjected to this pretreatment were determined voltammetrically and found to be  $\theta_{\text{S,o}} = 0.67 \pm 0.03$ , significantly lower than those found using the single-stage pretreatment. Thus there appears to be two types of  $\text{SO}_2$  associated with the electrode after soaking in  $\text{SO}_2$ -saturated  $\text{H}_2\text{SO}_4$ ; a strongly-bound  $\text{SO}_2$  covering approximately 67% of the surface, and a more weakly bound species which is removable by exposure to fresh 1 M aqueous  $\text{H}_2\text{SO}_4$ .

## DISCUSSION

The results show that sulfur layers derived from reduced  $\text{SO}_2$  have a pronounced effect on electrogenerative nitric oxide reduction. Both reaction rate (current) and selectivity are affected by the presence of adsorbed sulfur; results consistent with those found in a preliminary study[7]. In that earlier study, however, nitric oxide reduction currents were confounded with sulfur dioxide reduction currents, and true steady state could not be achieved. Here, controlled predeposition of the sulfur adlayer apparently creates a defined catalyst surface and simplifies the reacting system, allowing for attainment of steady state.

The results presented here can be discussed in terms of the mechanism of nitric oxide reduction, and surface modification of the platinum catalyst by adsorbed sulfur. As noted above, the presence of preadsorbed sulfur eliminates dinitrogen production and greatly inhibits ammonia production. Since the formation of both of these products involves the cleavage of an N-O bond, it is reasonable to conclude that sulfur on the catalyst surface inhibits N-O bond scission in one or more ways. This effect could be steric or electronic in nature. The N-O bond scission may require an array of surface sites, or specific active catalytic sites, analogous to the specific surface arrays proposed by Masel *et al.*[31-34] for dissociative adsorption of NO on platinum. Sulfur could adsorb randomly on the surface to limit the size of these arrays and inhibit NO bond breakage. More likely, sulfur is periodically distributed on the surface through preferential adsorption and perturbs those catalytic arrays which are active in NO bond scission. The sulfur might also affect the surface electronic environment in such a way that the N-O bond is not destabilized sufficiently to be broken in the course of the reduction. Our results do not permit a distinction between these various mechanisms at this time, though the results can be described adequately on the basis of steric considerations. There is an additional possibility that sulfur-induced faceting also occurs at the surface[35] to further influence electrocatalytic selectivity.

These results are consistent with high-vacuum studies of NO adsorption and reaction on clean and sulfur-covered catalysts[15-17] in that metallic free sites allow NO adsorption (and presumably electrochemical reduction), but NO dissociation (bond scission) seems to require larger surface ensembles[15, 31-34]. The relatively high NO reduction

currents which are observed indicate that nitric oxide is readily adsorbed and reduced on the sulfur-treated cathode, but the selectivity changes suggest a diminished rate of NO bond cleavage.

It is pertinent to briefly consider the nature of the observed limiting currents, principally the first (lower) limiting current. As mentioned earlier, this limiting current corresponds to production of  $N_2O$  and on an untreated cathode the current appears to be limited by the bulk reactant feed rate (at the limiting current, close to 100% conversion of the NO is achieved with both pure and dilute NO feeds). When the cathode is treated with reduced  $SO_2$ , however, limiting currents are still observed even though NO conversions are well below 100% (40% for the pure NO-fed cells). Given the nature of the sulfur deposition procedure, it is reasonable to postulate that after sulfur treatment the currents are limited not by bulk reactant flow but by the availability of the required free sites on the electrode surface and their turnover rate.

The results presented above support this view in several ways. First, with such a mechanism we would expect sulfur deposition to remove catalytic sites and thus to affect the pure NO-fed cells to a greater extent than those fed with dilute NO. With dilute NO (a lower reactant molecular feed rate) there is an excess of surface sites with respect to nitric oxide, and covering some (or even a majority) of these sites could still leave enough other sites to convert all or most of the NO. Our results show that whereas NO conversions for both pure and dilute NO feeds are 100% on untreated cathodes, with sulfur treatment overall conversion is near 90% for dilute NO cells but only 40% for pure NO cells.

Secondly, the magnitude of the effect of sulfur on the limiting current of a nitric oxide electrogenerative cell correlates well with the surface coverage of strongly-bound sulfur as determined by voltammetry. For cells with pure nitric oxide feeds sulfur treatment decreases the limiting current by about 65%, suggesting a 65% decrease in free surface. In the voltammetric experiments, strongly bound sulfur appears to decrease the free surface by about 67% ( $\theta_{s,o} = 0.67$ , based on the total number of surface sites available for hydrogen adsorption); an excellent agreement, especially considering the difference in experimental conditions and techniques. In making this comparison is the implicit assumption that the rate determining step (rds) in  $N_2O$  production is a first order process involving the fractional coverage of free surface sites ( $1 - \theta_s$ ). There is some uncertainty in the determination of the sulfur coverage by oxidation, since the valence of adsorbed sulfur on dispersed platinum is in dispute[12, 24]. Here we have assumed a zero valence state in accord with conventional practice. The results of a recent radiotracer study[24] have been used to argue that the product of  $SO_2$  reduction on platinized platinum is sulfur in the -2 valence state. The sulfur oxidation reaction (reaction 5) would then become an 8-electron reaction and the calculated sulfur coverage from appropriately modified equation 6 becomes  $\theta_{s,o} = 0.50$ ; a 50% decrease in free surface.

The electrogenerative reactor experiments reported here were performed using electrodes pretreated at only the first ( $SO_2$  adsorption) stage. From the above analysis, then, one would expect both strongly and

weakly bound  $SO_2$  to be present during the reduction step and the resulting sulfur coverage to be near  $\theta_{s,o} = 1.00$  in the reactor experiments. With such a coverage one might expect that the nitric oxide reaction would be strongly inhibited; however, the experimental results show that significant reaction does take place on these electrodes (Figs 2 and 5). These observations could be explained by the occurrence of some oxidation of a portion of the adsorbed sulfur during cell operation, perhaps through contact with nitric oxide.

The above results demonstrate the possibility of utilizing surface modification for industrial chemical production in the electrogenerative mode. Thus, controlled deposition of sulfur dioxide followed by reduction in an electrogenerative nitric oxide reduction cell can very favorably alter its selectivity toward hydroxylamine production, with only a limited effect on overall NO conversion levels. These results, together with previous studies using  $Cl^-$  and CO addends[9], suggest that the effect of preadsorbed sulfur on nitric oxide electroreduction could be generalized to represent the effect of many other surface adsorbates on the electrogenerative nitric oxide system. The use of selective inhibition also can be envisioned in small-scale preparatory devices where catalytic surface modifications can be renewed by periodic treatment if required.

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