

Electrocatalytic reduction of NO_3^- on palladium/copper electrodes

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Abstract

The reduction of NO_3^- on palladium/copper electrodes has been studied using differential electrochemical mass spectroscopy (DEMS), rotating ring-disk electrodes (RRDE) and quartz microbalance electrodes (ECQM). In acidic electrolytes, the activity increases linearly with Cu coverage, in alkaline electrolytes, a different dependence on coverage is observed. One monolayer of Cu gives a different selectivity from bulk copper. The adsorption of NO_3^- is competitive with SO_4^{2-} , whereas Cl^- adsorption blocks the reduction. Competitive adsorption lowers both the activity and the selectivity to N_2 . Copper activates the first electron transfer, the role of palladium is to steer the selectivity towards N_2 . The trends in activity and selectivity are explained in terms of coverage of N-species. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The reduction of nitrate has gained renewed attention due to environmental problems like overfertilisation and the increasing costs of the purification of drinking water. The usual techniques (ion-exchange and biofiltration) have major disadvantages [1], and for this reason, the direct reduction with H_2 using a catalyst is being investigated. Noble metals are the best hydrogenation catalysts and, therefore, the first choice for reducing nitrate. As the noble metals

have very low activity, a promoter is necessary. Known promoters are germanium (for the production of hydroxylamine) [2], copper [1], tin [3] and indium [3] (for the production of N_2).

A number of articles have been published on the catalytic reduction of nitrate with H_2 [1,3–8] or formic acid [3] as a reductor using palladium/copper on silica. It was observed that with increasing copper percentage, the activity increases but the selectivity towards N_2 decreases. NH_3 and NO_2^- are formed as side products, whereas only traces of N_2O could be detected [4]. The reduction is strongly dependent on pH: in alkaline solvents, NH_3 is formed, in acidic solvents, NO_2^- [5]. The selectivity to NH_3 increases with higher hydrogen flow rates [1].

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To explain the increase in NO_2^- and NH_3 , the reduction of NO_2^- has also been investigated (the first step in the reduction of nitrate is the formation of NO_2^- [1,2]). Both activity and selectivity towards N_2 are decreased by copper [6].

The activity and selectivity of the palladium/copper catalyst is very dependent on the preparation method [7,9]. CO-FTIR experiments on palladium/copper alloy catalysts [10] show that different preparation methods can give differences in surface composition: bulk segregation, surface segregation and alloying have all been observed. For a better understanding, it would be useful to be able to control the surface composition of the catalyst. This can be achieved electrochemically by underpotential deposition of copper (copper is able to form a reversible UPD layer, e.g., Ref. [11]). The amount of copper at the surface can be tuned by varying the deposition potential.

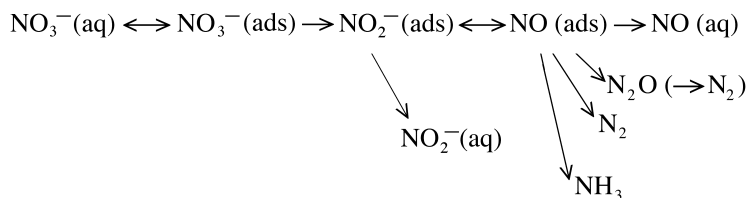
The mechanism of the reduction of nitrate is independent of the reductor, e.g., hydrogen or formic acid. This fact leads to two possible mechanisms: (1) NO_3^- reacts with adsorbed H on the surface. (2) NO_3^- reacts by a local cell mechanism, i.e., by reduction of NO_3^- on one part of the surface and oxidation of the reductor at another part of the surface; electrons go through the metal and protons go through the solution to make the stoichiometry complete. In both cases, electrochemical methods should be useful for clarifying the mechanism and the role of copper in the elementary steps. In the second case, this is obvious, in the first case, there is no difference between H(ads) formed by the dissociation of H_2 or by the reduction of a proton, $\text{H}^+ + \text{e}^- \rightarrow \text{H(ads)}$.

The conventional Langmuir–Hinselwood kinetic approach [8] show that hydrogen and NO_3^- adsorb on different sites, which would be an indication for the second mechanism. To translate the electrochemical to the catalytic experiments, the hydrogen partial pressure would relate to the potential and the activity to the electrical current.

The reaction scheme that is proposed from the kinetic approach [8,12] is shown in Scheme 1.

The first step (adsorption of NO_3^-) is a fast and reversible process. This was derived from the observation that the kinetic order to NO_3^- is 0.7 [8]. This value is typical for a reaction with a relatively low coverage of reacting species at the surface (if the coverage was high, the order would be zero). Since the reaction is kinetically controlled, not diffusion controlled, this suggests that NO_3^- is bonded weakly to the surface. This could make the reaction liable to competitive adsorption effects. Our first objective is to determine the effects of competitive adsorption on the reaction.

The second step (reduction of NO_3^- to NO_2^-) is known to be the rate-determining step. This is verified by electrochemical experiments which showed the first electron transfer to be rate determining [13], both on palladium and copper electrodes and in acidic electrolytes. NO_2^- has been observed as an intermediate during the reaction, (e.g., Ref. [8]). Our second objective is to determine the role of copper in the rate-determining step (palladium has no activity for NO_3^- reduction). The pH of the solution has also an effect on the activity [5], so the measurements will be performed in both acidic and alkaline electrolytes. We decided not to measure



Scheme 1.

in pH-neutral electrolytes because the solution would have to be buffered. As will be shown in our results, the buffering ions will probably have an effect on the reaction, and the result would differ from NO_3^- being reduced in drinking water.

The third step is the selectivity controlling reaction step. NO_2^- , NO , N_2O , N_2 , and NH_3 are the possible products; N_2 is the desired product. The selectivity towards N_2 decreases with the copper content, but pure palladium gives a high selectivity towards N_2 , (e.g., Refs. [1,14]). The selectivity is also dependent on pH [14]. Sometimes [14,15] the direct pathway for producing N_2 from NO is omitted, N_2O is written as a necessary intermediate in the formation of N_2 . In another case [12], N_2O is not mentioned as a possible product. Our third objective is to identify the roles of copper and palladium on the selectivity, both in the NO_3^- reduction as in the reduction of the intermediates. If possible the path by which N_2 is formed will be identified.

Overall, we will determine the dependence of the reaction on the copper coverage, on different anions in the solution and on the pH. From these measurements, we will formulate a model involving all three described steps.

2. Experimental

Cyclic voltammetry, amperometry, rotating disk (RDE), and rotating ring-disk electrode (RRDE) measurements were carried out with an Autolab Pgstat 20 with bipotentiostat module. Detection of non-gaseous oxidizable products was performed in the RRDE setup by applying a constant potential to the palladium/copper disk and scanning the platinum ring.

The selectivity to gaseous products was defined as the amount of gaseous products divided by the Faradaic current and determined using differential electrochemical mass spectroscopy (DEMS). DEMS measurements were performed with a Leybold Quadruvac PGA 100 Mass Spectrometer. Details of the experimental setup

are given elsewhere [16]. The products were examined for N_2 ($m/z = 28$) and N_2O ($m/z = 44$). The signal was calibrated by oxidation of a monolayer CO to CO_2 and corrected for sensitivity and fragmentation probability [17]. Activities and selectivities were determined potentiostatically using steady state currents.

The quartz microbalance system consists of palladium deposited on a gold-covered quartz crystal (5 MHz, Phelps electronics) in a Teflon encasing [18]. The frequency was measured with a Philips PM 6680/016 frequency counter.

We have tried to establish the NO-coverage during the reduction of NO_3^- using IR-spectroscopy (Bio-Rad FTS 45A spectrometer, equipped with a liquid nitrogen cooled MCT detector). The setup is described in detail in Ref. [19]. Useful IR-spectra can only be obtained in a potential window of at least 0.1 V in which Faradaic current is virtually absent. No such region is available for the Pd/Cu system, and no conclusive results could be obtained.

Submonolayers of copper were obtained by underpotential deposition between 0.25 and 0.6 V from a solution of 20 mM Cu^{2+} in either 0.1 M HClO_4 or H_2SO_4 depending on the electrolyte during nitrate reduction. The coverage of copper was determined after each measurement from the oxidation charge of $\text{Cu} \rightarrow \text{Cu}^{2+}$ compared to the oxidation charge of a monolayer CO:

$$\Theta_{\text{Cu}} = \frac{Q_{\text{Cu-ox}}}{Q_{\text{CO-ox}}} \quad (1)$$

Palladium electrodes were prepared by electrodeposition from a 5×10^{-2} M PdCl_2 in 0.2 M $\text{HCl} + 0.3$ M HClO_4 solution on a palladium foil. A deposition current of 10 mA/cm² was used.

An Hg/HgSO₄ electrode in saturated K₂SO₄ was used as a reference electrode in acidic electrolytes, a Hg/HgO electrode in 0.1 M KOH was used in alkaline electrolytes. All potentials in the text will be referred to the reversible hydrogen electrode (RHE).

All chemicals were obtained from Merck (p.a. grade). NaNO_3 was used as the source of NO_3^- , unless otherwise specified. NO (purity 2.0, washed in a solution of 2 M KOH) and N_2O (purity 2.5) were provided by Hoekloos. Great care was taken to avoid contact between oxygen and NO. Ultrapure water (18.2 M Ω), obtained with an Elga purifying system, was used for all electrolytes.

3. Results

3.1. Reduction of nitrate

3.1.1. DEMS measurements

The activity of the electrode at 0.02 V vs. copper coverage at pH = 0.3 and $[\text{NO}_3^-] = 0.1$ M is plotted in Fig. 1a. The reduction current increases linearly with the copper coverage. Electrolytes containing HClO_4 show a higher

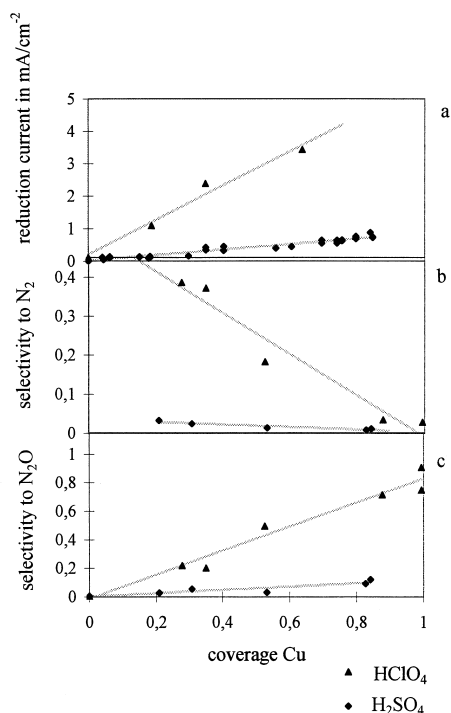


Fig. 1. Activity and selectivity vs. Cu coverage in HClO_4 and H_2SO_4 , $V = 0.02$ V, pH = 0.3, $[\text{NO}_3^-] = 0.1$ M.

activity than those containing H_2SO_4 . Electrolytes containing only HNO_3 give the same results as NaNO_3 in HClO_4 . Both trends have been observed at any potential between 0 and 0.3 V. A bulk copper electrode has the same activity as a UPD-copper electrode at high coverages. The actual activity, however, does change with the applied potential with a Tafel slope of 111 mV/dec.

The selectivity to N_2 vs. copper coverage is plotted in Fig. 1b, to N_2O in Fig. 1c. The selectivity to NO could not be determined accurately because N_2O fragments to NO inside the mass spectrometer and this interferes with the determination of the selectivity. The amount of NO produced, however, is small.

In both HClO_4 and H_2SO_4 , the selectivity towards N_2 decreases with θ_{Cu} , while the selectivity towards N_2O increases linearly. In an electrolyte containing HClO_4 , far more N_2O is produced than if H_2SO_4 is used as an electrolyte. Like the trends in the activity, both trends are seen at different potentials. The selectivity changes only slightly with potential. For instance, at a copper coverage of 1, the selectivity to N_2O increases from 80% at 0.02 V to 95% at 0.22 V. The same holds for low copper coverages. For instance, at a copper coverage of 0.28, the selectivity to N_2 increases from 40% at 0.02 V to 50% at 0.22 V. This can be attributed to increased NH_4^+ formation at more negative potentials. Besides, NH_4^+ , also NO_2^- is formed during the reduction (as will be discussed in the Section 3.1.2) and, for this reason, the combined selectivity to N_2 and N_2O is always less than 100% at any given copper coverage. If bulk copper is deposited (the copper coverage will be above 1), the selectivity to N_2O decreases and NO is formed in large quantities.

The kinetic order of the NO_3^- concentration with respect to the activity is 0.7, which has also been reported in literature for the drinking water catalyst [5].

The selectivity vs. the nitrate concentration at 0.02 V at a copper coverage of 0.9 is plotted in

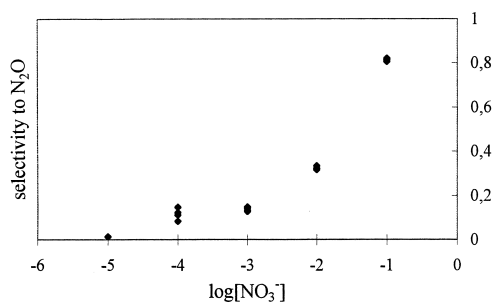


Fig. 2. Selectivity vs. $[\text{NO}_3^-]$, $V = 0.02$ V, $\text{pH} = 0.3$, Cu coverage is 0.9.

Fig. 2. The selectivity to N_2O increases with concentration. The other products are NH_4^+ and NO_2^- .

3.1.2. RRDE measurements

The species detected at the ring are incompletely reduced products of the nitrate reduction. The most likely products are HNO_2 or NO as the cyclic voltamograms (Fig. 3a) show reduction and oxidation currents at approximately the same potentials as in a solution containing HNO_2 or NO (Fig. 3b). The reduction of HNO_2 to NO is very fast and reversible [20]. Therefore, no difference can be observed between the two species. The other products (NO_3^- , N_2O , N_2 and NH_4^+) cannot be oxidized in water. No potential range in the cyclic voltamograms is available at which the current is proportional to the NO concentration, so it is difficult to quantify the NO concentration.

3.1.3. Quartz microbalance experiments

To follow the adsorption of anions and its effect on the current, the mass of the electrode was monitored during NO_3^- reduction. The mass should increase when SO_4^{2-} is adsorbed to the surface, and simultaneously, the current should decrease. The results of this experiment, however, do not show a clear increase in mass when SO_4^{2-} is adsorbed. We have not been able to determine the reason.

In a subsequent experiment, we added Cl^- to the solution. Cl^- was chosen since Cl^- binds

strongly to metal electrodes and, therefore, the anion effect should be more pronounced. When we adsorbed Cl^- , the mass of the electrode decreased regardless of the presence of NO_3^- in the solution. Presumably, the decrease in mass is due to the chloride ions displacing either nitrate or perchlorate ions from the double layer or change the adsorption of the water molecules to the surface.

In Fig. 4, the results of the Cl^- adsorption during the NO_3^- reduction are plotted. At $t = 0$ s, a small amount of Cl^- was added (the total concentration Cl^- in the cell was 10^{-3} M). The change in mass at $t = 0$ s can be attributed to the change in water level above the electrode. At $t = 92$ s, the solution was stirred to transport the Cl^- towards the electrode. At $t = 142$ s, the

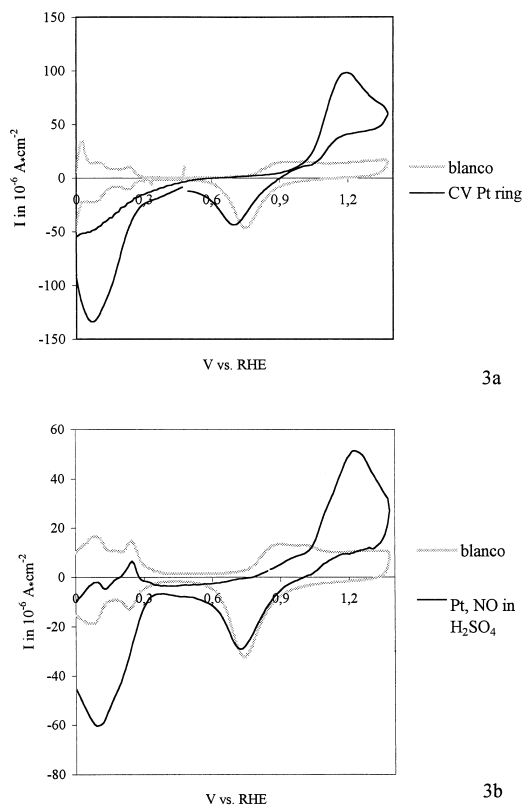


Fig. 3. (a) Cyclic voltamogram of platinum ring during reduction of NO_3^- , $\text{pH} = 0.3$, $[\text{NO}_3^-] = 0.1$ M. (b) Cyclic voltamogram of NO in H_2SO_4 on platinum, $\text{pH} = 0.3$, $[\text{NO}_2^-] = 10^{-3}$ M.

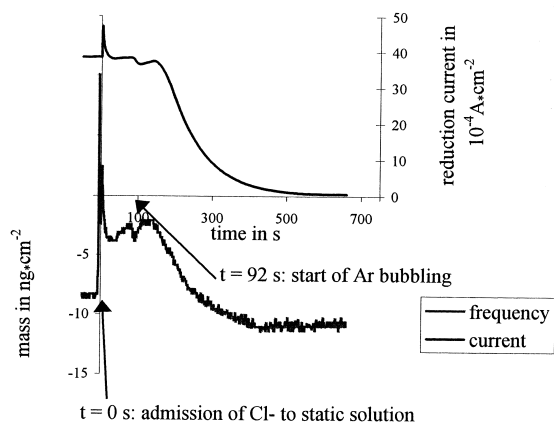


Fig. 4. PdCu, activity and mass of electrode upon adsorption of Cl^- , $V = 0.07$ V, $[\text{NO}_3^-] = 0.1$ M, supporting electrolyte is 0.5 M HClO_4 , Cu coverage is 1.

Cl^- reached the electrode and adsorbed to the surface, resulting in a decrease in mass. Simultaneously, the reduction current decreases due to competitive adsorption of the Cl^- ions. Note that the decrease in mass and current run parallel. No attempts were made to interpret the change in mass in Fig. 4 in terms of the number of adsorbed ions and molecules.

When Cl^- was replaced by I^- , a similar decrease in current is observed parallel to a large increase in mass. The same mass decrease and increase, respectively, has been observed in experiments without NO_3^- .

3.2. Reduction of intermediates

To study the reactions following the first step ($\text{NO}_3^- + 2\text{H}^+ + 2e^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O}$), the reduction of the intermediates, NO_2^- , NO and N_2O , was studied. Pure palladium and palladium with a copper coverage of 1 were taken as electrodes.

3.2.1. Nitrite reduction

Rotating disk experiments (RDE) show a difference in activity between palladium and copper in H_2SO_4 of about 10:1.

A large difference in selectivity, using DEMS, is observed between palladium and copper on palladium electrodes. The main product on a

palladium electrode is N_2 , copper deposited on palladium produces N_2O with only traces N_2 . At more negative potentials, the selectivity to gaseous products decrease for both electrodes, so the major product becomes NH_4^+ . A change from HClO_4 to H_2SO_4 has little effect on the selectivity.

3.2.2. NO reduction

The reduction of NO shows the same selectivity as the reduction of NO_2^- . Copper on palladium shows a large production of N_2O , palladium of N_2 . The reduction becomes diffusion limited due to the low solubility of NO , so an RDE setup was used.

The reduction of NO on palladium does not depend on the use of H_2SO_4 or HClO_4 . The rate on copper electrodes, however, does depend on the anion used. The activity electrode in HClO_4 was higher than in H_2SO_4 . The activity of the palladium electrode was about seven times higher than that of a monolayer copper on palladium electrode in H_2SO_4 , in HClO_4 the ratio is about 4:1 (Pd vs. Cu on Pd). These results were obtained in a copper containing solution (10 mM Cu^{2+}) at 0.24 V vs. RHE, i.e., at the potential between the UPD layer deposition and the bulk deposition. This was done to prevent changes in the copper coverage due to simultaneous oxidation of copper and reduction of NO , which leads to poor reproducibility.

3.2.3. N_2O reduction

The reduction of N_2O on palladium (Fig. 5) shows an anion effect, just as NO_3^- did, and the

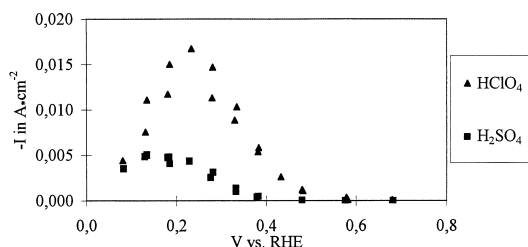


Fig. 5. N_2O reduction on Pd in HClO_4 and H_2SO_4 , $P_{\text{N}_2\text{O}} = 1$ atm, $\text{pH} = 0.3$.

reduction is inhibited by H-adsorption. The selectivity to N_2 is always 100%. Copper on palladium shows little activity for N_2O reduction.

3.3. Alkaline electrolytes

3.3.1. NO_3^- reduction

In alkaline electrolytes, the activity is increased by copper, but the activity reaches a plateau value (Fig. 6a). Bulk copper electrodes have the same activity as copper at high coverage on palladium. This trend is independent of the potential (the activity itself shows a Tafel slope of 106 mV/dec). The kinetic order of the concentration at high copper coverages is 0.7.

The selectivity to N_2 decreases with increasing copper coverage (Fig. 6b). The anions used in the deposition of the copper could have an effect on the selectivity, but the reproducibility of the experiments was too poor to state this with certainty. Only traces of N_2O are formed.

During RRDE experiments on the reduction of NO_3^- , NO_2^- is formed, since the cyclic voltammogram of the ring shows the same features as

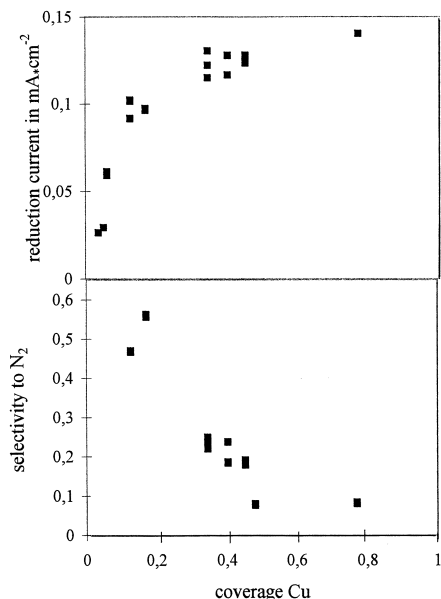


Fig. 6. Activity and selectivity of NO_3^- reduction vs. copper coverage in NaOH, $V = 0.02$ V, $pH = 13.7$, $[NO_3^-] = 0.1$ M.

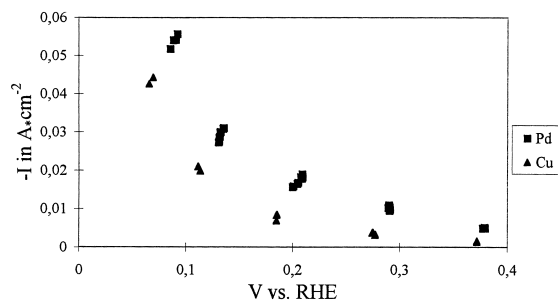


Fig. 7. Activity of Pd and Cu for NO_2^- reduction in KOH, $pH = 13.7$, $[NO_2^-] = 0.1$ M, bulk Cu and Pd.

the cyclic voltammogram of NO_2^- , similar to the situation in acidic electrolytes. The cyclic voltammogram of NO_2^- shows little concentration dependence, so that the amount of NO_2^- produced could not be determined.

The addition of ClO_4^- or SO_4^{2-} to the solution has no effect on activity or selectivity. This is also the case during the reduction of NO_2^- and N_2O . The addition of Cl^- only deactivates the electrode slightly, unlike in the case of acidic electrolytes. I^- , however, does deactivate the electrode.

3.3.2. NO_2^- reduction

In Fig. 7, the reduction of NO_2^- on a palladium and a palladium/copper electrode with high copper coverage are compared. Copper is less active than palladium. Copper is also less active for the reduction of NO_2^- than for the reduction of NO_3^- .

The selectivity changes from N_2 on palladium to a combination of N_2 and N_2O on copper. This is similar to acidic electrolytes, the change is, however, less. The rate of reduction of NO_2^- on a palladium electrode shows a kinetic order of virtually zero, indicating a strong adsorption of NO_2^- and a relatively slow reduction. On a copper electrode, the kinetic order of the concentration is about 0.5, indicating weaker adsorption.

3.3.3. N_2O reduction

The reduction of N_2O at palladium in alkaline electrolytes starts at more positive poten-

tials than in acidic electrolytes. Copper shows little activity compared to palladium. The selectivity to N_2 is 100% under all conditions.

4. Discussion

4.1. Activity

The first step in mechanism 1 is the adsorption of NO_3^- to the surface. The importance of this step is shown by the difference in activity between NO_3^- in $HClO_4$ or H_2SO_4 . This can only be explained by the difference in adsorption between the ClO_4^- and SO_4^{2-} ions. The adsorption of NO_3^- can be hindered by adsorp-

tion of SO_4^{2-} , as has been shown on platinum [21].

We tried to confirm this by EQMB experiments. The mass difference upon SO_4^{2-} adsorption was, however, too small to observe the expected results. When an ion is used that adsorbs even stronger, the expected result was observed: upon adsorption of Cl^- , as seen by a mass decrease, the activity decreases, as seen by a decrease in Faradaic current. The mass decrease due to Cl^- adsorption runs parallel to the current decrease of the NO_3^- reduction. This implies that Cl^- blocks the NO_3^- reduction sites in a one to one fashion. The anion effect can be seen during the reduction of N_2O as well, as has been reported in the literature [22].

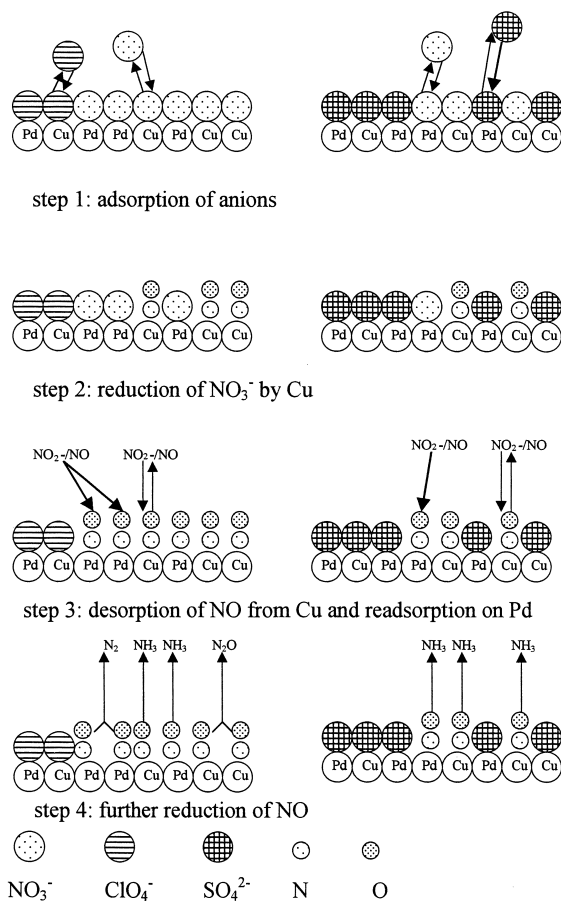


Fig. 8. Depiction of the model for activity and selectivity in acidic electrolytes.

The anion effects, together with the kinetic order of approximately 1, show that the activity is determined by the number of NO_3^- ions at the surface. This is depicted in Fig. 8 as step 1.

The second step in mechanism 1 is the reduction of NO_3^- . For acidic electrolytes, the activity of the electrode is linear with copper coverage at coverages below 1 and constant above 1. This shows the role of copper as a promoter very clearly; the initial step of the reduction only takes place at the copper sites. The activity as a function of the copper coverage gives a straight line through the origin. This step is depicted in Fig. 8 as step 2. The electrical current does not only depend on activity, but also on the number of electrons consumed per reduced NO_3^- ion, i.e., on the selectivity. In this case, however, the effect would be small: the number of electrons “consumed” per NO_3^- would change from 5 (N_2) at low copper coverages to 4 (N_2O) at high copper coverages. This change is too small to be detected, given the statistical uncertainty of the measurements.

The third step in mechanism 1 is desorption or reduction of NO_2^- . The activity for this step will depend on the rate of desorption vs. the rate of reduction. This will be discussed for palladium and for copper. It should be noted that the reduction from NO_2^- to NO is very fast, and NO is probably the adsorbate (as for platinum and rhodium [23]). This explains the similarity of the cyclic voltamograms of NO_2^- and NO.

NO adsorbs strongly on palladium. The first argument is the absence of an anion effect of the reduction of NO. A second argument comes from adsorbate studies, where NO will not desorb upon changing of the electrolyte with a blank solution. A third argument comes from gas phase experiments: NO adsorbed on palladium desorbs at a much higher temperature (400–500 K, e.g., Ref. [24]) than NO adsorbed on copper (150–200 K at low coverage NO [25]).

NO adsorbs weakly on copper. This can be seen during RRDE experiments on palladium/copper electrodes: NO_2^- or NO can be detected

at the ring, proving that NO_2^- , or NO, desorbs from the copper surface. The RRDE experiments could not be performed on pure palladium electrodes since these have little activity towards NO_3^- reduction. Secondly, NO adsorbs competitively with SO_4^{2-} . In alkaline electrolytes, the kinetic order is not zero, also indicating weak adsorption on copper.

This step is depicted in Fig. 8 as step 3. It is assumed that NO will either diffuse in the bulk solution and readsorb or that it will diffuse over the surface to palladium sites. The reason for this assumption will be discussed in Section 4.2.

There is still one paradox. NO is expected to be reduced quickly compared to NO_3^- , because the rate-determining step of the latter is the first step. The fact that NO can be detected during RRDE experiments would suggest that the reduction of NO is relatively slow compared to the reduction of NO_3^- . For acidic solutions, this paradox can be solved. The absolute values of the current of NO_3^- reduction on Cu on Pd and NO_2^- on Pd are comparable. If a low kinetic order for NO_2^- in acidic electrolytes is assumed, as is the case in alkaline solutions, then the reduction current at the same concentration are comparable. This would explain why it can be detected at the ring, but will not be the rate-determining step. In alkaline solutions, however, the reduction of NO_2^- is approximately 100 times faster than the reduction of NO_3^- at the same concentration, potential and electrode (Figs. 6 and 7).

4.2. Selectivity

The selectivity determining step in mechanism 1 is the third step, after the rate-determining step has been performed. The selectivity towards N_2O is increasing with increasing copper coverage. In the case of HClO_4 as an electrolyte, the selectivity is even linear with the coverage. The difference can also be seen during the reduction of NO_2^- : palladium electrodes produce mainly N_2 , copper deposited on palladium produces mainly N_2O .

Bulk copper electrodes give a different selectivity from UPD-copper electrodes, NO instead of N_2O . This shows that palladium plays a role in the catalysis by influencing the copper at the surface. A comparison of palladium/copper with similar systems (copper deposited on platinum and gold) indicates the same. Copper on platinum shows a relative increase of the selectivity towards NH_3 and copper on gold towards NO at high copper coverages. This shows that the substrate has an influence on the selectivity of copper.

Electrolytes containing $HClO_4$ and H_2SO_4 show not only a large difference in activity, but also in selectivity. The difference in activity was attributed to the difference in the adsorption strength of the ions and would result in a difference in the concentration of NO_3^- ions at the surface. The result would be a different concentration of N-intermediates at the surface (step 2 in Fig. 8), and this would determine the selectivity. The way this influences the reaction is depicted in Fig. 8 as step 4. At low N-coverage NH_3 is formed, at high N-coverage N_2O . The N-species in acidic electrolytes is most likely NO, given the stability of NO on platinum [19,23], rhodium [23], and iridium [26] surfaces. This large effect of the anion on selectivity is not observed during the reduction of NO_2^- , probably because NO and NO_2^- adsorb more strongly than NO_3^- .

Between steps 2 and 4 in Fig. 8, a desorption/readorption step is included to bring NO to the palladium sites. Such a step is likely, since NO is formed on copper, but adsorbs weakly on copper and strongly on palladium.

The selectivity is also dependent on concentration: as the concentration increases, the selectivity towards N_2O increases. The increase in selectivity to N_2O with concentration can be explained by an increase of the concentration N-species at the surface.

It should be noted that palladium at a high coverage of N-species would produce N_2 , as can be seen during the reduction of NO. This explains the increase in selectivity to N_2 with

decreasing copper coverage (Fig. 1b). This situation will, however, not occur during the NO_3^- reduction: palladium has little activity for the reduction of NO_3^- , and therefore the N-coverage will be low at high palladium coverages (i.e., at low copper coverages).

4.3. Model for acidic electrolytes

The anion effect and the concentration effect on the selectivity show that the selectivity of the reaction is coupled to the activity of the reaction. To show the relationship between activity and selectivity, we propose a model based upon the coverage of N-species at the surface. This model is shown in Fig. 8.

In step 1, NO_3^- adsorbs to the surface, hindered by SO_4^{2-} , if present.

In step 2, NO_3^- reduces to NO_2^-/NO at the copper sites.

In step 3, NO_2^-/NO desorbs from the copper sites into the solution. Next, it either adsorbs on a palladium site, on a copper site or diffuses into the bulk solution. Surface diffusion of the NO-species is also possible.

In step 4, NO is further reduced. NO at high coverage on palladium sites will be reduced to N_2 . NO at high coverage on copper sites will be reduced to N_2O . NO at low coverage on either palladium or copper will be reduced to NH_3 .

4.4. Alkaline solutions

The activity in alkaline electrolytes vs. the copper coverage shows a change in slope between low and high coverages. It is unclear whether the slope becomes zero at high coverages. A possible explanation would be a shift in selectivity (from N_2 to NO_2^-) and, therefore, a decrease in electrons “consumed” per NO_3^- (5 to form N_2 and 2 for NO_2^-). The result would be a decrease in slope of 2/5 in the current vs. copper coverage plot. The decrease in slope is larger, so another effect must play a role as well.

The reduction shows only an anion effect when I^- is added and only slightly with Cl^- . This can be explained by assuming that OH^- bonds strongly to the surface.

As in acidic electrolytes, the selectivity to N_2 decreases with increasing copper coverage in alkaline electrolytes.

A lower activity and selectivity for the reduction of NO_2^- on copper compared to palladium has been observed, similar to acidic electrolytes.

The model proposed for acidic electrolytes will now be compared to the situation in alkaline electrolytes.

The adsorption, as described in step 1, shows the anion effect like in acidic electrolytes, but only with very strongly adsorbing anions.

The rate-determining step is the first electron transfer, similar to step 2 in the model. In both electrolytes, a kinetic order to NO_3^- concentration of 0.7 is observed. The coverage dependence with copper is, however, different.

The desorption and readsorption of NO_2^- (step 3) is similar, NO_2^- can be detected at a ring electrode during RDE experiments, both in alkaline and acidic electrolytes.

Step 4, the further reduction of NO_2^- , shows the same decrease in selectivity to N_2 as in acidic electrolytes. The selectivity to N_2O , however, is virtually absent.

The similarities between the model in acidic electrolytes and the measurements in alkaline are too large to be ignored. It is likely the mechanism is the same, or has at least the same essential steps. However, there are some differences that have not been explained yet. Therefore, it is not possible to prove that the mechanism is the same.

4.5. Reduction of NO to N_2

According to the reaction in Scheme 1, N_2 can be formed by the reduction of N_2O and by a direct pathway from NO. If N_2 is formed by the reduction of N_2O , sites should be available for producing N_2O and there should be sites avail-

able for reducing N_2O . It is observed that reduction of N_2O is relatively slow on copper and relatively fast on palladium, so it is possible that copper sites produce N_2O and palladium sites reduce N_2O to N_2 . Palladium sites have to be available, so the selectivity to N_2 would increase with the palladium coverage and the selectivity to N_2O would increase with copper coverage. This is consistent with the data produced in acidic electrolytes. This does not exclude parallel paths for the formation of N_2 , as also described in reaction in Scheme 1.

The reduction of N_2O in alkaline solutions starts at very positive potentials, even within the oxide regime, as has been reported earlier [27]. This could be an explanation for the low selectivity to N_2O in alkaline electrolytes as N_2O is easily further reduced to N_2 . It is expected from the measurements in acidic electrolytes that at high coverages of copper, the selectivity to N_2O would increase. If all the N_2O would reduce further, the selectivity to N_2 would increase since N_2 is the only product of N_2O reduction. In our case, however, we find a decrease in selectivity to N_2 with increasing copper coverages. This does not fit with N_2O as the intermediate for N_2 production; N_2 has to be produced by a pathway different from the reduction of N_2O .

This reasoning assumes that the reaction follows Scheme 1 as described in Section 4.3, in both acidic and alkaline electrolytes. If the mechanism would change in alkaline electrolytes, then the argumentation does not hold and the mechanism would have to be solved in both cases separately.

4.6. Comparison with drinking water purification catalysts

In this section, we compare the predictions from our model for the mechanism with the data from the catalyst used for NO_3^- reduction in drinking water [1,3–5,7,9,14,28].

An increasing activity is observed with an increasing Pd:Cu ratio, as is predicted [1]. What

is not predicted, however, is that at Pd:Cu ratios above 4:1 the activity decreases, but in alkaline solutions, there was a decrease in slope of the activity vs. copper coverage. It must be noted that the Pd:Cu ratios can not be translated directly to a Cu-coverage, the Cu-coverage depends on the preparation method [7,10]. The preparation method used in Ref. [1] would give a relatively high Cu coverage [7,10]. It might be that at Pd:Cu ratios of higher than 4:1, the surface is almost totally covered with copper and that the hydrogen dissociation becomes the rate limiting step instead of the NO_3^- reduction, which could not be the case during an electrochemical experiment.

At Pd:Cu ratios higher than 1:4, the selectivity to NO_2^- increased [14]. This is predicted in our model as well, especially if the surface coverage of copper becomes greater than 1, i.e., if bulk copper is formed at the surface. It would be important to check if bulk copper exists at the surface, because copper deposited on palladium reacts differently from bulk copper. The preparation method has to be chosen to avoid this problem.

Our model predicts that at a more negative potential, the selectivity to NH_3 would be higher. A more negative potential corresponds to a higher partial pressure or concentration of reductor. A higher selectivity to NH_3 at higher partial pressures of hydrogen has indeed been observed.

HCl is used as a neutralizer of the produced OH^- [1,3–5,7,9,14,28]. For acidic electrolytes, this decreases the activity and selectivity to N_2 greatly, as is shown in Fig. 4. However, this is not the case for the drinking water catalyst, where in neutral environments the addition of Cl^- shows an increase in activity and selectivity [28]. This is probably due to changes in the pH near the surface; during the reduction of NO_3^- the pH near the surface becomes more alkaline and this decreases both activity and selectivity to N_2 . During a reduction of NO_3^- with Cl^- the pH stayed lower than without Cl^- . Both SO_4^{2-}

and HCO_3^- act as a pH-buffer and, therefore, improved the selectivity. As the solution becomes more alkaline, more NH_3 is produced.

The catalyst for NO_3^- reduction in drinking water (pH between 5 and 9) shows similarities with a Pd/Cu-electrode in alkaline electrolytes. The selectivity to N_2O is very low in both cases [4]. Another resemblance is the absence of the anion-effect. It would be interesting to check the dependence of the activity of the drinking water catalyst with the copper coverage, but unfortunately, the surface composition is unknown.

It should be noted that the value for the selectivity towards N_2 reported by Tacke [4] (> 98%) is much higher than in our results (max. 60%). Our model predicts that if palladium is added to the PdCu catalyst, the intermediate NO_2^- will be reduced to N_2 , and this has indeed been observed [14]. It might be possible that the preparation method of the PdCu catalyst does not create uniform particles, but leaves some palladium uncovered. This will increase the selectivity compared to only PdCu catalyst. The increased selectivity can of course be attributed to other differences, like, for instance, the pH and experimental setup.

5. Conclusion

The role of copper in the Pd/Cu-catalyst is to enhance the reduction of NO_3^- to NO_2^- , both in the initial adsorption of NO_3^- and in the electron transfers. Copper has a negative influence on activity and selectivity after this step, and for this reason the yield of N_2 goes through a maximum. The reaction is very dependent on the electrolyte composition, both with regard to pH and anions in the solution. The anion dependence is explained in terms of the coverage of N-species at the surface; a high coverage of N-species gives high activity and selectivity to N_2 and N_2O , a low coverage of N-species gives NH_3 .

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