Electrochimica Acta xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrocatalytic Reduction of Nitrate on Tin-modified Palladium Electrodes

Y.Y. Birdja, J. Yang, M.T.M. Koper*, [1]

Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

ARTICLE INFO

Article history:
Received 15 January 2014
Received in revised form 2 June 2014
Accepted 2 June 2014
Available online xxx

Keywords:
Nitrate reduction
Sn-modification
Pd film
On-line electrochemical mass spectrometry
Ion chromatography

ABSTRACT

The electrocatalytic reduction of nitrate was investigated in acidic media on Sn-modified polycrystalline palladium and Sn-modified palladium film electrodes (deposited on gold) by means of voltammetry in combination with on-line electrochemical mass spectrometry and on-line ion chromatography. The catalytic activity for this reaction is strongly enhanced by modification with Sn as pure Pd is not found to have a measurable activity for the nitrate reduction. Dominant volatile products are found to be N_2O and in a smaller amount N_2, while NH_2OH is found to be the dominant non-volatile product. Furthermore, the influence of hydrogen absorption in Pd is investigated by using a multilayer Pd film and a submonolayer Pd film on a polycrystalline Au electrode. By comparing the product distribution of these electrodes with the bulk Pd electrode the effect of hydrogen absorption is found to be of negligible importance for the nitrate reduction as the product distribution and formation as a function of potential are similar compared to the bulk Pd electrode.

1. Introduction

Living organisms need nitrogen compounds in order to produce more complex organic molecules such as proteins, nucleic acids and amino acids. Air is composed of approximately 79% of dinitrogen gas (N_2), which is the simplest and most stable form of nitrogen. However, N_2 cannot be used in this form by most organisms. Plants use nitrogen which is incorporated in compounds such as nitrate ions (NO_3^-), ammonium ions (NH_4^+) and urea ($(NH_2)_2CO$) while animals consume plants or herbivors for their nitrogen supply. The inorganic compounds of nitrogen are controlled by the so-called nitrogen cycle. Human activities such as combustion and agriculture affect the nitrogen cycle, which leads to an increase in the amount of nitrate in groundwater. According to the Council of the European Union for the water quality for human consumption, nitrate concentrations should be kept below 50 ppm [1]. A higher concentration can pose health threats such as blue baby syndrome, cancer and eutrophication of water reservoirs. From this point of view the removal of nitrate is an important process. In nature this is taken care of by the bacterial denitrification process. The electrochemical removal of nitrate is similar to this process as the enzymes are then replaced by redox catalysts. It is very important to understand this electrocatalytic process from a fundamental point of view in order to identify possible limitations of the catalysts and other factors that complicate the implementation of this process on a large scale. Nitrogen compounds formed by electrocatalytic reduction of nitrate can also be of economic value. Examples are: N_2O as anesthesia, NH_3 as fertilizer and NH_2OH as precursor for the nylon production. The formation of N_2 from nitrate is important as N_2 is harmless for the environment. Most research has been done on noble metal catalysts, often modified by another adatom. Platinum has been widely studied for the nitrate reduction together with the influence of various promoters. The promoters influence the activity and selectivity of the nitrate reduction significantly [2–5]. It has been found that the rate determining step is the reduction of (adsorbed) nitrate to nitrite, which is the step that is enhanced by the promoters, for which p-block metals are often used [6]. Unfortunately, the exact role of these promoters is not well understood.

Palladium itself is a poor catalyst for the nitrate reduction but more active compared to platinum [7–9]. Research has been done on the modification of Pd for promoting the nitrate reduction. De Vooys et al. investigated Pd/Cu catalysts, on which nitrate is reduced to N_2 with a selectivity that was found to be inversely proportional to the Cu coverage [10]. Here Cu enhances the rate determining step of the nitrate reduction, whereas Pd is active for NO and N_2O reduction [11]. Also Ge has been investigated as

---

* Corresponding author. Tel.: +31 71 5274250; fax: +31 71 5274451.
E-mail address: m.koper@chem.leidenuniv.nl (M.T.M. Koper).

[1] ISE member.

http://dx.doi.org/10.1016/j.electacta.2014.06.011
0013-4686/© 2014 Published by Elsevier Ltd.

promoter for the nitrate reduction on Pd. N_2O was found to be the main product from a certain minimum Ge coverage [12], with the selectivity towards hydroxylamine increasing for higher Ge coverages [13]. Shimazu et al. have studied tin modified Pd [14]. They have investigated the electrocatalytic activity of Pd thin films of varying thickness in $HClO_4$, and found that the electrocatalytic activity of PdSn electrodes is strongly dependent on the thickness of the Pd layers and on the Sn coverage. However, the product distribution, with the dominant product N_2O, was not affected by these parameters.

Palladium is well known for its unique ability to absorb hydrogen [15]. The hydrogen evolution on a metal usually takes place following a Volmer-Heyrovsky-Tafel process [16–18]. In case of Pd, there exists a so-called penetration reaction where adsorbed H atoms penetrate the surface layer and move into a bulk site [17]. This occurs at similar potentials as the hydrogen UPD and HER [15,19,20]. As a result, large currents are observed, which complicate the study of surface processes such as anion adsorption and the oxidation/reduction of adsorbed species. The use of Pd thin layers deposited on a substrate circumvents this problem as the amount of hydrogen that can be absorbed in the bulk is limited and therefore it is possible to differentiate between surface processes. In the literature Pt and Au are often used as substrate for the deposition of Pd films.

In this work Sn, the best promoter for the nitrate reduction on Pt, is investigated for the enhancement of the reduction of nitrate on Pd. A comparison will be made of the activity and the selectivity towards volatile and non-volatile products between bulk Pd electrodes and Pd multi- and submonolayer films in the absence and presence of strongly adsorbing anions. Our study will employ a combination of cyclic voltammetry with online electrochemical mass spectrometry and online ion chromatography, as this allows a direct and detailed comparison between activity, selectivity and electrolyte compositions.

2. Experimental

The voltammetric experiments were all carried out at room temperature in a typical three-electrode, one compartment electrochemical cell. First the cell and all glassware were boiled in a 1:1 concentrated sulfuric and nitric acid mixture. Ultrapure water (Millpore MilliQ, resistivity > 18.2 MΩ· cm) was used to boil, rinse and clean all glassware prior to each experiment and to prepare the electrolytes with Suprapur (Merck) reagents. The details of the cleaning procedure can be found elsewhere [21]. Before each measurement argon (purity grade 6.0) was purged through the cell for deaeration. The Sn-modification of Pd was done using $SnCl_2$ (99.99+%, Sigma-Aldrich). Other used chemicals were $CuSO_4$ (99.995+%, Sigma-Aldrich) and HNO_3 (Merck, suprapur, 65%).

In this work a polycrystalline palladium electrode and a (ultra)thin palladium film deposited on a polycrystalline gold electrode were used as working electrodes. The bulk Pd electrode was pretreated by immersing in concentrated nitric acid for 5 minutes. Next the electrode was polished mechanically with alumina pastes with particle sizes of 5 μm and 0.3 μm followed by sonication in ultrapure water. Before the experiment the electrode was cycled in the blank electrolyte until a stable voltammogram was obtained to verify a clean state of the surface. The gold electrode for the Pd films was cleaned by first applying a potential of +10 V in a 10% H_2SO_4 solution for 30 seconds followed by 15 seconds rinsing in a 6 M HCl solution. After this the electrode was flame-annealed and cooled down in air. In the blank electrolyte, electrochemical cleaning consists of 200 cycles between 0 and 1.75 V_{RHE} at a scan rate of 1 V/s. The charge needed for the reduction of the surface oxide of a stable voltammogram obtained at 50 mV/s was used to calculate the active surface area of this electrode. For the bulk Pd working electrode the geometric area is used as active surface area. A palladium wire and a reversible hydrogen electrode (RHE), mounted via a Luggin capillary in the same electrolyte, were used as counter and reference electrode, respectively, unless mentioned otherwise (e.g. for special procedures as the Pd deposition on Au or Cu UPD on Au). Electrochemical cleaning and blank voltammetric experiments were performed in a cell separate from the cell in which experiments on nitrate reduction were performed.

The voltammetric measurements for the On-Line Electrochemical Mass Spectrometry (OLEMS) were carried out with an Ivium A06075 potentiostat and the OLEMS measurements with an EvoLution mass spectrometer (European Spectrometry Systems Ltd.). The system, a Quadrupole Mass Spectrometer Prisma QMS200 (Pfeiffer), is brought to vacuum with a TMH-071P turbo molecular pump (60 l/s, Pfeiffer) and a Duo 2.5 rotary vane pump (2.5 m^3/h, Pfeiffer). During voltammetric measurements a hydrophobic tip placed close underneath the working electrode ($\sim 10\,\mu$m) collected volatile products from where they flow to the MS. The pressure inside the MS was always kept below 10^{-6} mbar. During OLEMS measurements the voltammetric scan rate was always 1 mV/s. The configuration and pretreatment of the tip is described elsewhere [22,23]. Before use the tip is cleaned in a solution of 0.2 M $K_2Cr_2O_7$ in 2M H_2SO_4 and rinsed with ultrapure water. All mass fragments decay during measurement, because it takes a long time for the pressure to reach a steady state. We correct for this by subtracting a double exponential function fitted to data points where there is no activity observed. In this work all the results are background corrected in this manner. Furthermore, fragmentation ratios were used for NO and N_2 as these mass fragments are partly the result of fragmentation of N_2O. The fragmentation ratio between N_2O (m/z = 44) and NO (m/z = 30) was found to be 0.202 while between N_2O and N_2 (m/z = 28) it was 0.0685 [24]. A SEM voltage of 1500 V was used for all species (m/z = 2, 14, 15, 28, 30, 31, 33, 44, 45, 46). Unfortunately it is not straightforward to deduce quantitative information in terms of faradaic efficiencies for the reaction products from OLEMS measurements. Our setup is able to detect volatile products only, while non-volatile products are formed as well. It is difficult to calibrate the OLEMS together with e.g. ion chromatography simultaneously as this is required to be able to derive the quantitative amounts of all the reaction products. Furthermore a whole range of products is formed depending on the applied potential. It would be better to perform long term electrolysis at a single potential to calculate faradaic efficiencies.

The IC experiments were performed on an ion chromatography unit (Shimadzu, Prominence), which is equipped with a conductivity detector (CDD-10A vp, Shimadzu). The voltammograms related to the IC measurements were recorded with an Autolab potentiostat (Pgstat20). The samples analyzed with IC were collected with an automatic fraction collector (FRC-10A, Shimadzu) during voltammetry by a small teflon tip positioned close to the working electrode in the cell [25]. The parameters for the fraction collector (flow rate and sample volume) were set in such a way that during voltammetry with a scan rate of 1 mV/s, each sample contains the average reaction products over a 60 mV potential difference (for the OLEMS measurements this potential range is approximately 5 mV at a scan rate of 1 mV/s). By employing an IC Y-521 cation column (Shodex) the cations NH_4^+ and $HONH_3^+$ were detected. A 2.5 mM nitric acid solution (Merck, Suprapur, 65%) was used as eluent. The column temperature was set to 30 °C and the flow rate of the eluent at 0.8 ml/min. The cation concentration of the analyzed samples could be calculated by the use of standard solutions of the corresponding cation for characterization of the retention time and calibration of the concentration.

Please cite this article in press as: Y.Y. Birdja, et al., Electrocatalytic Reduction of Nitrate on Tin-modified Palladium Electrodes, Electrochim. Acta (2014), http://dx.doi.org/10.1016/j.electacta.2014.06.011

3. Results & Discussion

3.1. Nitrate reduction on bulk palladium

3.1.1. Unmodified palladium

In Fig. 1 the blank voltammogram of the bulk Pd electrode is shown together with the CV for nitrate reduction on this electrode. The current is mainly due to hydrogen adsorption/absorption and desorption. With nitrate in the solution (0.1 M HNO_3) the current remains unchanged which suggests that nitrate is not reduced on a bare Pd electrode. This was verified with on-line electrochemical mass spectrometry and ion chromatography. No significant amount of reaction products was observed in this potential range. This is in agreement with the results reported previously [26].

3.1.2. Palladium modified with tin

The modification of the Pd electrode with Sn adatoms (PdSn) was carried out by spontaneous deposition with the Pd electrode immersed in a 250 μM $SnCl_2$ solution. The time during which the electrode was held in the solution determines the coverage of tin on the surface. The CVs of the modified and unmodified Pd electrode in blank solution at a relatively high scan rate of 1 V/s are shown in Fig. 2. The reason that such a high scan rate was used is to discriminate between the adsorption/absorption of hydrogen into the Pd bulk with and without the presence of Sn adatoms on the electrode surface.

Fig. 2 shows that the hydrogen adsorption/ desorption current is diminished due to Sn adsorption. The ratio of the charge accompanied by the hydrogen desorption on the modified (q_{PdSn}) and unmodified Pd surface (q_{Pd}) can be used to estimate the Sn-coverage of the electrode by $\theta_{Sn} = 1 - \left(\frac{q_{PdSn}}{q_{Pd}}\right)$. The charge is obtained by integrating the voltammogram in the hydrogen desorption region as seen by the shaded areas in Fig. 2. It should be noted that this value for the coverage is a rough estimation as Pd absorbs hydrogen in the bulk, which occurs in the same potential region. An alternative estimate (although also rather uncertain) can be based on the current observed at the most negative potential, which we assume to be mainly due to H adsorption/absorption and H_2 evolution: $\theta_{Sn} = 1 - \left(\frac{j_{PdSn}}{j_{Pd}}\right)$. Furthermore, one can observe that there is still Sn present on the surface after nitrate reduction, which suggests that Sn on the electrode surface is stable. However, it was observed that more scans lead to a slight decrease in the current for the nitrate reduction. This is probably due to the Sn desorption and poisoning of the electrode by adsorbed products. In this study we worked with a single Sn coverage of approximately 60-80% as obtained by keeping the electrode for 60 seconds in the Sn^{2+}-containing solution.

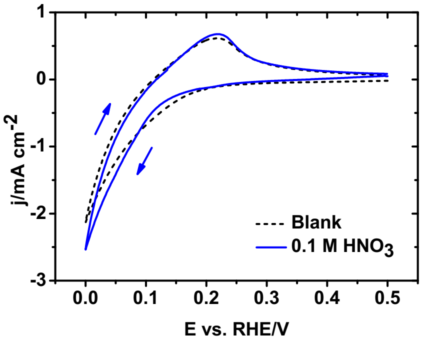

Fig. 1. The cyclic voltammogram for the nitrate reduction on the unmodified Pd electrode in 0.1 M H_2SO_4. Scan rate: 1 mV/s

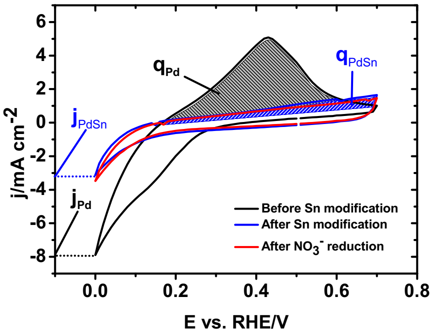

Fig. 2. Effect of Sn-modification on the Pd electrode in 0.1 M H_2SO_4. Scan rate: 1 V/s

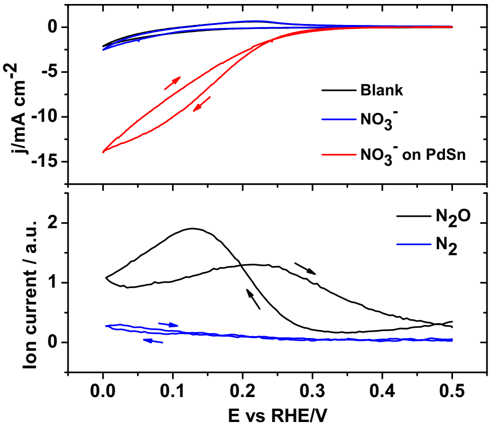

Fig. 3. Mass signals for the nitrate reduction on PdSn in 0.1 M H_2SO_4. Scan rate: 1 mV/s

3.1.3. On-Line Electrochemical Mass Spectrometry

The formation of volatile reaction products during voltammetry is determined by OLEMS. While an unmodified Pd electrode shows no volatile products, a Sn-modified Pd electrode shows several volatile reaction products. The CV together with the mass spectra are shown in Fig. 3. N_2O is the dominant product of the nitrate reduction on Sn-modified Pd. Small amounts of other mass fragments (m/z = 28, 14, 30, 45, 46) are also found. Mass signal 30 is associated with NO, while mass signals 45 and 46 are assigned to the nitrogen isotopes (N*) or oxygen isotopes (O*) of N_2O as they follow the same trend. The observation of a small amount of N_2 (m/z = 28) suggests that further reduction of N_2O is possible on a PdSn surface.

3.1.4. Ion Chromatography

The Faraday current in Fig. 3 for the Sn-modified Pd electrode differs from the profile of the mass signal vs potential as the mass signal shows a peak at $\sim$ 0.12 V and $\sim$ 0.22 V for the negative- and positive-going scan respectively, while the current does not. It is likely that other non-volatile products are formed and these were measured by ion chromatography. For the measurement of non-volatile products, samples were collected during a linear voltammetric scan in the same potential range and analyzed with IC. The voltammogram is given in Fig. 4 in blue together with the calculated concentration profile. It can be seen that hydroxylamine is formed dominantly together with some ammonia. The formation of these products starts at a potential just below 0.2 V. There is a difference in the voltammogram with and without sample collection (shown later in Fig. 11) as a result of the tip which presumably removes poisoning species from the electrode surface. The current is therefore a little higher and shows fluctuations during sample collection. In addition to nitrate reduction on a PdSn electrode,

Please cite this article in press as: Y.Y. Birdja, et al., Electrocatalytic Reduction of Nitrate on Tin-modified Palladium Electrodes, Electrochim. Acta (2014), http://dx.doi.org/10.1016/j.electacta.2014.06.011

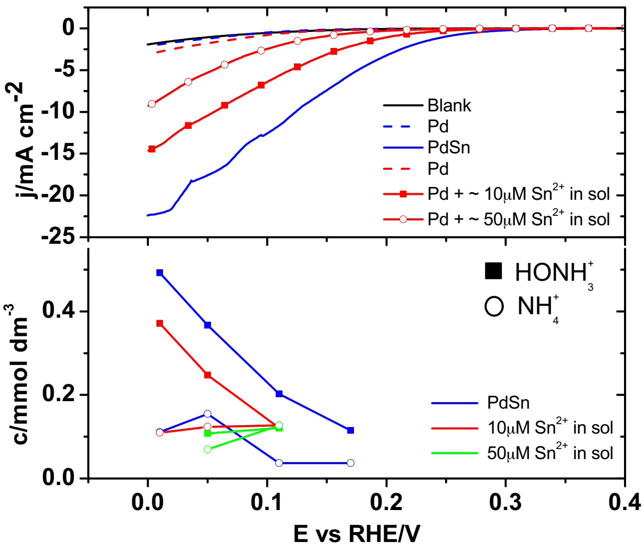

Fig. 4. Non-volatile reaction products for the nitrate reduction on PdSn in 0.1 M H_2SO_4 and Pd in a Sn^{2+} containing 0.1 M H_2SO_4 solution. Scan rate: 1 mV/s

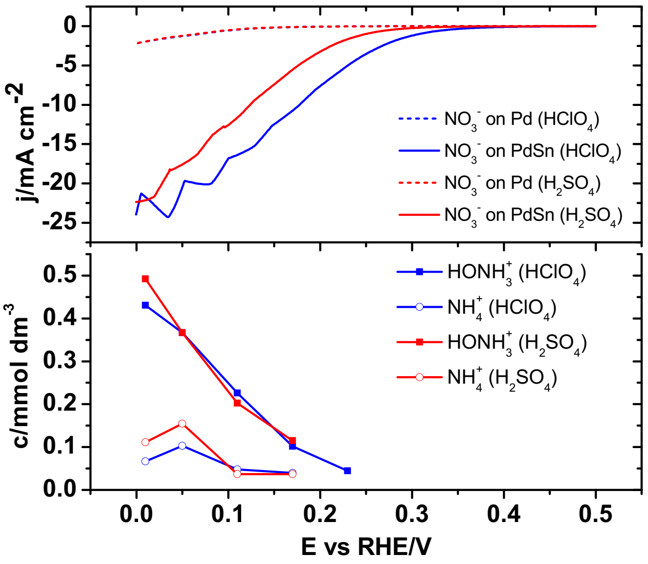

Fig. 5. Anion effect for the nitrate reduction on PdSn. Scan rate: 1 mV/s

the nitrate reduction was also investigated on a Pd electrode in a solution containing Sn ions. This leads to reversible adsorption of Sn during the voltammetric scan compared to irreversible adsorption of Sn which is the case for the Sn-modified Pd electrode. The corresponding CV's (in red) and the concentrations of protonated hydroxylamine and ammonia, $HONH_3^+$ and NH_4^+, as function of potential are also shown in Fig. 4. The dashed lines correspond to the pristine Pd electrode before adsorption of Sn adatoms. With Sn^{2+} in the solution it is observed that the onset of nitrate reduction is delayed and the current is lower (smaller amount of reaction products are formed) compared to the electrode with a Sn-modified Pd electrode. Furthermore, a higher concentration of Sn species in the solution has a negative influence on the catalytic activity for nitrate reduction, which could be ascribed to a blocking effect by the excess Sn ions.

3.1.5. Anion effect

From previous work on Pt it is known that the nitrate reduction is sensitive to the presence of other adsorbing species as nitrate first needs to adsorb on the surface for the reduction of NO_3^- to NO_2^-. Therefore the nitrate reduction has been investigated in two electrolytes: H_2SO_4 and $HClO_4$. Fig. 5 shows that in the presence of the non-adsorbing perchlorate anion the onset potential of nitrate reduction on PdSn is around 0.37 V while in H_2SO_4 it is around 0.3 V. The nitrate reduction is suppressed by the strongly adsorbed (bi)sulfate. This is similar to the results for nitrate reduction on platinum [27]. Furthermore, also in $HClO_4$ it is found that Pd is inactive for the nitrate reduction without addition of Sn species. The product distribution, however, is the same for both electrolytes and shows the same trend as a function of potential.

3.2. Nitrate reduction on (ultra)thin palladium films

3.2.1. Preparation of palladium films

Thin palladium overlayers have been extensively studied in the last decades as they are very interesting for electrocatalysis. Various electrochemical reactions have been studied on these systems such as adsorption and absorption of hydrogen [28], oxidation of formic acid [29,30], formaldehyde [31], CO adlayers [32] and the reduction of oxygen [33]. Different substrates have been investigated for the Pd deposition. Au(111) [28,34,35] and Pt(111) [29,36–38] are widely used and more recently also Rh(111) [39], Ru(0001) [40] and Ir, Re and PtRu [41].

In this work two methods have been used to prepare the thin films. The first is commonly used in literature and is simply Pd electrodeposition on the substrate which leads to films with a thickness of several multilayers. We used polycrystalline Au as substrate and the Pd electrodeposition was carried out at 0.27 V_{SCE} for 60 seconds in 0.1 M H_2SO_4 + 0.1 mM $PdCl_2$. The Pd film was characterized electrochemically by cycling in the blank electrolyte between 0 and 1.0 V_{RHE}. The voltammogram given in Fig. 6 (blue trace) shows the presence of the hydrogen adsorption/absorption and desorption as for bulk Pd (black trace). As expected the current is lower compared to the voltammogram of the bulk Pd electrode.

The second method for Pd film preparation is to deposit one single monolayer of Pd on the substrate (Au in our case). The monolayer palladium film is obtained by a spontaneous irreversible redox process in which a UPD Cu adlayer is replaced by Pd atoms. This technique has been demonstrated to result in a uniform 2D deposit

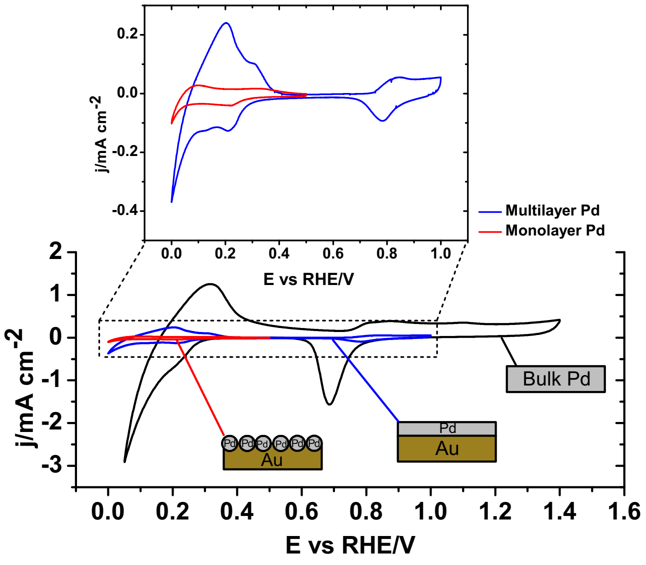

Fig. 6. Comparison of blank CV's for bulk Pd, multilayer and submonolayer AuPd electrodes. Scan rate: 100 mV/s

Please cite this article in press as: Y.Y. Birdja, et al., Electrocatalytic Reduction of Nitrate on Tin-modified Palladium Electrodes, Electrochim. Acta (2014), http://dx.doi.org/10.1016/j.electacta.2014.06.011

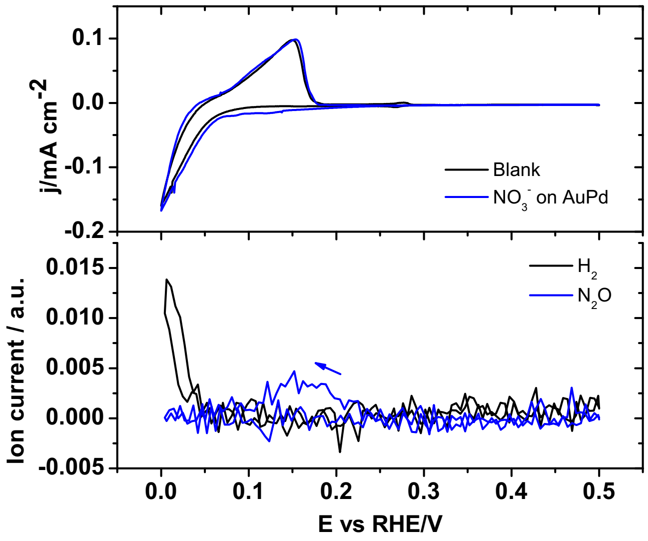

Fig. 7. Nitrate reduction on the unmodified multilayer AuPd including the formation of volatile products. Scan rate: 1 mV/s

covering the substrate [42–44]. First we deposited 1 monolayer of Cu on Au by UPD at 0.05 $V_{Ag/AgCl}$ for 3 minutes in 1 mM $CuSO_4$ + 0.1 M H_2SO_4. Next the electrode was immersed in 0.1 mM $PdCl_2$ + 0.1 M H_2SO_4 for 10 minutes. After rinsing the electrode was brought into the electrolye where the potential was cycled between 0 and 0.5 V_{RHE} until a stable voltammogram was obtained. The upper limit of the potential is kept relatively low to prevent the formation of oxides. This voltammogram is also shown in Fig. 6 (red trace). In comparison with the bulk Pd and the multilayer AuPd electrodes, the current is again much lower, and in this case it must be due to hydrogen adsorption only. In our experiments we have not investigated the coverage of Pd on Au with other techniques. As the charge for the hydrogen adsorption/desorption region for this Pd film is variable and lower compared to the charge of a fully covered Pd monolayer (in Fig. 6 the coverage from the H adsorption is approximately 0.5 ML), we will refer to it as a submonolayer Pd film throughout this work.

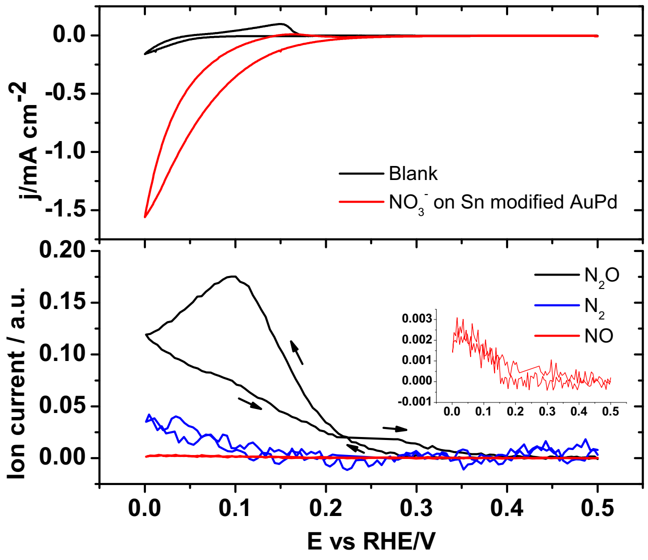

Fig. 8. Nitrate reduction on the Sn-modified multilayer AuPd electrode including the formation of volatile products (inset: zoom in on the NO mass signal). Scan rate: 1 mV/s

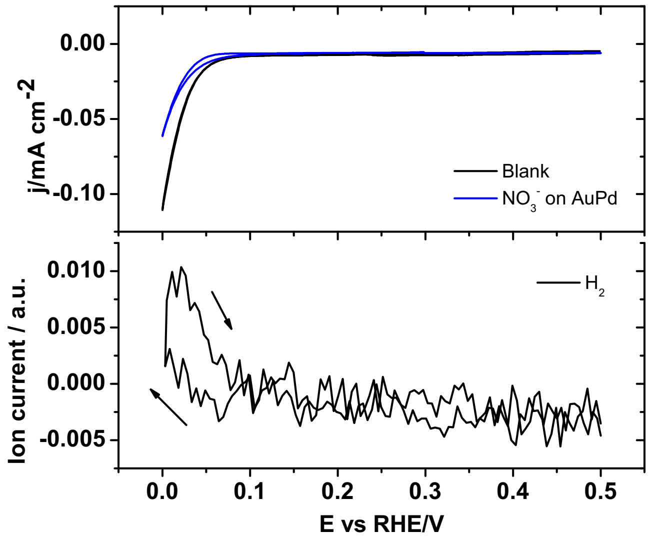

Fig. 9. Nitrate reduction on the unmodified submonolayer AuPd electrode including the formation of volatile products. Scan rate: 1 mV/s

3.2.2. *On-Line Electrochemical Mass Spectrometry*

In Figs. 7 and 8 the CVs and the mass signals as a function of potential are shown for the nitrate reduction on an unmodified- and Sn-modified multilayer Pd film on Au respectively. Without Sn on the surface H_2 (m/z =2) is the dominant product at potentials < 0.05 V_{RHE} together with trace amounts of N_2O (m/z = 44) only in the negative-going scan. When the electrode is modified by Sn a large current enhancement is observed similar to the bulk Pd electrode. The hydrogen formation is now strongly suppressed the signal is weaker compared to the lowest ion current of the products shown in the figures and large amounts of N_2O are produced together with a smaller amount of N_2 (m/z = 28). Furthermore a small amount of NO (m/z = 30, as mentioned this signal has been corrected for fragmentation of N_2O) is observed together with the mass fragments m/z = 14, 45 and 46. The latter three follow the same trend as N_2O and are therefore considered to be a fragment of N_2O after ionization, whereas the m/z = 14 (N) signal is also a fragment of N_2.

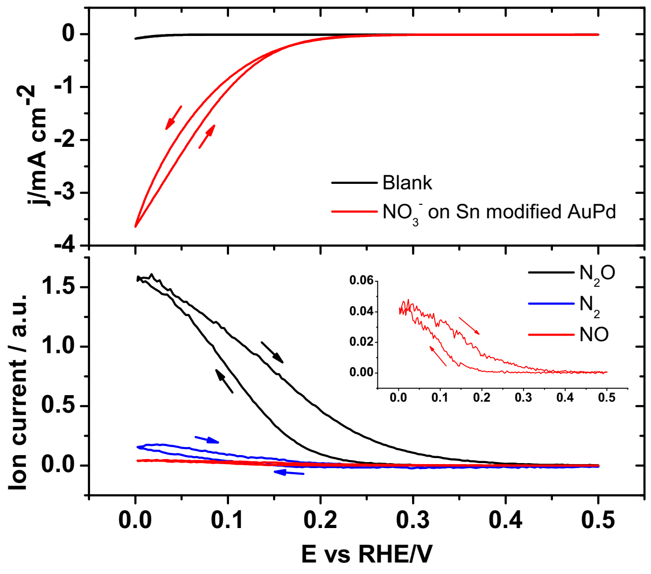

Fig. 10. Nitrate reduction on the Sn-modified submonolayer AuPd electrode including the formation of volatile products. Scan rate: 1 mV/s

Please cite this article in press as: Y.Y. Birdja, et al., Electrocatalytic Reduction of Nitrate on Tin-modified Palladium Electrodes, Electrochim. Acta (2014), http://dx.doi.org/10.1016/j.electacta.2014.06.011

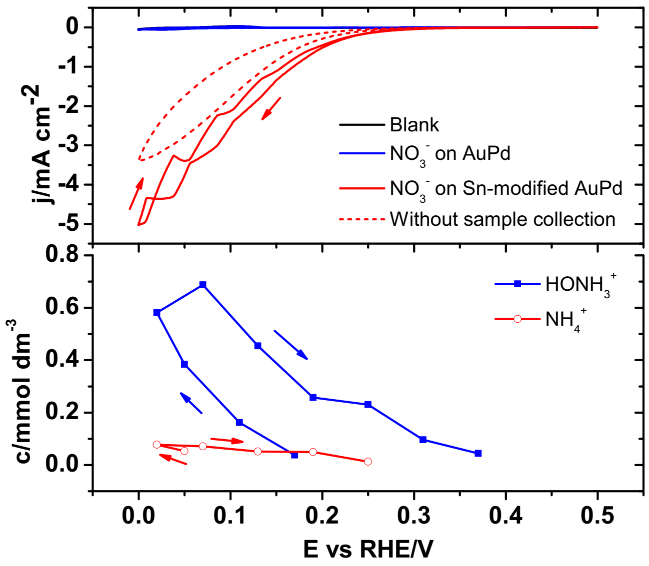

Fig. 11. Non-volatile product formation for nitrate reduction on the Sn-modified multilayer AuPd electrode. Scan rate: 1 mV/s

In Figs. 9 and 10 the formation of volatile products on a submonolayer AuPd electrode is shown with and without modification by Sn. Unmodified 1 ML AuPd results only in hydrogen evolution, while Sn-modification leads to a significant increase in activity. Again N_2O is the dominant product followed by N_2 and NO. This is similar to the Sn-modified multilayer Pd film and bulk Pd electrode.

3.2.3. *Ion Chromatography*

The non-volatile product formation using IC for the unmodified AuPd electrodes (multilayer and submonolayer Pd on Au) is not shown here as there were no products observed. After Sn-modification the non-volatile product formation as function of potential is shown in Fig. 11 for the multilayer AuPd and in Figure 12 for the submonolayer AuPd electrode. As seen before for the bulk Pd electrode the current is a little higher and shows fluctuations due to the sample collection. On both electrodes hydroxylamine and ammonia are formed. The Sn-modified multilayer AuPd produces about twice as much hydroxylamine compared to the Sn-modified submonolayer AuPd and is also more selective towards hydroxylamine than the Sn-modified submonolayer AuPd. The absolute current and the current profile are similar. Comparison of Figs. 8 and 11 (products on multilayer AuPd) to Figs. 10 and 12 (products on submonolayer AuPd) suggests that the Sn-modified submonolayer AuPd produces more NO and N_2O and is less efficient in the further reduction of NO to hydroxylamine and ammonia than the multilayer AuPd. An explanation for this may be related to the amount of Pd that is needed for the further reduction of NO to hydroxylamine or ammonia. The amount of Pd is less on the submonolayer AuPd compared to the multilayer AuPd which results in a lower amount of hydroxylamine and ammonia, but a higher amount of NO and N_2O.

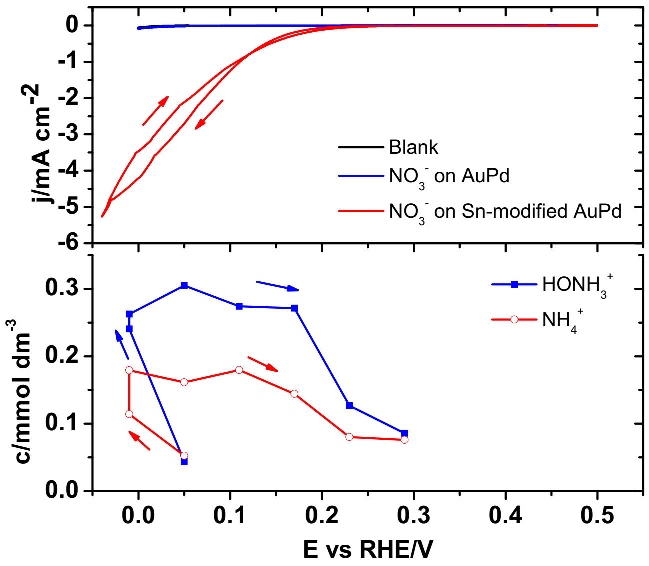

Fig. 12. Non-volatile product formation for nitrate reduction on the Sn-modified submonolayer AuPd electrode. Scan rate: 1 mV/s

4. Conclusions

Tin adsorbed on a Pd electrode can effectively increase the activity for the nitrate reduction in acidic media. It is believed that Sn catalyzes the rate determining step from NO_3^- to NO_2^- as it does on a platinum electrode. A pristine Pd electrode only shows hydrogen evolution and has no activity for the nitrate reduction, while on PdSn N_2O is found to be the dominant product together with a smaller amount of N_2. In addition to these volatile products hydroxylamine is produced dominantly together with a small amount of ammonia. Sn ions in the solution lead to a lower catalytic activity compared to the Sn-modified electrode as a higher concentration of Sn ions lowers the activity. It was also found that the nature of the anions influences the onset of the nitrate reduction. The stronger adsorbing sulfate anion delays the nitrate reduction compared to the non-adsorbing perchlorate anion. However, the product distribution is not affected.

In addition, this paper has shown that the ability of palladium to absorb hydrogen plays a negligible role in the nitrate reduction. The nitrate reduction on a multilayer and on a submonolayer Pd film deposited on Au without Sn-modification leads only to hydrogen evolution and no nitrate reduction in agreement with the lack of activity of bulk palladium. It should be noted that trace amounts of N_2O were observed in a small potential region for the multilayer AuPd but not on the submonolayer AuPd. When both AuPd electrodes are modified with Sn, on both electrodes N_2O is formed as the dominant volatile product and NH_2OH as the dominant non-volatile product. This is similar to the product distribution of the nitrate reduction on the Sn-modified bulk Pd electrode.This product spectrum is similar to the Sn modified platinum [6,24,25], whereas a Sn-modified rhodium electrode produces more ammonia [45], owing to the higher propensity of Rh to break the N-O bond.

Acknowledgements

The authors acknowledge a Chinese Scholarship Council (CSC) grant awarded to Jian Yang.

References

[1] Council Directive 98/83/EC. Official Journal of the European Communities, November 1998.
[2] K. Tada, K. Shimazu, J. Electroanal. Chem. 577 (2005) 303.
[3] G.E. Dima, V. Rosca, M.T.M. Koper, J. Electroanal. Chem. 599 (2007) 167.
[4] M.C.P.M. Da Cunha, J.P.I. De Souza, F.C. Nart, Langmuir 16 (2000) 771.
[5] O. Sureta-Zañartu, C. Yáñez, Electrochim. Acta 42 (1997) 6.
[6] J. Yang, F. Calle-Vallejo, M. Duca, M.T.M. Koper, ChemCatChem 5 (2013) 1773.
[7] V. Rosca, M. Duca, M.T. de Groot, M.T.M. Koper, Chem. Rev. 109 (2009) 2209–2244.
[8] J. Sa, D. Gasparovicova, K. Hayek, E. Halwax, J.A. Anderson, H. Vinek, Catal. Lett. 105 (2005) 209–217.
[9] U. Prusse, M. Hahnlein, J. Daum, K.D. Vorlop, Catal. Today 55 (2000) 79–90.
[10] A.C.A. de Vooys, R.A. van Santen, J.A.R. van Veen, Journal of Mol. Cat. A: Chem. 154 (2000) 203.

Please cite this article in press as: Y.Y. Birdja, et al., Electrocatalytic Reduction of Nitrate on Tin-modified Palladium Electrodes, Electrochim. Acta (2014), http://dx.doi.org/10.1016/j.electacta.2014.06.011

[11] A.C.A. de Vooys, M.T.M. Koper, R.A. van Santen, J.A.R. van Veen, Journal of Catalysis 202 (2001) 387.
[12] J.F.E. Gootzen, L. Lefferts, J.A.R. van Veen, Applied Catalysis A: General 188 (1999) 127.
[13] J.F.E. Gootzen, P.G.J.M. Peeters, J.M.B. Dukers, L. Lefferts, W. Visscher, J.A.R. van Veen, J. Electroanal. Chem. 434 (1997) 171–183.
[14] K. Shimazu, R. Goto, S. Piao, R. Kayama, K. Nakata, Y. Yoshinaga, J. Electroanal. Chem. 601 (2007) 161–168.
[15] F.A. Lewis, The Palladium Hydrogen System, Academic Press, London, 1967.
[16] M.R. Gennero de Chialvo, A.C. Chialvo, J. Electroanal. Chem. 372 (1994) 209.
[17] S. Szpak, C.J. Gabriel, J.J. Smith, R.J. Nowak, J. Electroanal. Chem. 309 (1991) 273.
[18] L.I. Antropov, Theoretical Electrochemistry, 2nd edition, Mir Publishers, Moscow, 1977.
[19] R. Woods, in: A.J. Bard (Ed.), Electroanalytical Chemistry, vol. 9, M. Dekker, New York, 1976.
[20] G. Jerkiewicz, Prog. Surf. Sci 57 (1998) 137.
[21] S.C.S. Lai, M.T.M. Koper, Faraday Discuss. 140 (2008) 399.
[22] A.H. Wonders, T.H.M. Housmans, V. Rosca, M.T.M. Koper, J. Appl. Electrochem. 36 (2006) 1215.
[23] M. Duca, V. Kavvadia, P. Rodriguez, S.C.S. Lai, T. Hoogenboom, M.T.M. Koper, J. Electroanal. Chem. 649 (2010) 59.
[24] J. Yang, M. Duca, K.J.P. Schouten, M.T.M. Koper, J. Electroanal. Chem. 662 (2011) 87–92.
[25] J. Yang, Y. Kwon, M. Duca, M.T.M. Koper, Anal. Chem. 85 (2013) 7645–7649.
[26] G.E. Dima, A.C.A. de Vooys, M.T.M. Koper, J. Electroanal. Chem. 554-555 (2003) 15–23.
[27] M. Duca, M.T.M. Koper, Energy Environ. Sci. 5 (2012) 9726.
[28] M. Baldauf, D.M. Kolb, Electrochim. Acta 38 (1993) 2145.
[29] M. Baldauf, D.M. Kolb, J. Phys. Chem. 100 (1996) 11375.
[30] L.A. Kibler, A.M. El-Aziz, D.M. Kolb, J. Mol. Catal. A 199 (2003) 57.
[31] H. Naohara, S. Ye, K. Uosaki, J. Electroanal. Chem. 500 (2001) 435.
[32] A.M. El-Aziz, L.A. Kibler, J. Electroanal. Chem. 534 (2002) 107.
[33] H. Naohara, S. Ye, K. Uosaki, Electrochim. Acta 45 (2000) 3305.
[34] H. Naohara, S. Ye, K. Uosaki, J. Phys. Chem. B 102 (1998) 4366.
[35] L.A. Kibler, M. Kleinert, R. Randler, D.M. Kolb, Surf. Sci. 443 (1999) 19.
[36] R. Hoyer, L.A. Kibler, D.M. Kolb, Electrochim. Acta 49 (2003) 63.
[37] G.A. Attard, A. Bannister, J. Electroanal. Chem. 300 (1991) 467.
[38] J. Inukai, M. Ito, J. Electroanal. Chem. 358 (1993) 307.
[39] R. Hoyer, L.A. Kibler, D.M. Kolb, Surf. Sci. 562 (2004) 275.
[40] S.R. Brankovic, J. McBreen, R.R. Adzic, Surf. Sci. 479 (2001) L363.
[41] L.A. Kibler, A.M. El-Aziz, R. Hoyer, and D.M. Kolb International Conference on Electrified Interfaces, Spa, Belgium, 11-16 July, 2004.
[42] S.R. Brankovic, J.X. Wang, R.R. Adzic, Surf. Sci. 474 (2001) L173–L179.
[43] L.B. Sheridan, J. Czerwiniski, N. Jayaraju, D.K. Gebregziabiher, J.L. Stickney, D.B. Robinson, M.P. Soriaga, Electrocatal 3 (2012) 96–107.
[44] L.B. Sheridan, D.K. Gebregziabiher, J.L. Stickney, D.B. Robinson, Langmuir 29 (2013) 1592–1600.
[45] W. Siriwatcharapiboon, Y. Kwon, J. Yang, R. L. Chantry, Z. Li, S. L. Horswell, and M. T. M. Koper ChemElectroChem1 (2014) 172.

Please cite this article in press as: Y.Y. Birdja, et al., Electrocatalytic Reduction of Nitrate on Tin-modified Palladium Electrodes, Electrochim. Acta (2014), http://dx.doi.org/10.1016/j.electacta.2014.06.011