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Promotion of the Electrocatalytic Reduction of Nitrate

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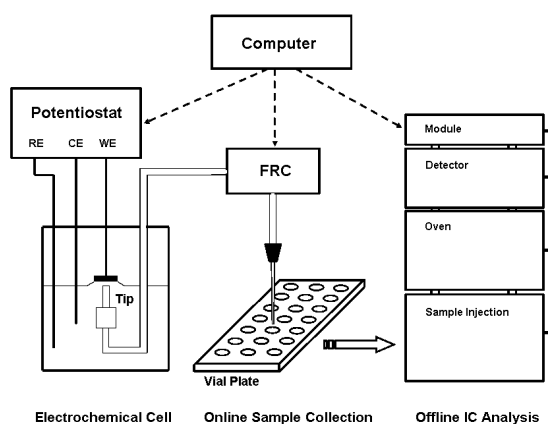
Combining voltammetry and ion chromatography: application to the selectivity reduction of nitrate on Pt and PtSn electrodes

Abstract

To overcome the shortcomings of electroanalytical methods (such as rotating ring-disk electrode voltammetry) in analyzing the ionic products that are seen as electrochemically inert or lack distinct “footprints” in electrochemistry, we suggest to combine voltammetry with ion chromatography by applying online sample collection to the electrochemical cell and offline analysis of ion chromatography. In this way, the potential dependence of product distribution can be obtained quantitatively. The method is used to investigate the non-volatile products from nitrate reduction on Pt and Sn-modified Pt electrode in acid. On Pt electrode, ammonia formation was demonstrated as the only product. After Sn modification of the Pt electrode, the selective formation of hydroxylamine as a dominant product rather than ammonia was observed. Moreover, the rate determining step of the nitrate reduction to nitrite on Pt electrode was enhanced by Sn modification and a certain concentration of nitrite was evidenced on Pt surface with high coverage of Sn.

4.1. Introduction

The quantitative detection of products of electrochemical and electrocatalytic reactions during (cyclic) voltammetry is an important prerequisite for the development of selective electrocatalysts. The detection of ionic products is most typically performed employing electrochemical analysis, usually based on the rotating ring-disk electrode (RRDE) setup, in which the ring electrode serves as the in situ detection electrode for the product generated at the disk.^{1, 2} However, the RRDE method relies on having a ring electrode material with a corresponding electrochemical specificity for the ionic product under consideration. Such conditions are not always met, for instance because the product cannot be reduced or oxidized easily, or because of the interference of other electrochemical reactions on the ring electrode.



Scheme 1. Schematic setup of the on-line sample collection with fraction collector (FRC) equipped with a micro-sized sample collecting tip that is close to the electrode surface during voltammetry, with subsequent analysis of sample fractions in a IC system. WE: working electrode, RE: reference electrode, and CE: counter electrode.

A typical example for which the RRDE method cannot be applied is the selective reduction of nitrate on platinum and modified platinum electrodes in acidic media to the ammonium and hydroxylammonium cations. This reaction is of practical interest in the selective production of hydroxylamine, an important intermediate in the industrial production of nylon-6.³⁻⁵ The RRDE method can qualitatively detect hydroxylammonium, though with some uncertainty as to the corresponding electrode reaction and not without the interference of other reactions,^{6, 7} but ammonium cannot be oxidized in acidic media at the Pt ring

electrode, and therefore RRDE measurements are not suitable for obtaining quantitative insight into the selectivity of various electrocatalysts for nitrate reduction.

In this Chapter, cyclic (linear-sweep) voltammetry of nitrate reduction on platinum and tin-modified platinum electrodes is combined with online ion chromatography to demonstrate the capabilities of this novel combination for studying selective electrocatalysis. The setup is illustrated in Scheme 1. The paper builds on a previous combination of cyclic voltammetry (CV) and high-performance liquid chromatography (HPLC), using online sample collection and subsequent off-line sample analysis.⁸ The combination of CV and HPLC has successfully been applied to the elucidation of the mechanism of the glycerol oxidation,^{9, 10} carbon dioxide reduction,¹¹ and glucose reduction.¹² With such a combination of CV and chromatography, it is possible to relate the current measured during voltammetry with the product distribution without the need to do long-term electrolysis, which is the customary way to gain insight into the product spectrum.

4.2. Experimental

Ultrapure water (Millipore MilliQ, resistivity > 18.2 MΩ cm) was used to prepare all solutions. The glassware was cleaned by Piranha solution (a mixture of concentrated sulfuric acid and 30% hydrogen peroxide in a ratio 3:1) and then boiled with ultrapure water three times before starting the experiment. Nitric acid (Merck, suprapur, 65%) and sodium nitrate (Merck, 99.99%) were used to prepare nitrate solutions. A Pt plate was applied as a working electrode. It was flame-annealed and then cooled down in an argon atmosphere before transferring it to the electrochemical cell. The modification of Pt electrode by Sn species was carried out by a dipping method involving spontaneous adsorption as was reported in detail before¹³. In all electrochemical measurements a Pt wire was used as the counter electrode and a reversible hydrogen electrode was used as reference electrode. All solutions were purged with argon (purity grade 6.0) to remove dissolved oxygen prior to electrochemical measurements, and voltammograms were recorded with an Autolab potentiostat (Pgstat20).

The experimental setup combines an ion chromatography unit (Shimadzu, Prominence), that is equipped a conductivity detector (CDD-10A vp, Shimadzu), with an automatic fraction collector (FRC-10A, Shimadzu) to collect samples by

using a small Teflon tip, which is positioned in solution, close to the surface of the working electrode in the electrochemical cell.⁸ The overall setup is similar to the CV+HPLC setup detailed previously.⁸ For cation (NH_4^+ and HONH_3^+) detection, hydroxylammonium sulfate (Merck, 99.99%) and ammonium sulfate (Merck, 99.99%) were used to prepare standard solutions, from which the retention time was characterized and the concentration was calibrated for each targeted cation. A IC Y-521 cation column (Shodex) was applied and nitric acid (Merck, suprapur, 65%) was used to prepare the eluent (2.5mM). The column was kept at a temperature of 30 °C and the flow rate was set at 0.8 mL/min. For anion (NO_2^-) measurement, sodium nitrite (Merck, 99.99%) was used to prepare the standard solutions. The anion column NI-424 (Shodex) that was used to separate nitrite from nitrate to detect nitrite formation during nitrate reduction was kept at a temperature of 40 °C with an eluent flow rate of 0.6 mL/min. The eluent consisted of 2.8 mM BIS-TRIS (Fluka, BioXtra, >99.0%), 2 mM phenylboronic acid (Fluka, purum, >97%), 8 mM 4-hydroxybenzoic acid (Aldrich, 99%), and 0.005 mM trans-1, 2-Diaminocyclohexane-N, N, N', N'-tetra acetic acid (Sigma-Aldrich, ACS reagent, >99.0%), which is the standard component suggested by Shodex for NI-424 column. The eluent was filtrated through a 0.45 μm PTFE membrane (Whatman) before being used in the IC system with the anion column.

As is well known there are homogeneous chemical reactions between the cation products and nitrite that could take place before samples are analyzed by IC,⁷ though their rates may be very slow due to the lower concentration of the reagents that are produced by electro-reduction of nitrate, especially of nitrite. At the same time the decomposition of nitrite in acid is significant,⁷ so that less nitrite would take part in the chemical reactions with cation products. In the detection of the cation products from nitrate reduction, we did not add metal hydroxide solution to adjust the sample pH to suppress these side-reactions, to avoid other metal cations from disturbing the targeted cation separation in the column. However, we did simulate the coexistence of cations with nitrite in the same acidic electrolyte and measured the hydroxylamine and ammonia concentrations in the same way as samples from the voltammetry measurement were analyzed, to find that there was a negligible loss of hydroxylamine and ammonia during sample analysis, as shown in Figure 1. Therefore, the IC measurement of the cations could be considered rapid enough to assure that the measured values of the concentration of cation products are approximately equal to the actual ones.

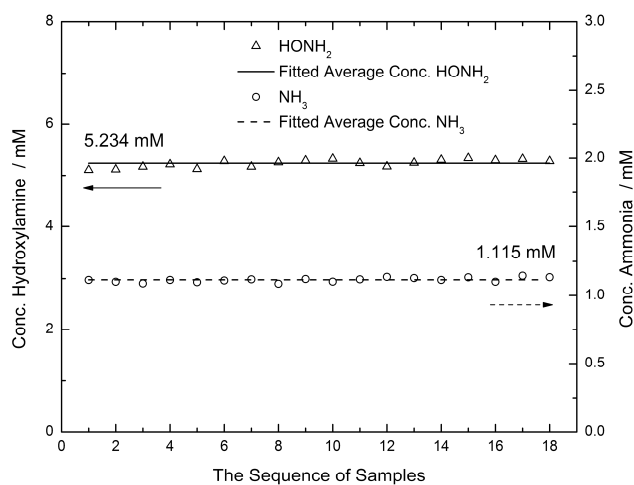


Figure 1. The variation of hydroxylamine and ammonia concentration during the IC analysis. The samples were simulated in an electrochemical experiment of nitrate reduction and contained 2.513 mM $(\text{HONH}_3)_2\text{SO}_4$, 0.504 mM $(\text{NH}_4)_2\text{SO}_4$, 0.131 mM NaNO_2 and 0.1 M HNO_3 in 0.1 M HClO_4 electrolyte.

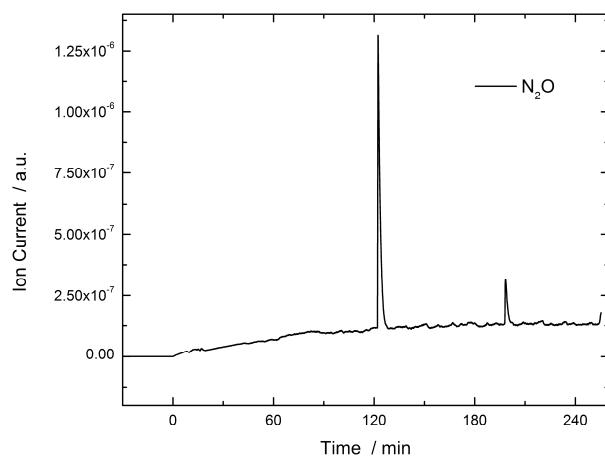


Figure 2. The mass spectrum of N_2O formation in the chemical reaction between 0.1 M NaNO_2 and 0.1 M $(\text{HONH}_3)_2\text{SO}_4$ in 0.1 M phosphate buffer of pH=7. The beginning of the reaction time is defined as the two solutions were mixed together in OLEMS cell. The spikes are due to the gas bubbles of N_2O that agglomerated around the sampling tip in solution.

However, these influences should be also considered during anion analysis. All experiments aimed at cation detection were performed in a solution of 0.1 M HClO_4 and 0.1 M HNO_3 , to avoid alkali cation interference with in the IC column. However, in order to inhibit the decomposition of nitrite in acid, the experiments of nitrate reduction were carried out in solution of a slightly lower pH, i.e. 0.1 M HClO_4 and 0.1 M NaNO_3 , and pH of the samples was neutralized to stabilize nitrite before IC analysis, assuming that acidity of solution around electrode surface is the same as the bulk pH during the nitrate reduction. LiOH (Aldrich, monohydrate, 99.995%) solution (0.1 M, 60 μL) was added to each sample vial by pipette to adjust sample pH before the IC analysis and pH value was checked by pH indicator strip (Merck) to be around 6. Even though the samples are neutralized, the chemical reactions between nitrite and cation products can not always be avoided. The chemical reaction between hydroxylamine and nitrite was reported to be independent on solution pH,¹⁴ and the formation of N_2O as the only product was checked by OLEMS measurement as shown in Figure 2; for the reaction between ammonia and nitrite, N_2 formation with a lower reaction rate in neutral medium was found out as well.¹⁵ Therefore, we emphasize that the measured values of the nitrite concentration are always lower than the actual ones. The OLEMS setup used for these experiments was described in detail elsewhere,¹³ and NaH_2PO_4 (Merck, 99.99%), Na_2HPO_4 (Merck, 99.99%) was used to prepared the phosphate buffer of pH=7 used for the experiment in Figure 2.

4.3. Results and Discussion

Most previous research on nitrate reduction on single crystal and polycrystalline Pt electrodes has concluded that ammonium is the main product in the potential region where hydrogen adsorption occurs on the Pt surface, with no significant formation of hydroxylamine.¹⁶⁻¹⁹ Figure 3 gives explicit evidence for the formation of the ammonium cation during nitrate reduction on a polycrystalline Pt electrode, and online sample collection causes only a minor influence on the voltammetry, as was observed and discussed previously for the CV+HPLC setup.⁸ The ammonium formation follows the peak in the Faradaic current variation as the electrode potential is scanned negatively, which is due to the competitive adsorption of hydrogen at relatively negative potential inhibiting the further reduction of nitrate to ammonia. Additionally, no hydroxylamine could be detected in the samples collected during the voltammetry measurement, demonstrating that ammonia is the main soluble product from nitrate reduction on a Pt electrode. Since previous

OLEMS measurements¹⁷ have shown that no volatile products are formed during nitrate reduction on unmodified platinum, ammonium is the overall dominant product.

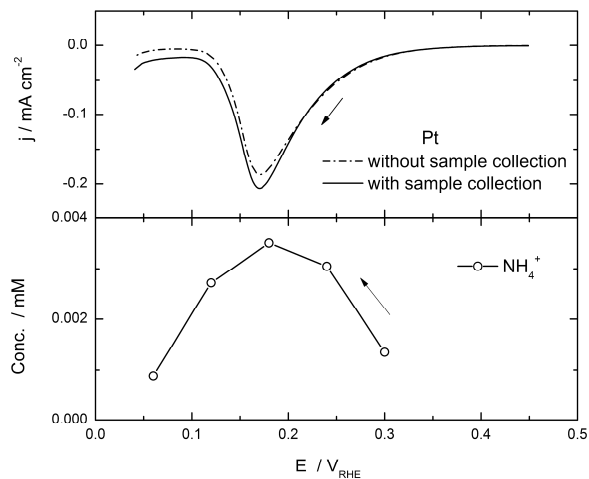


Figure 3. Linear sweep voltammogram and corresponding formation of ammonium during nitrate reduction on a Pt electrode in a solution of 0.1 M HNO_3 with 0.1 M HClO_4 at a scan rate of 1 mV/s.

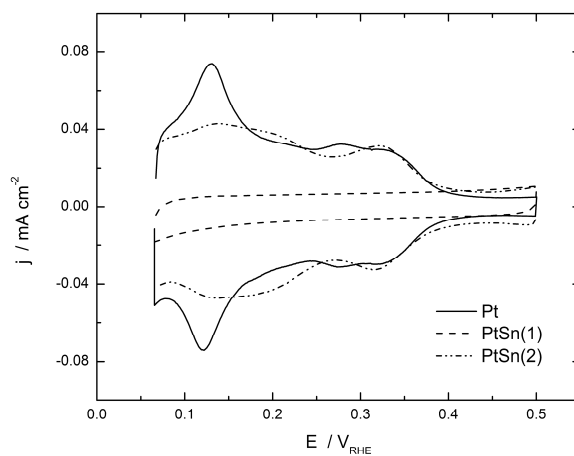


Figure 4. The cyclic voltammograms of Pt and Sn-modified Pt electrodes in 0.1 M HClO_4 solution at scan rate of 50 mV/s. The calculated coverage about Sn species on Pt surface: (1) 0.228; (2) 0.913.

The voltammograms of the Pt and Sn-modified Pt electrodes in 0.1 M HClO_4 solution are shown in Figure 4, where the coverages of Sn species were calculated from the hydrogen adsorption charge before and after Sn modification on polycrystalline Pt electrode.¹³ For the electrode with a low to intermediate coverage of Sn species (ca. 0.2 ML), as shown in Figure 5, the hydroxylammonium cation was found to be a more dominant reaction product than ammonia in essentially the entire potential range in which the PtSn electrode is active for nitrate reduction, although the formation of ammonia was also enhanced significantly in comparison to the unmodified Pt electrode. As for the volatile products from nitrate reduction on a polycrystalline Pt electrode with an intermediate coverage of Sn species, N_2O is the dominant product with a maximum yield at a potential of ca. 0.3 V, decaying to zero at 0 V.¹³ The formation of hydroxylamine and ammonia detected by IC was found to start at a potential a little negative from 0.3 V, suggesting that the maximum in N_2O production is due to a change in product distribution, i.e. towards soluble products. At the most negative potential, i.e. 0 V, we estimate the relative selectivity towards hydroxylammonium and ammonium to be ca. 82 % and 18 %, respectively. We ascribe the hysteresis of the IC signals to the faster rate of product formation than of sample collection resulting in the accumulation of products close to the electrode.

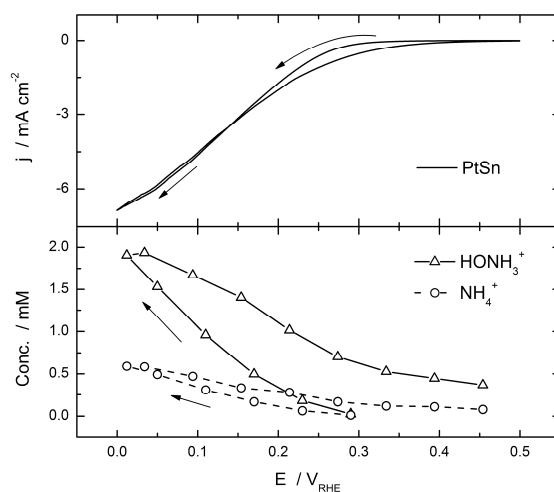


Figure 5. Cyclic voltammogram and corresponding formation of cation products from nitrate reduction on Sn-modified Pt electrode in solution of 0.1 M HNO_3 with 0.1 M HClO_4 at a scan rate of 1mV/s. The Sn coverage: 0.23.

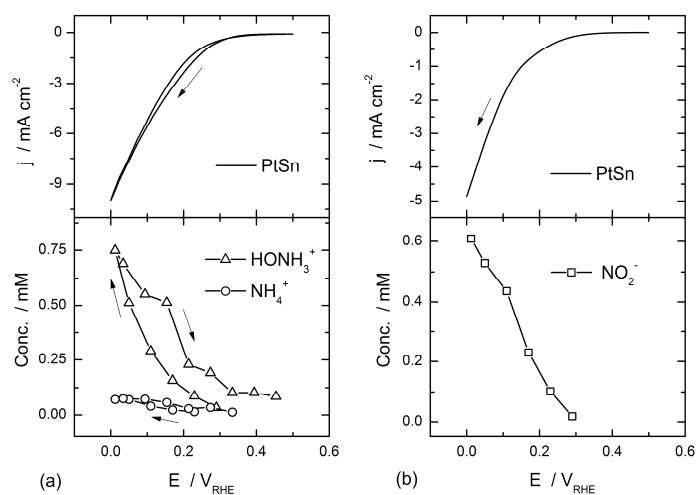


Figure 6. The voltammograms of Sn-modified Pt electrodes and corresponding non-volatile products from nitrate reduction at a scan rate of 1mV/s in solution of (a) 0.1 M HNO_3 + 0.1 M HClO_4 and (b) 0.1 M NaNO_3 + 0.1 M HClO_4 . The Sn coverage: 0.91.

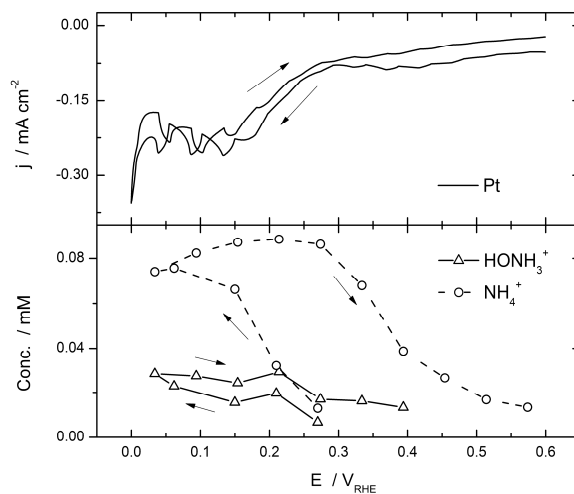


Figure 7. The cyclic voltammogram and corresponding formation of cation products for nitrite reduction on Pt electrode in solution of 2 mM NaNO_2 with 0.1 M HClO_4 at a scan rate at 1mV/s.

For a higher coverage of Sn species on the polycrystalline Pt surface (ca. 0.9 ML), a similar trend in the formation of hydroxylammonium and ammonium with potential variation is observed, as shown in Figure 6 (a). The measured

concentrations of hydroxylammonium and ammonium at this coverage of Sn are lower than at the intermediate coverage of Sn (Figure 5), indicating that the availability of free Pt sites on the Sn-modified surface is necessary to promote the formation of cationic products. Nonetheless, the relative selectivity to form hydroxylamine over ammonium increases to ca. 91 %. In terms of volatile products, NO is now the main product, as demonstrated in our previous paper.¹³ Therefore, it seems that the further reduction of NO is seriously hindered by a high coverage of Sn on the Pt surface. Moreover, as Sn is supposed to promote the reduction of nitrate to nitrite,²⁰ an anion column was applied to detect the formation of nitrite during the voltammetry. As shown in Figure 6 (b), a clear nitrite formation following the potential variation was found for the PtSn electrode, whereas there was no nitrite formation detected by IC on the unmodified Pt electrode. The difference in current density of Figure 6 (a) and (b) is ascribed to the solution pH since a higher concentration of protons in solution enhances nitrate reduction.²¹ Nonetheless, taking into consideration the instability of nitrite at low pH, the formation of nitrite on Sn-modified Pt electrode is expected to start at a potential more positive than the potential at which nitrite is first detected by IC. Moreover, the enhancement of the nitrate reduction by Sn species leads to the formation of NO as the dominant product at potentials more positive than 0.2 V,¹³ and NO formation would be mainly due to the decomposition of nitrite/nitrous acid in acid solution.^{7, 16} With more negative potential, the nitrite concentration increases.

Here it has to be kept in mind that both nitrite and NO in solution yield NO_{ad} on the Pt surface, which were both suggested to play an important role in the formation of cation products.^{7, 22} Therefore, Sn modification results in a higher coverage of NO_{ad} on Pt sites so that the formation of cation products is enhanced. However, we have to emphasize again that the real concentration of nitrite that was formed by electro-reduction of nitrate is higher than the measured one, due to the unavoidable chemical reactions involving nitrite.

Interestingly, nitrite reduction on a pristine Pt electrode in the same electrolyte gives rise to ammonia as the main product with much less formation of hydroxylamine, as shown in Figure 7. This suggests that there is a second role of the surface Sn species, i.e. not only to promote the conversion of nitrate to nitrite, but also to steer selectivity of nitrite/NO reduction to hydroxylammonium. In a recent paper, we concluded from DFT calculations that the presence of Sn on the Pt

surface enhances the adsorption energy of nitrate on the Pt surface, especially for the hydroxide state of Sn on the Pt surface.²⁰ The role of Sn in enhancing the selectivity towards hydroxylammonium is more likely related with the idea that Sn inhibits the N-O bond breaking through a third-body effect ⁶.

4.4. Conclusions

In this paper, we have introduced a combination of voltammetry and ion chromatography to study the selectivity to non-volatile products during nitrate reduction on Pt and Sn-modified Pt. This method can effectively detect hydroxylamine, ammonia, and nitrite individually during nitrate reduction on the timescale of conventional cyclic voltammetry. On a Pt electrode, ammonia was detected as the only product; on the Sn-modified Pt electrode, a 82 % selectivity to form hydroxylamine as the main (soluble) product was observed on Sn-modified Pt electrodes, especially at relatively negative potentials, where the formation of volatile products is negligible. Also, nitrite as an anion intermediate from nitrate reduction was detected on the PtSn surface with a high Sn coverage, in accordance with the model that Sn is able to enhance the first step of nitrate reduction to nitrite on the Pt surface. The current work also reveals a second role of the Sn adatom, namely in steering the selectivity from ammonia to hydroxylammonium, presumably through a third-body effect.

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