



Electrocatalysis



Electrocatalytic Oxidation of Amines by Ni(1,4,8,11tetraazacyclotetradecane)²⁺ Entrapped in Sol–Gel Electrodes

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Abstract: Nil²⁺ (L = 1,4,8,11-tetraazacyclotetradecane) was entrapped in sol-gel matrices in the presence of graphite. The matrices thus prepared serve as electrocatalysts for the oxidation of amines. The results point out that: (1) It is easy to prepare electrocatalytic electrodes by using this approach. (2) The properties of the electrodes thus prepared depend on the nature of the precursors used to prepare the matrices. (3) The mechanism of the electrocatalytic process differs from that observed in homogeneous solutions and depends on the nature of the electrode. (4) The matrix protects NiL²⁺ against the oxidation of the ligand.

Introduction

The simplicity and versatility of preparation of SiO₂ matrices by the sol–gel method, as well as the relative inertness and stability of the matrices, have promoted their use in a wide range of applications.^[1] A variety of active species can be incorporated into these matrices, including organic^[1b] and inorganic compounds,^[2] metals and metal oxide nanoparticles,^[3] bacteria,^[4] yeasts,^[5] and enzymes.^[1a,4,6] The matrices thus prepared can, among other things, act as catalysts,^[7] photocatalysts,^[8] electrocatalysts,^[9] slow-release agents,^[10] ion-exchange columns,^[11] and electron-exchange columns.^[2]

The advantages of electrodes consisting of an electrocatalyst entrapped in a sol-gel matrix coating a good conductor are: (1) The electrocatalyst can be recycled many times.^[12] (2) The electrode can operate in a medium in which the electrocatalyst is insoluble and/or unstable.^[2,12b]

The applications of these matrices in electrocatalysis are limited, because the matrices are insulators^[13] and therefore the plausible current densities are low.^[14] Furthermore, the diffusion of the substrate to the electrocatalyst is slow.^[13,15] There-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201500985. fore, the main applications of such electrodes are for analytical purposes and as sensors. $\ensuremath{^{[16]}}$

It seemed of interest to check whether the incorporation of a redox catalyst into a sol-gel matrix synthesized in the presence of graphite powder, introduced to improve conductivity, transforms it into an electrocatalyst. Nil²⁺ (L = 1,4,8,11-tetraazacyclotetradecane) was chosen as the potential electrocatalyst for the oxidation of amines, as it acts as an electrocatalyst for this process in homogeneous solutions^[12b] and when it is adsorbed onto active carbon.^[13] The following questions were asked:

(1) Does the nature of the precursors used to prepare the solgel matrix affect the electrocatalytic properties of the electrode?

(2) Does the entrapment of NiL²⁺ protect it from oxidative decomposition? In homogeneous solutions, NiL³⁺ decomposes by a second-order process^[17] oxidizing the ligand. This reaction is base-catalyzed,^[17a] that is, the life time of Ni^{III}L in neutral and alkaline solutions is very short.^[17a] It was shown that Ni^{III}L entrapped in a sol-gel matrix is stable even at pH 10.^[3] This observation was attributed to the inhibition of the reaction between two Ni^{III}L complexes in the matrix. However, in electrochemical experiments the electrode can, in principle, replace the second Ni^{III}L and thus decompose the catalyst.

In the present study, we decided to check whether electrodes consisting of a mixture of graphite, as the conducting component, and a sol–gel matrix containing NiL²⁺ can be used for the oxidation of $(CH_3)_nNH_{3-n}$. This choice is based on the following arguments:

(1) NiL²⁺ is a known electrocatalyst for the oxidation of amines in aqueous solutions^[18] and in heterogeneous systems.^[19]

(2) These amines are formed in a variety of industrial processes as byproducts,^[20] that is, as pollutants, and therefore their oxidation is of environmental interest.



Results and Discussion

The sol-gel electrodes were prepared by modifying the procedure reported in the literature.^[9d] A-1 and A-2 electrodes consist only of graphite and the corresponding precursor of the sol-gel matrix. A-1 electrodes were prepared with trimethoxymethylsilane (MTMOS) as the precursor, and A-2 electrodes were prepared with trimethoxyphenylsilane (TMOP) as the precursor. The Ni electrodes are identical to the A-*i* electrodes but contain NiL(PF₆)₂. The composition of the electrodes is summed up in Table S1 in the Supporting Information.

Leakage Study

One of the major disadvantages of sol-gel matrices is the plausible leakage of the active species from the matrix. The leakage of Ni^{III/II}L from the electrodes was studied. Details of the leakage study are given in the Supporting Information (Part S2). The results indicate that the leakage is negligible (less than 1 %) for both kinds of electrodes. This is lower than that reported for Ni^{III/II}L entrapped in sol-gel matrices.^[2] The source of this difference is probably the presence of graphite that affects the nature of the matrices either by adsorption of Ni^{III/II}L on the graphite and/or by affecting the structure of the matrices.

Oxidation of Amines

The electrochemical oxidation of three amines, methylamine, dimethylamine, and trimethylamine, was studied by using sol-gel electrodes without entrapped NiL²⁺ [glassy carbon (GC), A-1, and A-2 electrodes]. Figure 1 depicts the electrochemical oxidation of methylamine on glassy carbon, A-1, and A-2 electrodes. At lower pH values, the catalytic currents are small. As the sol-gel electrodes have a large surface area, the double-layer-charging current interferes with the exact measurement of the catalytic current at pH < 10. Therefore, a pH value of 10 was chosen. The results point out that the three amines studied are oxidized above 0.90 V vs. Ag/AgCl, when NiL²⁺ is not entrapped in the electrode.





Figure 1. Voltammograms of methylamine on different electrodes (50 mV/s; solution containing 3.0 \mbox{M} CH₃NH₂, 0.10 \mbox{M} NaClO₄ at pH 10.0; black: glassy carbon electrode, red: A-1 and green: A-2 sol–gel electrodes).

The cyclic voltammograms of Ni-*i* electrodes in NaClO₄ solutions at pH 10.0 (insets in Figures 2 and 3) point out that the entrapped NiL²⁺ is pseudo-reversibly oxidized at about 0.8 and 0.9 V in the Ni-1 and Ni-2 electrodes, respectively. These oxidation potentials are similar to the potential at which NiL²⁺ is oxidized in homogeneous solutions,^[21] 0.78 V vs. Ag/AgCl at pH 2.2. It is important to note that these cyclic voltammograms are not affected by many repetitions of the cycles or by using the electrodes in the presence of amines and then, after washing, in the absence of amines. This result indicates that the ligand in NiL²⁺ is not oxidized in the process, as the matrix protects it.



Figure 2. Voltammograms on sol-gel electrodes (50 mV/s; solution containing 3.0 $\,$ M (CH_3)_2NH, 0.10 $\,$ M NaClO4 at pH 10.0; red: Ni-1 and black: Ni-2 sol-gel electrodes; inset: 0.10 $\,$ M NaClO4 at pH 10.0; red: Ni-1 and black: Ni-2 sol-gel electrodes).

In the presence of amines (Figures 2 and 3), considerable oxidation currents are observed at values greater than 0.6 V vs.



E (V) vs. Ag/AgCl

Figure 3. Voltammograms on a Ni-2 sol-gel electrode (50 mV/s; all solutions contained 0.10 M NaClO₄ at pH 10.0 and 3.0 M each of N(CH₃)₃, NH(CH₃)₂, and NH₂CH₃; inset: 0.10 M NaClO₄ at pH 10.0).





Ag/AgCl. The results are similar to the electro-oxidation of these amines on glassy carbon electrodes in the presence of NiL²⁺ in solution.^[18] Thus, the results demonstrate that NiL²⁺ acts as an electrocatalyst also when it is immobilized in sol–gel matrices.

It is of interest to note that the results (Figure 3) point out that $N(CH_3)_3$ is oxidized through an electrocatalyzed process by the Ni-2 electrodes though this does not happen in the presence of NiL^{2+} in homogeneous solutions.^[12b] This result suggests that the mechanism of oxidation in homogeneous solutions differs from that in the sol-gel electrodes.

The current was studied as a function of the scan rate with and without dimethylamine in the solution, Figure 4 describes the results.

The linear dependence of the current on (scan rate)^{1/2} suggests that the observed electrochemical oxidations are governed by diffusion-controlled mechanisms. In the absence of the amines, it is the oxidation of the NiL²⁺ complex, in the presence of amines it is the oxidation of the amines. However, the intercepts in Figure 4 and the plateau observed for the catalytic oxidation of NH(CH₃)₂ on Ni-2 at the high scan rates (Figure 4) indicate that the mechanism is not simply diffusion-controlled. Similar results were reported for the oxidation of NiL²⁺ covalently bound to a sol-gel matrix embedded in a Nafion membrane adsorbed onto a glassy carbon electrode.^[22] These results are not surprising, as the entrapped NiL²⁺ species clearly do not diffuse freely in the matrix. The observation that the dependence of the current on (scan rate)^{1/2}, for the electrocatalytic oxidation of amines on Ni-2 electrodes, changes from linear to independent at higher scan rates suggests a change in the ratedetermining step, which implies a change in mechanism from diffusion-controlled to electron-transfer-controlled. To check this possibility, the dependence of the current on the concentration of $NH(CH_3)_2$ at the high scan rate was studied (Figure 5). The results clearly point out that for Ni-2 electrodes, the current

is nearly independent on $[NH(CH_3)_2]$, that is, that diffusion is not the rate-determining step in the process. Even for the Ni-1 electrodes, the results suggest that at high concentrations of the substrate the dependence of the current on the concentration is no longer linear and approaches an asymptotic value, that is, also for these electrodes at high scan rates and high concentrations, the electrocatalytic process is not diffusion-controlled.



Figure 5. Current as a function of $[(CH_3)_2NH]$. All solutions containing 0.10 M NaClO₄ at pH 10.0, 200 mV/s. Red squares: Ni-1 sol–gel electrode; black circles: Ni-2 sol–gel electrode.

The results point out that the composition of the electrodes, that is, the nature of the precursors used to prepare the matrices, affects the efficiency of the electrocatalytic process considerably (Figure 4). This result is in accord with previously reported results.^[13,23] The decrease in the current in the Ni-2 electrodes relative to that in the Ni-1 electrodes is attributed to the steric hindrance caused by the phenyl groups in the pores and to the increased hydrophobicity of the electrodes. Furthermore, the double-layer-charging current of Ni-1 is larger than that of Ni-2, which indicates that the surface area of Ni-1 is considera-



Figure 4 – Current as a function of (scan rate)^{1/2}. All solutions at pH 10.0.

Figure 4. Current as a function of (scan rate)^{1/2}. All solutions at pH 10.0. Red squares: Ni-1 sol-gel electrode; solution containing 3.0 \times (CH₃)₂NH, 0.10 \times NaClO₄; 1.1 V. Blue diamonds: Ni-1 sol-gel electrode; solution containing 0.10 \times NaClO₄; 1.0 V. Blue circles: Ni-2 sol-gel electrode; solution containing 3.0 \times (CH₃)₂NH, 0.10 \times NaClO₄; 1.0 V. Blue circles: Ni-2 sol-gel electrode; solution containing 3.0 \times (CH₃)₂NH, 0.10 \times NaClO₄; 1.0 V. Blue circles: Ni-2 sol-gel electrode; solution containing 3.0 \times (CH₃)₂NH, 0.10 \times NaClO₄; 1.0 V. Blue circles: Ni-2 sol-gel electrode; solution containing 3.0 \times (CH₃)₂NH, 0.10 \times NaClO₄; 1.0 V. Blue circles: Ni-2 sol-gel electrode; solution containing 3.0 \times (CH₃)₂NH, 0.10 \times NaClO₄; 1.0 V. Blue circles: Ni-2 sol-gel electrode; solution containing 0.10 \times NaClO₄; 0.96 V. Inset: magnification of the results in the absence of (CH₃)₂NH. The original voltammograms are presented in Figures S4–S7.





bly larger than that of Ni-2; this might clearly also contribute significantly to the differences in the observed catalytic current. (We thank one of the reviewers for pointing this out.)

Formaldehyde, a known product of the oxidation of $NH_n(CH_3)_{3-n}$, n = 1-3, was identified as a product of the electrocatalytic processes studied, by applying a literature procedure.^[24] The yield of the process, about 30 %, was calculated from the spectrophotometric results. The source of the relatively low yield might be the electrocatalytic oxidation of the CH_2O formed in the pores near the electrocatalyst. The analytical method is outlined in the Supporting Information (Part S3).

Concluding Remarks

The results presented herein point out that:

(1) The sol-gel electrodes prepared by this simple method are efficient electrocatalysts; reactive electrocatalysts can be entrapped by this technique.

(2) The ligand of the electrocatalyst, Ni^{II}L²⁺, is not oxidized during the catalytic oxidation of the substrates, although it is oxidized at pH 10 in homogeneous solutions. It should be noted that the pH in the pores of the matrices might be lower than that in the homogeneous solution because of the $(Si-O)_3$ -SiOH groups.

(3) The mechanism of the electrocatalytic process clearly differs from that in homogeneous solutions. Thus, $(CH_3)_3N$ is catalytically oxidized on the sol–gel electrodes, although it is not oxidized on glassy carbon electrodes.^[12b]

(4) The mechanism of oxidation of the substrate depends on the concentration and the nature of the electrode, moving from a diffusion-controlled to an electron-transfer-controlled processes with an increase in the scan rate and with an increase in the concentration of the substrate.

(5) The choice of the precursors used to prepare the sol-gel matrices has a major impact on the performance of the electrode in electrocatalytic processes. Clearly this has to be optimized.

Experimental Section

Materials and Methods

A.R. grade sodium perchlorate, perchloric acid, trimethoxyphenylsilane (TMOP), trimethoxymethylsilane (MTMOS), methylamine, graphite, dimethylamine, and trimethylamine were purchased from Aldrich. The ligand, L = 1,4,8,11-tetraazacyclotetradecane, and the complex, Ni^{II}L(Cl₂)₂, were synthesized by a previously reported method.^[25] This complex was transformed into Ni^{II}L(PF₆)₂ by adding an equivalent amount of AgPF₆ and recrystallizing.

All the solutions were prepared in deionized water that was further purified by passing through a Milli Q Millipore setup to obtain a final resistivity greater than 10 M Ω /cm. Ar from Maxima was used to deaerate the solutions for at least 5 min.

All the experiments were performed in solutions with an ionic strength of 0.10 $_{\rm M}$, which was maintained by the addition of NaClO₄.

Spectra were measured with a UV/Vis Agilent 8453 Diode Array spectrophotometer. The electrochemical experiments were per-

formed with a Metrohm Autolab potentiostat, Multi-channel, which is connected to Autolab hardware GPES software. All potentials are vs. Ag°/AgCl. In all the experiments, the counter electrode was Pt. The sol-gel electrodes were connected to the electrochemical cell by a Pt wire.

Preparation of the Electrodes

Sol-gel electrodes were prepared by modifying the procedure reported in the literature^[9a,9d] in order to optimize the electrodes for our applications. The amounts of the graphite, precursors (MTMOS/ TMOP), and Ni^{II}L(PF₆)₂ components were studied. The optimal conditions were chosen on the basis of the quality of the cyclic voltammograms and the leaching of the active species, Ni^{II}L²⁺. The precursor effect on the drying time of the electrodes indicates that the drying process takes several days longer when TMOP is used relative to the process with use of MTMOS. Table S1 sums up the composition of each type of electrode. The nominal surface area of the electrodes is (7 ± 1) mm²; however, as a result of the porous nature of the electrodes, it is actually significantly larger, and the capacity of the double layer is large and inhibits observations of small Faradaic currents. As the exact surface area of each electrode differs somewhat from those of other electrodes, the points for each type of electrode in one plot were all measured with the same electrode. Figure S1 describes a sol-gel electrode.

After each set of cyclic voltammetric measurements with a given Ni-*i* sol-gel electrode as a working electrode, the electrode was checked in a NaClO₄ solution. The results pointed out that the cyclic voltammograms were similar to those shown in the inset of Figure 2. These experiments point out that the entrapped Ni^{II}L²⁺ remained intact during the experiments and the ligand was not oxidized, as was reported for Ni^{II}L²⁺ electrolyzed in alkaline homogeneous solutions by using solid working electrodes.^[26]

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