

Heterogeneous electro-catalysis by Ni(II)Cyclam

Ariela Burg^a, Dror Shamir^b, Lina Apelbaum^c, Eric Maimon^b, Dan Meyerstein^{d,e}

^a. Chemical Engineering Department, Sami Shamoon College, Beer-Sheva, Israel.

^b. Nuclear Research Centre-Negev, Chemistry Department, Beer-Sheva, Israel.

^c. R & D, Makhteshim Chemical Works Ltd, Beer Sheva, Israel.

^d. Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel.

^e. Biological Chemistry Department, Ariel University, Ariel, Israel.

The simplicity and versatility of preparation of porous SiO₂ matrices, using the sol-gel method, as well as the relative inertness and stability of the matrices, have promoted their use in a wide range of processes. It was decided to check whether sol-gel matrices in which a redox agent, NiL²⁺ (L=1,4,8,11-tetraazacyclotetradecane), is entrapped can be used as an electro-catalyst for waste treatment. The oxidation of (CH₃)_nNH_{3-n}⁺ at sol-gel electrodes was studied. Preliminary results indicate that electro-catalytic processes based on sol-gel electrodes can be developed.

Advantages of heterogeneous electro-catalysts:

1. The redox reagent is entrapped in the matrix and therefore it has not to be separated from the product and can be easily recycled.
2. Often the redox reagent in its active oxidation state decomposes via a second order mechanism, e.g. NiL³⁺, and NiL⁺ and thus shortens its effective lifetime as an electro-catalyst. Entrapment in the matrix can inhibit these reactions.
3. Such electrodes can operate in solvents in which the electro-catalyst is insoluble.

Goal

Study the electro-activity of NiL²⁺ incorporated in a sol-gel matrix via the electro-catalytic oxidation of (CH₃)_nNH_{3-n}⁺.

NiL²⁺ is a known electro-catalyst for the oxidation of amines in aqueous solutions.

These amines are formed in a variety of industrial processes as by products i.e. as pollutants. Therefore their oxidation is of environmental interest.

Two different electrodes were made:

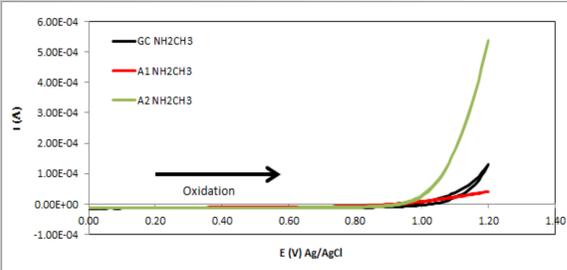
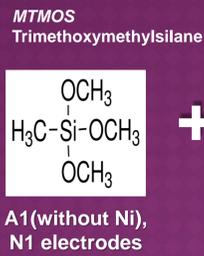
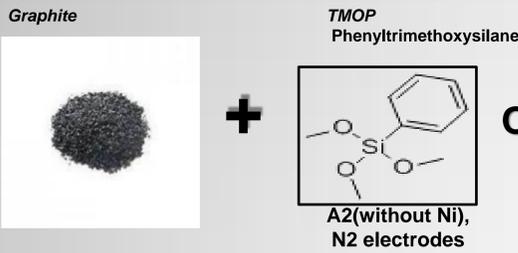


Figure 1 – Voltammogram of different electrodes, 500 mV/s. In 3.0 M CH₃NH₂, 0.10 M NaClO₄ at pH 10. — Glassy carbon electrode, — A1 sol-gel electrode, — A2-sol gel electrode.

The oxidation of three amines was studied with sol-gel electrodes without incorporated NiL²⁺. Figure 1 shows cyclic voltammograms of methyl amine by A1, A2 and GC as working electrodes. The results indicate that the three amines studied are oxidized at > 0.90 V, in the absence of NiL²⁺.

The results in figures 2 and 3, indicate that the first reaction that occurs is reaction (1). In analogy to the reaction occurring in aqueous solutions, oxidation of NiL²⁺ to NiL³⁺:

The oxidation of dimethyl amine is shown in figures 4 and 5. The results point out that NiL²⁺ acts as a heterogeneous electro-catalyst, when it is immobilized in the sol-gel matrix.

The current was studied as a function of the scan rate with and without dimethyl-amine in the solution, figure 6 describes the results.

The tendency of the results is a linear tendency which suggests that the rate of the catalytic oxidation of the amines is limited by diffusion. The intercepts in figure 6 and the plateau in N2 NH(CH₃)₂ graph, figure 6, indicate that the mechanism is not controlled only by diffusion. It can be explained by the competition between mass transfer and electron transfer. At high scan rates the electron transfer is slower than the mass transfer, therefore the oxidation current doesn't change. Interestingly the results indicate that the composition of the electrodes affects the activity of the NiL²⁺. The N1 matrix includes methyl residues, and the N2 matrix includes phenyl residues. The phenyl residues might cause larger steric effects in the pores relatively to the methyl groups. The species that have to move in the redox process might be slowed down by the larger residues in the pores, thus decreasing the catalytic current.

The identification of one of the known catalysis products, formaldehyde, was done according to a known procedure. The formaldehyde identification results, inset figure 7, point out that the second reaction occurring on the electrode surface is the mechanism described in figure 7.

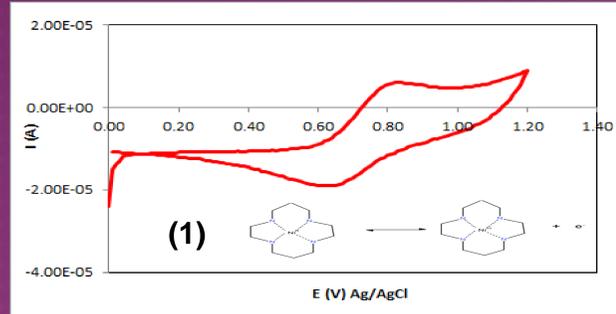


Figure 2 – Voltammogram of N1-sol-gel electrode, 50 mv/s, solution contains 0.10 M NaClO₄ pH 10.

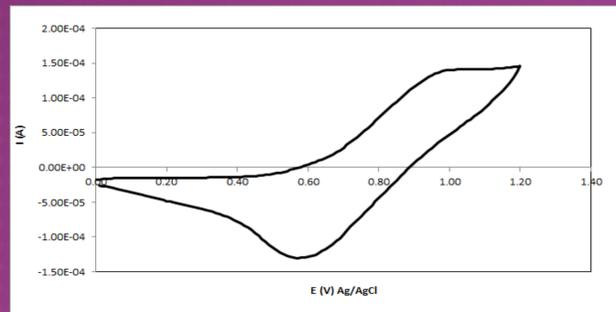


Figure 3 - Voltammogram of N2-sol-gel electrode, 50 mv/s, solution contains 0.10 M NaClO₄, pH 10.

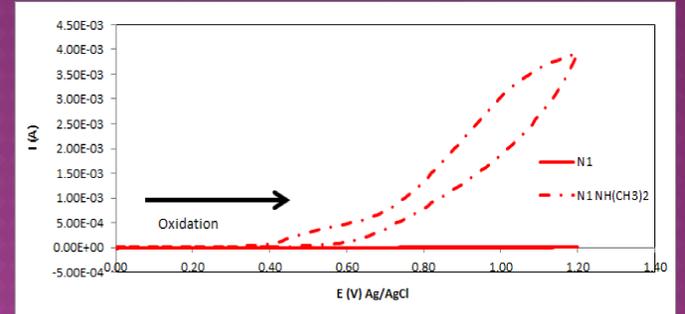


Figure 4 – Voltammogram of N1-sol-gel electrode, 50 mv/s, solution contains: 0.10 M NaClO₄, pH 10. — 3.0 M (CH₃)₂NH, 0.10 M NaClO₄, pH 10.

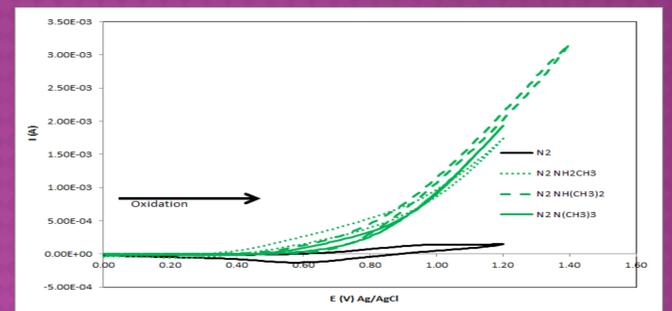


Figure 5 – Voltammogram of N2-sol-gel electrode, 50 mv/s, solution contains: — 0.10 M NaClO₄ pH 10. — 3.0 M NH₂CH₃, 0.10 M NaClO₄ at pH 10. — 3.0 M NH(CH₃)₂, 0.10 M NaClO₄ at pH 10. — 3.0 M N(CH₃)₃, 0.10 M NaClO₄ at pH 10.

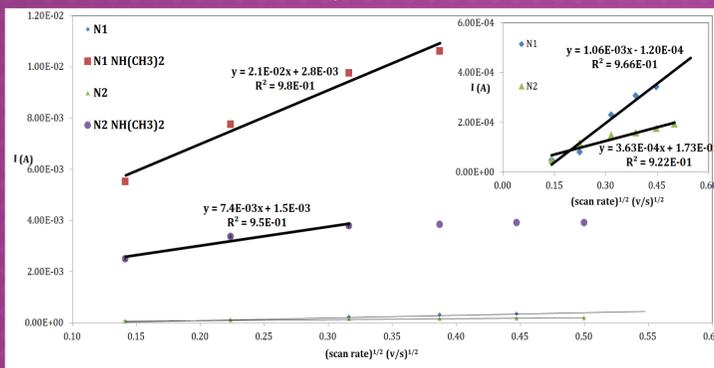


Figure 6 – Current as a function of the root of the scan rate. The experiments were done using the N1-sol-gel electrodes as working electrodes solution contains: ● 3.0 M (CH₃)₂NH, 0.10 M NaClO₄, pH 10, ▲ 0.10 M NaClO₄, pH 10. N2-sol-gel electrodes as working electrodes solution contains: ■ 3.0 M (CH₃)₂NH, 0.10 M NaClO₄, ◆ 0.10 M NaClO₄, pH 10.

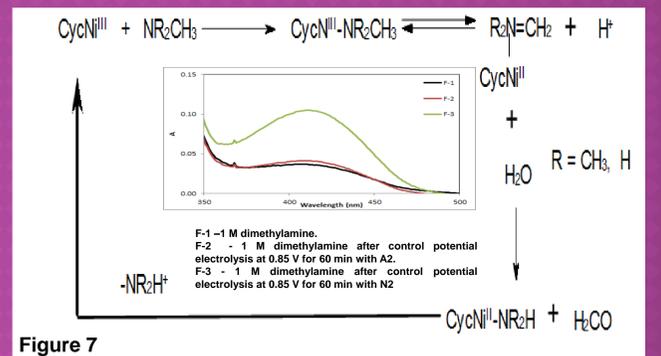


Figure 7

Conclusions:

- The oxidation of the amines is observed at amine concentrations above 0.10 M, while in a homogenous system the oxidation is observed at lower concentrations.
- All the results described above were obtained using only two electrodes. The active specie, in this case, NiL²⁺, can be recycled and reused.
- An additional advantage of these electrodes is the small amount of NiL²⁺, 1.8×10⁻⁵ mol, that is needed for the catalysis.

- At least part of the redox process occurs inside the pores, therefore the nature of the precursor of the sol-gel matrix affects the rate of the diffusion process.
- Practical conclusion for industrial catalysis is that this process and a variety of processes can be controlled by the choice of the building blocks of the sol-gel matrices.