Electrocatalytic Oxidations on Chemically Modified Electrodes prepared by Anodic Deposition of a Nickel Complex with a Tetra-azamacrocyclic Ligand

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A precipitate is formed on anodes in alkaline solutions containing 1,4,8,11-tetra-azacyclotetradecane-5,7-dionatonickel(II); this precipitate acts as an electrocatalyst for the oxidation of water, alcohols, and chloride.

Our interest in the stabilization of trivalent nickel complexes in aqueous solutions[1] prompted us to study the electrochemical oxidation of 1,4,8,11-tetra-azacyclotetradecane-5,7-dionato-(2−)nickel(II), $Ni^{II}L$. This complex was chosen as its redox potential in aprotic media is rather low[2] and therefore it was hoped that its trivalent complex would be stable also in neutral and alkaline solutions. During the study it was observed that a precipitate is formed on Pt anodes when preparative oxidation of $Ni^{II}L$ is carried out in alkaline media, pH > 10.5. The formation of the precipitate is also observed when repetitive cyclic voltammetry is carried out. We report here some preliminary results concerning the electrochemical properties of this precipitate.[3]

Chemically modified electrodes were prepared by keeping platinum or graphite electrodes at potentials of >1.0 V *vs.* standard calomel electrode (S.C.E.) in solutions containing 5×10^{-4} M $Ni^{II}L$ at pH 13.0 for 1—5 min. The electrode was then rinsed with triply-distilled water and transferred into the sample solution. Figure 1 shows the cyclic voltammograms obtained. Two major features were noted.

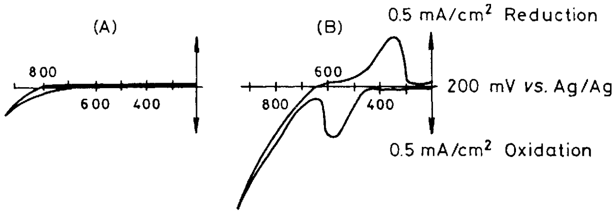

Figure 1. Effect of chemical modification on cyclic voltammograms at pH 12.0, using a 0.75 cm² platinum coil electrode, a scan rate of 15 mV/s, and a solution composition of 10^{-2} M NaOH and 0.1 M Na_2SO_4. (A) Bare electrode; (B) electrode modified by keeping it in a solution containing 2×10^{-4} M $Ni^{II}L$ at pH 12 and 1.200 V for *ca.* 10 min. The electrode was then rinsed and transferred into the test solution.

i, An anodic peak at *ca.* 575 mV *vs.* S.C.E. and a cathodic peak on the reverse scan with a similar area. This process is attributed to the oxidation of precipitated $Ni^{II}L$ to $Ni^{III}L$ probably by hydroxide or oxide ions, present with sodium counter ions, in the precipitate. The presence of an organic ligand was deduced from an Auger spectrum of the precipitate which indicated the presence of both nickel and nitrogen, but it was not clear whether this is the original ligand or one modified by oxidation. The area under the anodic peak (which depends on the time and potential used for preparing the modified electrode) indicates that the precipitate is several hundred layers thick. The shape, peak potential, and peak current but not the integrated current depend on pH, thickness of the precipitate, and scan rate.‡ The precipitate dissolved at pH ⩽ 9.0.

ii, A comparison of the voltammogram of the unmodified electrode with that of the modified one clearly indicates that the latter catalyses the oxidation of OH^-, *i.e.*, water. The

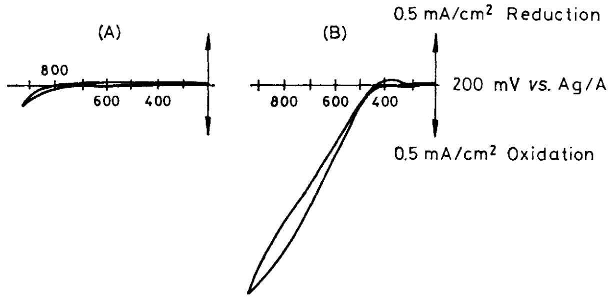

Figure 2. Catalysis of methanol oxidation on modified electrodes. Solution composition and conditions as in Figure 1 but solutions containing also 2% v/v of methanol. (A) Bare electrode; (B) modified electrode.

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† Dr. Gregory Ginzburg passed away August 5, 1981.

‡ Thus, for example, the anodic peak occurs at *ca.* 425 mV at pH 13.0 with a thinner precipitate.

modified electrode was kept at 1000 mV *vs.* S.C.E. in a solution at pH 13 for half an hour. No decrease in the catalytic current was observed and a cyclic voltammetry experiment proved that the nickel content of the precipitate did not change.

In Figure 2 are plotted voltammograms obtained using the same electrodes in a solution containing 2% methanol at pH 12.0. The result clearly indicates that the precipitate acts as a good electrocatalyst for the oxidation of methanol. The observation that the cathodic peak nearly disappears in the presence of methanol suggests that the electrode reaction, which probably involves two electrons in the rate determining step, follows a mechanism of the type shown in equation (1).

$$\mathrm{Ni^{III}L + Red} - e^- \rightarrow \mathrm{Ni^{II}L + Ox} \qquad (1)$$

If the electrode is transferred, after extended methanol oxidation catalysis, into a solution containing no methanol at pH 12.0, voltammograms similiar to those observed for the modified electrode, Figure 1, are obtained.

The modified electrode also electrocatalyses the oxidation of other alcohols, *e.g.*, ethanol and propanol, and of chloride. Similar results are obtained with analogous nickel complexes.

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3 A similar precipitate was reported in (edta)nickel (H_4edta = ethylenediaminetetra-acetic acid) solutions. (E. Fuchs, G. Ginzburg, J. Lati, and D. Meyerstein, *J. Electroanal. Chem.*, 1976, **78**, 83).