

# Ni(II)1,4,8,11-tetraazacyclotetradecane electrocatalytic films prepared on top of surface anchored PAMAM dendrimer layers. A new type of electrocatalytic material for the electrochemical oxidation of methanol

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Gold electrodes, previously prepared with surface anchored PAMAM dendrimers, were further modified with a Ni-containing tetraazamacrocycle resulting in a novel electrocatalytic material which proved to be particularly efficient for the electrochemical oxidation of methanol in basic aqueous medium.

Substantial research efforts have been devoted by different groups around the world towards the development of fuel cells which, it is widely believed, will provide a clean technology for specific energy requirements in the near future. Among the problems on which the researchers in this area have focused for some years now, the design and preparation of effective electrocatalysts for the oxidation of methanol stands out for its important technological potential.<sup>1</sup> In this context, metal-containing macrocycles have attracted the attention of many research groups due to the specificity of the electrooxidation reaction and the absence of poisonous effects that characterize the behavior of some other materials.<sup>2,3</sup> Among the compounds that have shown a good electrocatalytic activity for this reaction, Ni(II)1,4,8,11-tetraazacyclotetradecane, commonly known as Ni-cyclam, is a compound that can be easily prepared<sup>3</sup> and attached to different conductive surfaces to prepare promising new electrocatalytic substrates.<sup>3,4</sup>

Dendrimers on the other hand, are polymeric compounds, similar to covalent micelles, that bear well defined cavities and peripheric groups that can be used for several different applications.<sup>5</sup> PAMAM (poly(amidoamine)) dendrimers, for instance, are a type of commercial dendritic polymer, characterized by an ethylenediamine core with hydrophobic interiors and hydrophilic terminal groups, that also have been employed in the surface modification of different materials.<sup>6</sup> Due to their permeability as well as the ability to use their terminal functional groups to position these molecules on a previously modified electrode surface, these materials have also shown their ability to concentrate in the interfacial region hydrophobic and electrocatalytic molecules.<sup>7</sup> In this work, we show that a modified electrode-containing surface-confined PAMAM dendrimers can be further modified with electroformed Ni-cyclam in basic medium to increase the electroactivity of the substrate towards the electrochemical oxidation of methanol.

Au bead electrodes with roughness factors close to 1 were prepared as has been previously described<sup>8</sup> and modified with 2-aminoethanethiol hydrochloride (**1**) by immersion of the freshly

prepared electrode in a 1 mM methanolic solution of the relevant thiol for 12 h. Surface coverage determinations of **1** were carried out by electrochemical reductive desorption (using a BAS-Epsilon<sup>®</sup> Potentiostat/Galvanostat) of the thiol in KOH 0.5 M deoxygenated solutions revealing that, as shown in previous reports,<sup>9</sup> the thiol molecules do adsorb onto the electrode surface in a sub-monolayer fashion (approximately 24% of the full surface coverage).

As can be seen in Fig. 1, the thiol modified electrodes were then exposed to 20  $\mu$ M methanolic solutions of PAMAM generation 3.5 dendrimer (**2**, obtained from Aldrich, bearing 64 carboxylic acid terminal groups) also containing 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC), 0.25 mM, in order to promote the formation of amide linkages between the surface-confined thiol and the dendrimer molecules.<sup>10</sup>

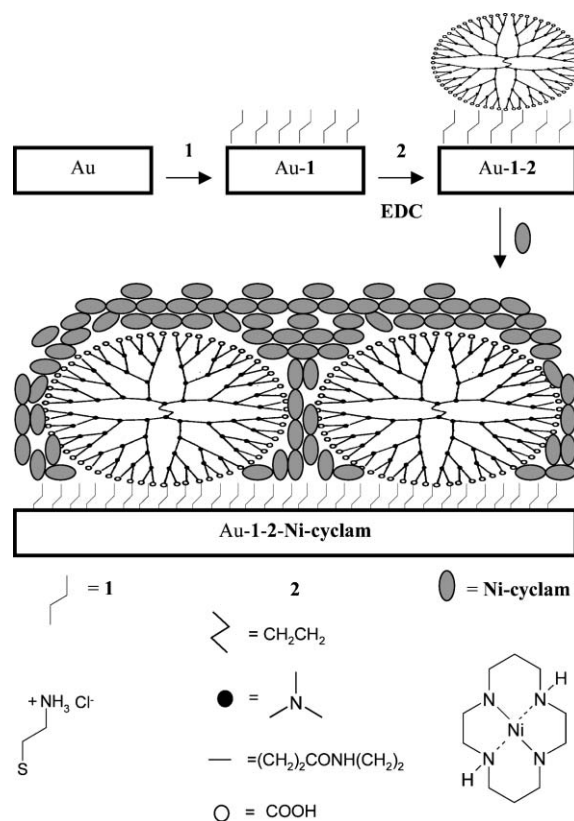


Fig. 1 Scheme showing the electrode surface modification protocol.

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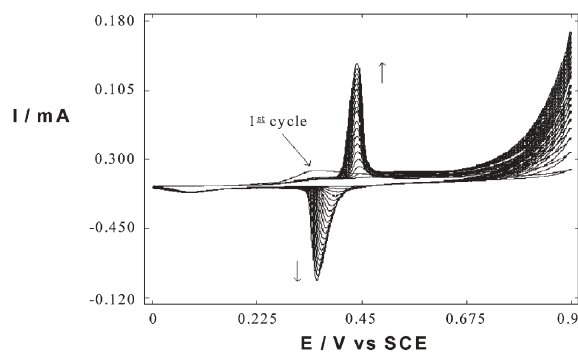
As has been previously observed,<sup>7c</sup> dendrimer confinement was verified by monitoring the electrochemical response of the  $\text{Ru}(\text{NH}_3)_6^{3+}$  (2.0 mM) species in the presence and in the absence of PAMAM dendrimer molecules revealing that, upon dendrimer covalent adsorption, the voltammetric response of the electroactive probe molecule substantially changes.

Clean, thiol (Au-1) and thiol-PAMAM (Au-1-2) Au modified surfaces were then immersed in a 0.1 M NaOH aqueous solution also containing 0.5 mM of Ni-cyclam and cyclic voltammetry (CV) experiments were carried out in the 0–0.9 V vs. SCE potential window for 20 consecutive cycles at  $100 \text{ mV s}^{-1}$ . As can be appreciated in Fig. 2, the CV response of the electrolytic solution in the three substrates is characterized by a redox wave whose shape suggests an electroformed film of Ni-cyclam, which increases linearly with the number of cycles.<sup>3</sup> Consistent with reports that have identified robust Ni–O–Ni linkages<sup>4c</sup> between Ni-cyclam molecules, it was observed that after careful rinsing of the electrode with NaOH solution and deionized water, the CV response of the electrodes remained unchanged in a pure supporting electrolyte solution. A plot of the anodic peak current vs. the scan rate further supported a strongly adsorbed film since a linear behavior, characteristic of the electrochemical response of a surface-confined species, was observed.<sup>8</sup> Integration of the charge involved in the anodic and cathodic peaks on the other hand, allowed computation of the amount of Ni-cyclam confined on the different surfaces under study. In this way, whereas a surface coverage for the clean Au electrode was measured as  $8.0 \times 10^{-9} \text{ mol cm}^{-2}$ , the corresponding value for both Au-1 and Au-1-2 substrates happened to be slightly smaller ( $6.7$  and  $6.8 \times 10^{-9} \text{ mol cm}^{-2}$  respectively) probably due to the presence of the previously adsorbed compounds.

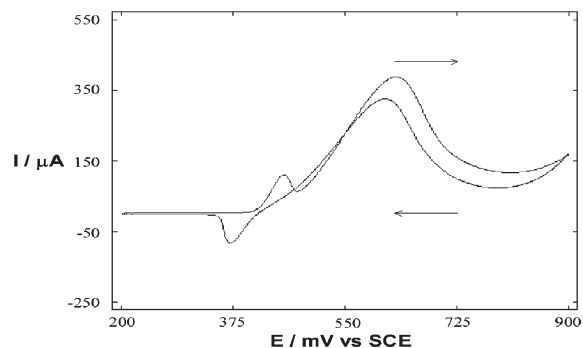
Immersion of the different Ni-cyclam modified electrodes considered in this study in 0.1 M NaOH solutions also containing 0.4 M methanol, resulted in characteristic electrocatalytic CV responses, of which a representative one is shown in Fig. 3.

Consistent with previous reports in the literature,<sup>3</sup> the electrochemical oxidation of methanol starts at fairly low anodic potentials due to the catalytic effect of the Ni oxidation event that takes place in the tetraaza compound at approximately 420 mV vs. SCE.

Experiments carried out at different concentrations of methanol in the same alkaline aqueous solution with the three modified surfaces under study, gives rise to titration curves on which the



**Fig. 2** CV response (20 consecutive cycles at  $100 \text{ mV s}^{-1}$ ) of a 0.5 mM solution of Ni-cyclam in 0.1 M of NaOH on a Au-1-2 modified electrode. Similar responses were obtained for Au and Au-1 electrodes.



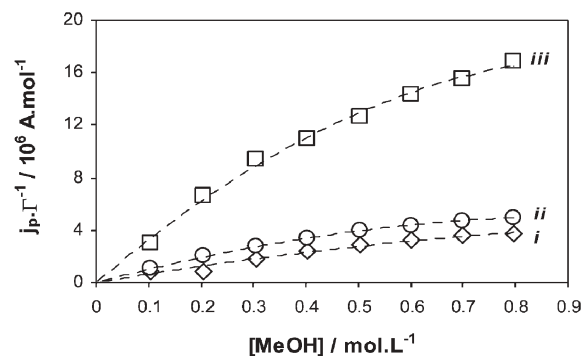
**Fig. 3** CV response of NaOH 0.1 M + 0.4 M methanol solution on a Au-1-2-Ni-cyclam modified electrode at  $100 \text{ mV s}^{-1}$  and 298 K.

current density of the first oxidation peak ( $J_p$ ) can be measured and normalized to the amount of Ni-cyclam confined on the electrode surface ( $\Gamma$ ). The relevant data is presented in Fig. 4 and it is interesting to note that the presence of the surface-confined PAMAM dendrimer, increases the normalized current density of the methanol electrooxidation by about a factor of 4 when compared to the response of either Au-Ni-cyclam or Au-1-Ni-cyclam modified electrodes.

PAMAM dendrimer molecules have a large affinity for methanol (the commercially available compound is actually sold in methanolic solutions) and therefore a reasonable explanation of these results could be based on a dendrimer induced interfacial effect that increases the concentration of methanol at the modified electrode surface. In this way, the improved behavior of the modified substrate reported in this work could rely on the positioning of two complementary units at the electrode surface. Whereas on one hand, the PAMAM dendrimer molecule would concentrate methanol molecules at the electrode-solution interface, the Ni-cyclam would act as the electrocatalytic unit necessary to promote the electron transfer events at accessible potentials.

Studies on the detailed interfacial structure of these modified electrodes as well as the electrocatalytic activity of different dendrimers combined with metallomacrocycles towards methanol electrooxidation, are currently being carried out in our laboratory.

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**Fig. 4** Titration curves obtained from the first oxidation peak of methanol using (i) Au-Ni-cyclam, (ii) Au-1-Ni-cyclam and (iii) Au-1-2-Ni-cyclam in 0.1 M NaOH at 298 K.

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