Electropolymerized nickel macrocyclic complex-based films: design and electrocatalytic application

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The voltammetric behaviour of electropolymerized nickel macrocyclic complexes in alkaline aqueous solution is described. The nickel-based modified electrodes were prepared by oxidative polymerization of nickel porphyrin, nickel salen and nickel cyclam complexes by repeated potential scans in 0.1 M NaOH solution. All the electroformed films exhibited the same behaviour which is similar to that shown by nickel hydroxide-modified electrodes. In addition, the nickel complex-based polymers act as efficient materials for the electrocatalytic oxidation of methanol, ethanol and hydrazine.

Electropolymerized metalloporphyrin-coated electrodes have been developed intensively in recent years owing to the fact that the resulting materials can act as efficient electrocatalysts for chemical, photochemical and/or analytical applications.[1–3] Recently it has been shown that electropolymerized nickel porphyrin films can be used as sensors for the determination of nitric oxide[4] in aqueous and biological solutions and a fruitful example of calibration of such electrochemical sensors has been reported.[5] Indeed, recent research in developing new electrode materials seems to be directed towards the use of porphyrins as well as macrocyclic complexes (*e.g.* of cobalt, iron and nickel) in the form of conducting polymer films[1,6,7] that behave as fast electron-transfer mediators for solution species. Although the electrochemistry and the electrocatalytic properties of nickel macrocyclic complexes, phthalocyanines and porphyrins have been well studied in various solvents[1,8–14] few data exist on their behaviour as electropolymerized films in aqueous alkaline solution. Recently, it has been shown that nickel tetraazamacrocyclic complexes can be easily electropolymerized on to an electrode surface in alkaline solutions to form stable modified electrodes that catalyse the oxidation of several substrates.[8,15–19] However, the reason why the voltammetric behaviour of the films formed from various kinds of nickel planar macrocyclic complexes[4,8,15–22] is nearly the same in aqueous basic solution has not been fully understood and has been a point of discussion. Two postulates have been put forward; one considers that upon the electrochemical polymerization of the nickel complex in alkaline media, the nickel–nitrogen tetracoordination of the complex incorporated in the polymeric film is lost and the films behave in a similar manner as a nickel hydroxide electrode.[8,16] Even though that coordination of the nickel centres was probably absent, they remain entrapped inside the polymeric skeleton and exhibit stable redox behaviour. The second postulate considers that the complexes do not decompose upon electropolymerization but are attached to the electrode surface and are interconnected *via* oxo-bridges.[15,18]

The aim of the present work is to extend the above observations to more examples of nickel macrocyclic-based conducting polymers (see structures in Fig. 1) with a direct characterization of their electrochemical properties and redox catalysis towards the electrocatalytic oxidation of methanol, ethanol and hydrazine in alkaline solution.

Experimental

Electrochemical instrumentation

All the electrochemical studies were performed with a conventional three-electrode potentiostatic system (GSTP4/PJT 24-1, Solea-Tacussel). The working electrodes were either a vitreous carbon electrode (CVJ, Tacussel) of 3 mm diameter polished prior to all experiments, or an indium tin oxide (ITO) transparent electrode (Balzers). The potentials were measured with reference to the saturated calomel electrode (SCE) placed in a separate compartment containing the supporting electrolyte. All the experiments were performed at room temperature and under an argon atmosphere.

Absorption spectra of the monomeric complexes and polymer films on ITO were obtained with a Shimadzu 160 UV–VIS spectrophotometer.

Chemicals

The insertion of Ni^{II} into the free porphyrin base tetrakis(4-sulfonatophenyl)porphyrin (Aldrich) giving NiTPPS, the free porphyrin base tetrakis(*p*-aminophenyl)porphyrin (Aldrich) giving NiTAPP and into the macrocycle cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane; Aldrich) giving NiTCTD was carried out as previously reported.[15,18,19] NiSalen [H_2Salen = bis(salicylidine)ethylenediamine; Aldrich) and all other chemical products were reagent grade and used as received.

Results and Discussion

Polymerization and characterization of the nickel complexes

Fig. 2A shows the evolution of the cyclic voltammogram obtained for NiTPPS porphyrin film growth, denoted poly-NiTPPS, on an ITO electrode. The potential was continuously cycled between 0 and 1.0 V at 100 mV s^{-1} while the ITO electrode was immersed in a monomer solution of 2 mM NiTPPS in aqueous 0.1 M NaOH. As has been previously reported,[20] an ill defined redox couple appears during the first

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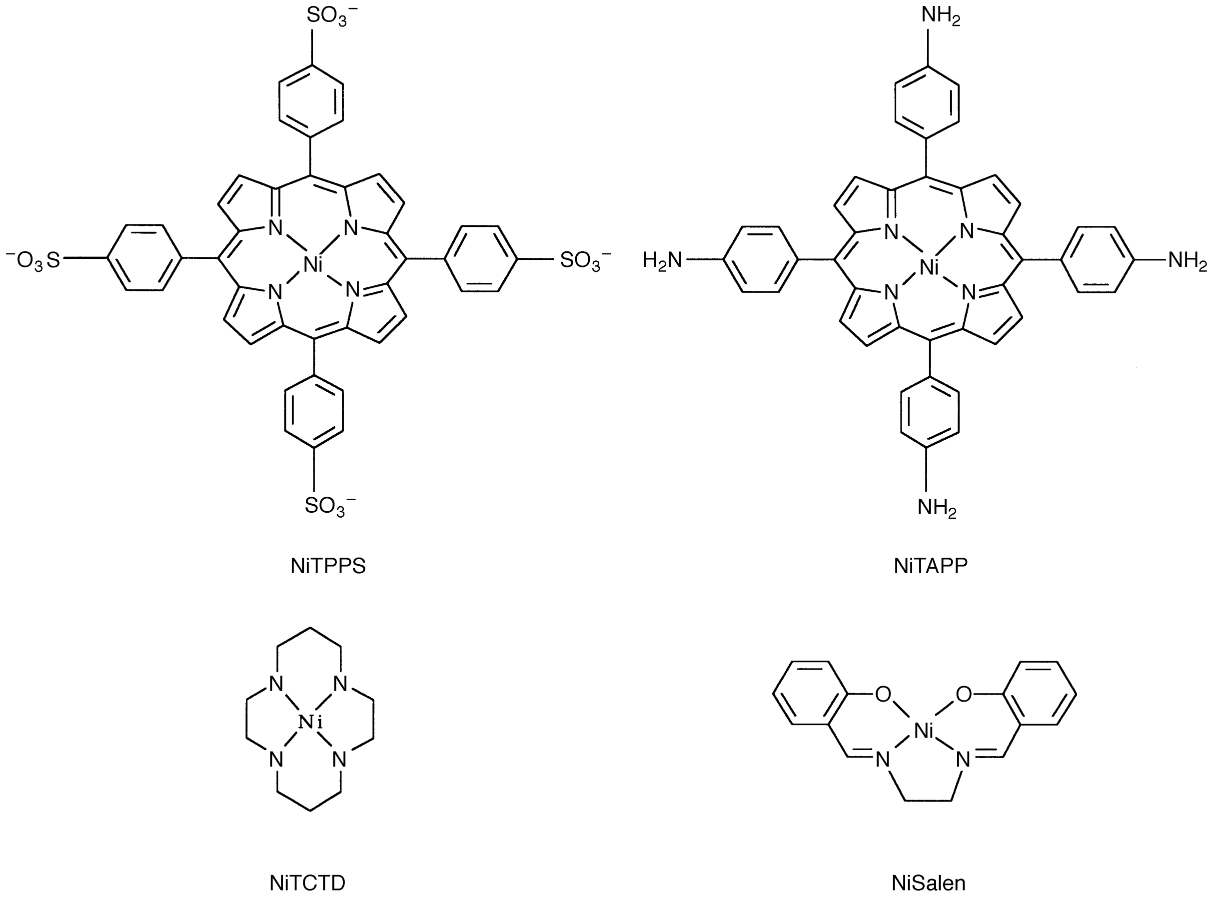

Fig. 1 Structure of the studied nickel complexes

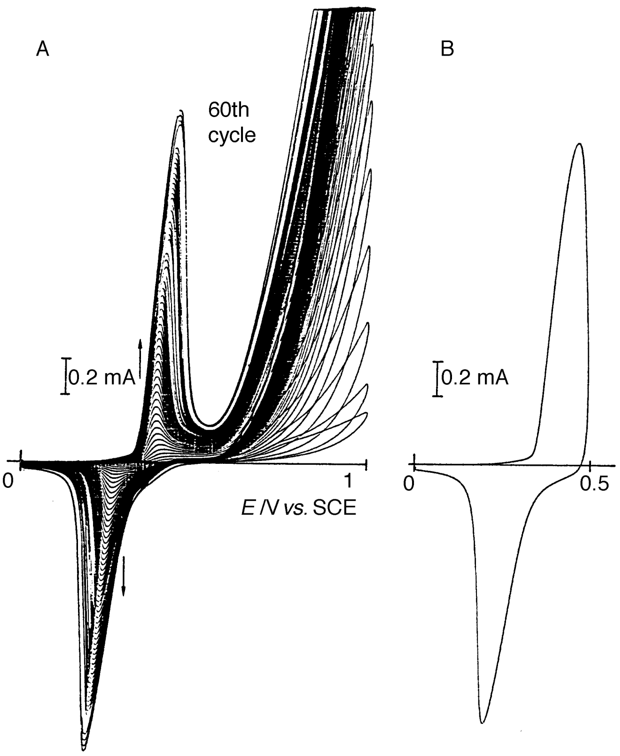

Fig. 2 A, Evolution of repeated cyclic voltammograms of ITO electrode in 0.1 M NaOH aqueous solution +2 mM NiTPPS monomer (60 scans are shown). B, Cyclic voltammogram of poly-NiTPPS film coated electrode prepared by 60 electropolymerizing scans, as indicated in A (potential scan rate 100 mV s^{-1}).

scan which increases and becomes well defined when the potential scans are repeated. The continuous increase in the amplitude of the voltammometric peaks, around 0.34 V, indicates that the film has been formed as a result of the anodic electropolymerization of the porphyrin complex.

After a period of scanning, the electrode was transferred, after careful rinsing with water, to a 0.1 M NaOH aqueous solution (containing no monomer). The cyclic voltammogram of the poly-NiTPPS film is shown in Fig. 2B and exhibits the previously observed electrochemical behaviour assigned to the Ni^{III}–Ni^{II} process[20] at 0.34 V. Similar results were obtained on vitreous carbon electrodes.

The apparent surface coverages Γ_{Ni} of the poly-NiTPPS film electrodes by the nickel porphyrin were calculated from the cyclic voltammograms of these films, the calculation being based on the charge under the Ni^{III}–Ni^{II} oxidative or reductive peak. Fig. 3A shows how Γ_{Ni} varies with the number of electropolymerizing potential scans n (at 100 mV s^{-1}, at an ITO electrode): Γ_{Ni} increases over the first 150 potential scans and then remains constant. We have previously reported such evolution of Γ with n for several kinds of polyporphyrin films[1,23,24] and the origin of such an evolution can be explained by a change of the polymer (electronic and/or redox) conductivity, in the thickening films (the film thickness can be measured in terms of the number of electropolymerizing potential scans n used to prepare the poly-NiTPPS polymer). Fig. 3B shows that the potentials of the redox couple of the peaks and their separation depend on the conditions of film formation. It appears that the cathodic peak is shifted towards negative potential values to a greater extent than the anodic peak was shifted to positive potential. This indicates that the kinetics of the forward and reverse electron transfer processes are affected differently by the thickness of the film.

The formation of poly-NiTPPS films on ITO transparent electrodes was confirmed by UV–VIS spectrophotometry. The

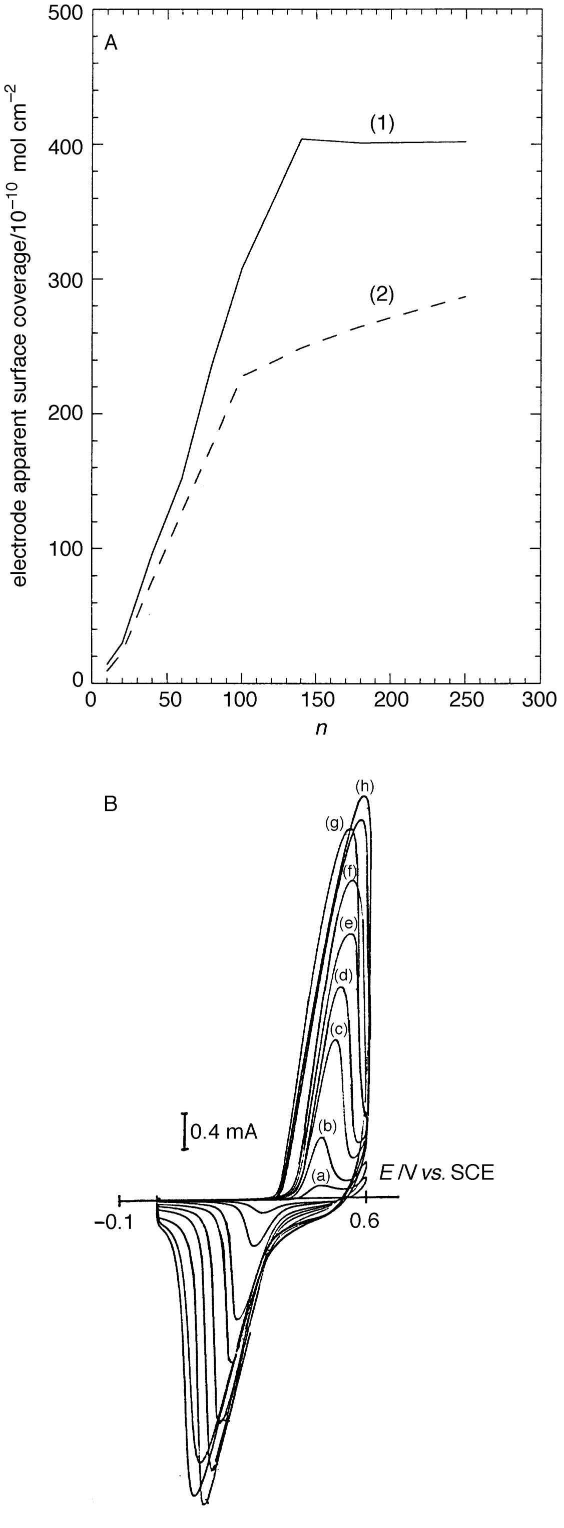

Fig. 3 A, Plot of the electrode apparent surface coverage by NiTPPS, Γ_{Ni}, *vs.* the number of electropolymerizing scans. Calculations of Γ_{Ni} were based on the anodic peak (curve 1) or on the cathodic peak (curve 2). ITO electrodes were modified as indicated in Fig. 2A and the apparent surface coverage was determined after each scan in a fresh NaOH solution. B, Cyclic voltammetry of poly-NiTPPS films, in 0.1 M NaOH aqueous solution, prepared by different numbers of electropolymerizing scans *n* as indicated in Fig. 2A [(a) $n=10$; (b) $n=20$; (c) $n=40$; (d) $n=60$; (e) $n=80$; (f) $n=100$; (g) $n=140$; (h) $n=180$]; scan rate 100 mV s^{-1}.

absorption spectrum of NiTPPS in solution (Fig. 4A; curve 1) is compared with that of the poly-NiTPPS film on a transparent electrode (Fig. 4A; curve 2). This clearly indicates that a nickel porphyrin film is present on the electrode surface. Peak broadening is observed for the Soret band in the film with a hypsochromic shift. Considerable broadening of the Soret band was previously observed for several supported porphyrins and was attributed to some degree of aggregation and stacking of the porphyrin molecules on the electrode surface. Fig. 4B shows absorbances of films ($\lambda=403$ nm, the wavelength of the Soret band) as a function of the number of electropolymerizing potential scans *n*. The electropolymerization of the porphyrin seems to occur monotonously for $n<100$ since the absorbance of the Soret band is essentially proportional to the number of scans. However, a decrease of the absorbance is observed when the thickness of the film is increased further. The origin of this behaviour is, as yet, not understood.

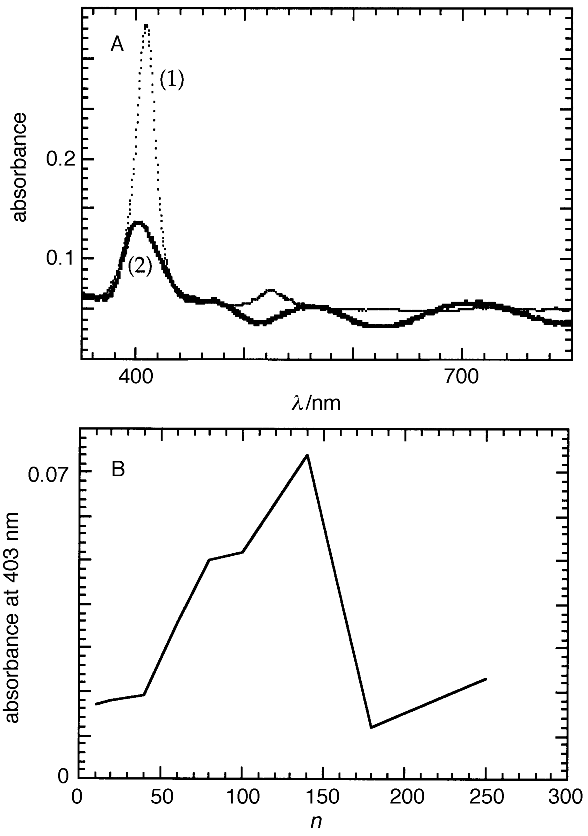

Fig. 4 A, Absorption spectra of NiTPPS in NaOH solution (curve 1) and poly-NiTPPS film on ITO (curve 2). B, Absorbances (at $\lambda=403$ nm) of poly-NiTPPS films on ITO electrodes as a function of the number of electropolymerizing scans. Electrodes were prepared as indicated in Fig. 2A.

A typical example of the cyclic voltammogram obtained for the electrochemical growth of poly-NiSalen on a vitreous carbon electrode is shown in Fig. 5A. A large anodic current at 0.75 V was observed during the first cycle and which may be caused by the anodic oxidation of the Salen ligand, as previously reported in acetonitrile solution.[25] This peak vanished after a few scans (2–10) and the presumed Ni^{III}/Ni^{II} redox system was clearly evident by the third scan. The intensities of the observed reversible couple of the voltammetric peaks increased regularly after each potential scan. The characterization of the films was carried out by transferring the electrode (after rinsing with water) to a 0.1 M NaOH aqueous solution (containing no monomer). The cyclic voltammogram of the modified electrode (Fig. 5B) still shows the Ni^{III}–Ni^{II} process. It should be noted that the voltammometric parameters evolve in a similar way as with the poly-NiTPPS films. The potential of the redox couple and peak separation depend on the condition of film formation. For thin poly-NiSalen films formed after 5–20 scans $E_{1/2}$ is at 0.44 V with a peak separation of 65 mV. For thicker films, the potential of the Ni^{III}–Ni^{II}

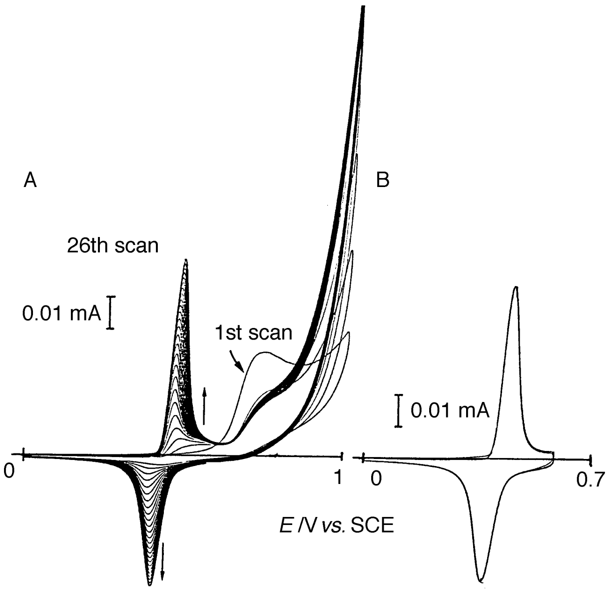

Fig. 5 A, Evolution of repeated cyclic voltammograms of vitreous carbon electrode in 0.1 M NaOH aqueous solution +2 mM NiSalen monomer (26 scans are shown). B, Cyclic voltammogram of poly-NiSalen film coated electrode prepared by 26 electropolymerizing scans, as indicated in A (potential scan rate 100 mV s^{-1}).

couple shifts to more positive values and the peak separation increases. It should be noted that the formation of poly-NiTCTD films occurs similarly to poly-NiSalen but the amount of nickel per cm^2 is about 20 times that for poly-NiSalen films (for the same number of electropolymerizing scans at a scan rate of 100 mV s^{-1}).

The mechanism of electrooxidative polymerization of the nickel complexes is not clear at present. However, by taking into account the previously reported data of anodic oxidation of nickel tetrakis(3-methoxy-4-hydroxyphenyl)porphyrin,[19,26] nickel tetramethyldibenzotetraaza[14]annulene,[8] nickel substituted-cyclam[15,18] and nickel curcumin[17] in basic aqueous solution, our complexes are probably electropolymerized in the same manner. Although the electrochemistry of nickel tetraazamacrocyclic complexes and porphyrins has been well studied in organic solvents[1,8–14] few data exist on their electrochemical behaviour as electropolymerized films in aqueous alkaline solution. Roslonek and Taraszewska[15] have proposed a tentative explanation for the electrochemical polymerization process by suggesting that the attachment of the nickel complexes to the electrode surface is connected to oxidation of OH$^-$ anions. Indeed, a pH value of 13 is critical for film formation and one would expect that the oxidation of OH$^-$ would create a variety of functional groups on the electrode surface. It is important to note that no electropolymerization process occurred when the potential scan was limited to a range before the beginning of the oxidation of OH$^-$ (*i.e.* $E<0.8$ V).[15] Thus, coupling the complexes to the electrode surface *via* an $-\mathrm{O}-\mathrm{Ni}^{\mathrm{II}}$ bond seems probable.[15] During further scans, the attached nickel(II) complexes undergo oxidation to Ni$^{\mathrm{III}}$ and bind to incoming nickel species, supplied to the electrode surface by diffusion, *via* oxo-bridges.[15] It appears clear from our data, and also from previously reported data[18,16–19,26] that the redox process shown by the nickel complex-based films in alkaline solution is similar to that shown by electrochemically formed $\mathrm{Ni(OH)_2}$ electrodes[27,28] in which the observed redox process is usually related to the α-$\mathrm{Ni(OH)_2}$/γ-NiOOH transformation [for hydrated nickel(II) structures]. Although the electrochemical behaviour of nickel hydroxide electrodes has been extensively investigated because of their practical and technological use in the anode material of batteries, there are still many discussions about the effective mechanism of the actual redox reaction.

In order to further elucidate the origin of the redox process displayed by all the studied nickel complex-based films in alkaline aqueous solutions, the voltammetric behaviour of a nickel porphyrin film prepared in acetonitrile solution was also studied. Fig. 6A shows the polymerization of the porphyrin complex NiTAPP performed on an ITO electrode by cyclic voltammetry between −1.6 and 1.2 V in acetonitrile–0.1 M $\mathrm{Bu_4NBF_4}$, at a scan rate of 100 mV s^{-1}. The cyclic voltammograms exhibit the expected well known reversible one-electron porphyrin-ring oxidation NiP–NiP$^+$ and reversible one-electron ring reduction NiP–NiP$^-$ at +0.77 and −1.36 V, respectively.[1,29] The evolution of the cyclic voltammograms during repeated potential scans shows a continuous increase in the amplitude of the peaks as for the previously described systems and this indicates that a film was formed on the electrode as a consequence of electrochemical oxidative polymerization of the attached aminophenyl groups. It should be noted that the anodic irreversible process observed at $E>+1.0$ V may be related to the oxidation of the attached amino-substituted phenyl groups. Further, after two potential scans, one cathodic prepeak appears at −1.25 V. The intensity of this peak increased with the number of scans and its potential shifted gradually to lower values. This new cathodic process may depict the electroactivity of the polymer matrix formed during the electropolymerizing scans. Such an electropolymerization behaviour was previously reported for pyrrole-substituted nickel porphyrins[1,6,30] and amino-substituted nickel phthalocyanine.[11]

The characterization of the poly-NiTAPP film was first

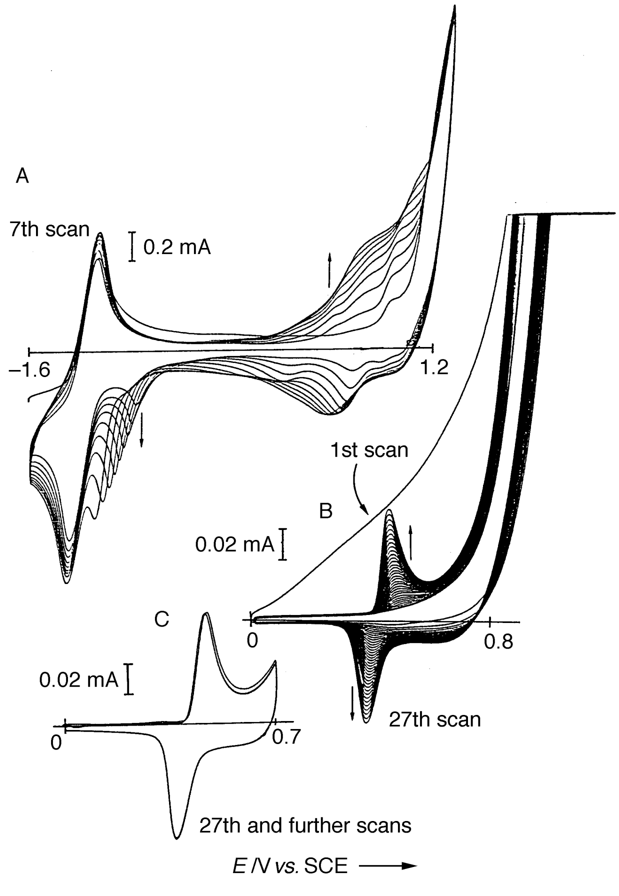

Fig. 6 A, Repeated cyclic voltammograms of 2 mM NiTAPP in acetonitrile–0.1 M $\mathrm{Bu_4NBF_4}$, at an ITO electrode (7 cycles are shown). B, Evolution of the cyclic voltammograms of the ITO electrode coated by poly-NiTAPP (prepared as indicated in A) and transferred to fresh 0.1 M NaOH aqueous solution. C, 27th and further scans. Potential scan rate 100 mV s^{-1}.

carried out in acetonitrile–0.1 M Bu_4NBF_4. The cyclic voltammogram of the film exhibited similar electrochemical responses as the starting monomer which indicates that the polymeric film contains the nickel porphyrin. When the poly-NiTAPP film was studied in 0.1 M NaOH solution, different features were observed (Fig. 6B). During the first scan, a huge irreversible anodic peak was observed at $E > +0.8$ V showing that a transformation of the film was occurring. As soon as the second scan was performed, the intensity of the previously reported anodic peak became significantly smaller indicating the end of the irreversible transformation of the film. In addition, a new well defined redox system appeared with $E_{1/2} = 0.4$ V that grew continuously until it reached a steady state. The shape of the final cyclic voltammogram (Fig. 6C) was very similar to those obtained with the electropolymerized nickel macrocyclic-based films obtained in alkaline solution, which are also similar to those of a $Ni(OH)_2$ electrode.[27,28] The redox process observed at 0.40 V remained stable and showed that during the electrochemical treatment of poly-NiTAPP in alkaline media, the nickel porphyrin (or macrocyclic complexes in general) incorporated into the polymeric film behaves in a similar manner to a nickel hydroxide electrode.[27,28] It should also be noted that during this process the colour of the film (observed on ITO electrodes) changes from deep blue to dark gold. This may be explained by changes in the axial occupation of the Ni sites as a consequence of the formation of the O—Ni oxo bridges in alkaline solution.

This fundamental observation mirrors the behaviour reported by Cataldi and co-workers[8] for poly-nickel(II)-tetramethyldibenzotetraaza[14]annulene formed in dichloromethane and transformed in alkaline aqueous solution. Upon electrochemical polymerization of the nickel complex in an organic solvent and treatment of the film in alkaline solution, the complex incorporated in the polymeric film behaves in a similar manner to a nickel hydroxide electrode. It is important to note that (*i*) the redox process exhibited by all the nickel-based films (either directly prepared by electropolymerization in alkaline solution or in organic solvent followed by treatment in alkaline solution) and assigned to Ni^{II}–Ni^{III}, is similar to that observed with nickel hydroxide films and shows the same pH dependence,[8,15–22,27,28,31] and (*ii*) the UV–VIS spectra of the films (particularly in the case of nickel porphyrins) indicate very clearly that the macrocyclic configuration of the nickel complexes remained intact upon electrochemical polymerization (see Fig. 4A).

Electrocatalytic effects

The electrocatalytic capabilities of the nickel-based polymer films towards the electro-oxidation of methanol, ethanol and hydrazine have been examined. The modified electrodes act as catalysts for the oxidation of methanol, ethanol and hydrazine in 0.1 M NaOH aqueous solution, as clearly shown in Fig. 7, in the case of poly-NiTCTD. Indeed, for methanol and ethanol, the voltammograms have the typical well known shape commonly reported in the case of the electrocatalytic oxidation of alcohols.[32,33] Similar shapes of cyclic voltammograms were obtained with poly-NiSalen and poly-NiTPPS films in the presence of methanol, ethanol and/or hydrazine and these results are similar to those reported for the well known electrocatalytic oxidation of methanol on modified electrodes by nickel hydroxide and or nickel macrocyclic-based polymers.[8,15–17,19,26,32,33] The oxidation currents of methanol, ethanol and hydrazine at the nickel-based polymer films appear at 0.65, 0.62 and 0.60 V, respectively, and the amplitudes of the catalytic peaks remain stable upon several repeated potential scans. Fig. 8A shows the relationship between the ethanol concentration and the catalytic current developed at poly-NiSalen films containing different amounts of nickel (*i.e.* with different Γ_{Ni}). It can be seen that for all films the extent of the

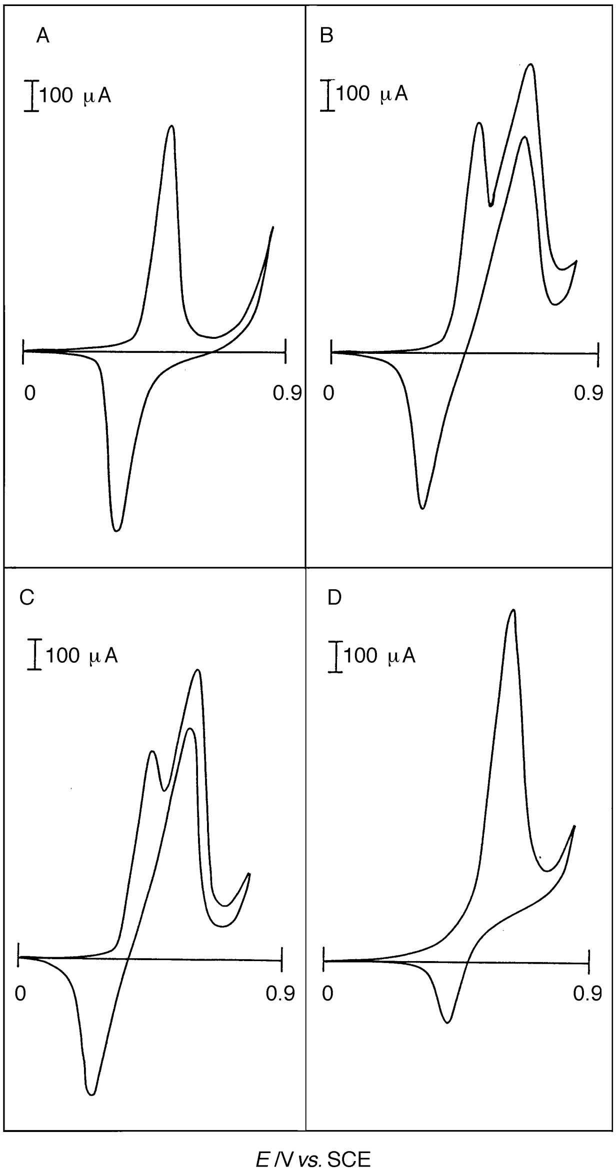

Fig. 7 A, Cyclic voltammetry of poly-NiTCTD film on vitreous carbon electrode ($\Gamma_{Ni} = 9.7 \times 10^{-8}$ mol cm^{-2}) in 0.1 M NaOH aqueous solution and with B, 40 µM methanol, C, 70 µM ethanol, D, 540 µM hydrazine. Scan rate 100 mV s^{-1}.

oxidation current increases and reaches a steady state for ethanol concentrations higher than 1.5 mM. It can also be clearly seen that the catalytic current increases with Γ_{Ni}, the amount of nickel incorporated in the film. For an ethanol concentration of 1.5 mM, the catalytic current varies with Γ_{Ni} as shown in Fig. 8B and this logically indicates that the electrocatalytic behaviour of the film increases with the amount of the nickel centres. However, for thick films ($\Gamma_{Ni} > 10^{-7}$ mol cm^{-2}) the catalytic current did not increase significantly with ethanol concentration. This may be explained by the fact that the electrocatalytic effect depends also on the thickness of the film (in terms of the surface concentration of available electroactive sites). Indeed, it was shown that oxidation of alcohols on nickel hydroxide electrodes depends on the morphology, thickness, permeability, surface concentration of active sites and charge transport of the modifying films.[8,15–17,19,26,29,32,33]

Fig. 9 shows the electrocatalytic behaviour of thin and thick poly-NiTCTD films towards methanol, ethanol and hydrazine oxidation. It appears from these data that (*i*) the films were found to be better catalysts for methanol than for ethanol and hydrazine, and (*ii*) the catalytic activity obviously depends on

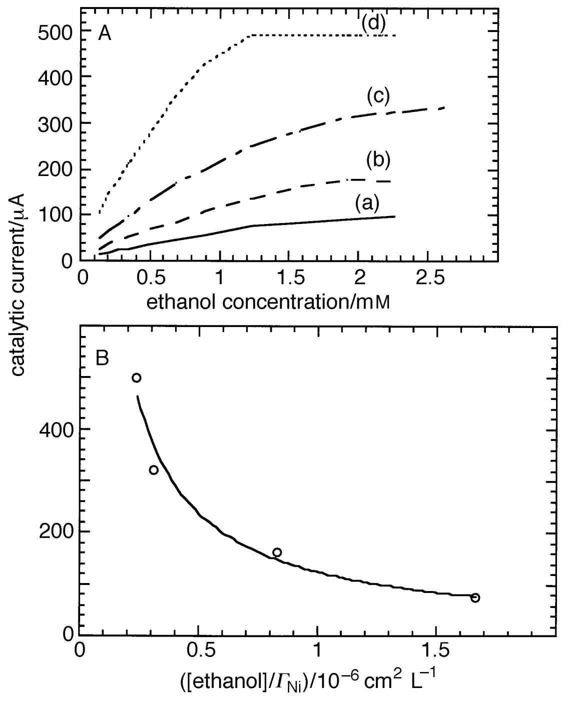

Fig. 8 A, Electrocatalytic oxidation peak currents of ethanol measured at poly-NiSalen films on vitreous carbon electrodes with different Γ_{Ni} as a function of the ethanol bulk concentration. (a) $\Gamma_{Ni} = 0.9 \times 10^{-9}$ mol cm^{-2}; (b) $\Gamma_{Ni} = 1.8 \times 10^{-9}$ mol cm^{-2}; (c) $\Gamma_{Ni} = 4.75 \times 10^{-9}$ mol cm^{-2}; (d) $\Gamma_{Ni} = 6.2 \times 10^{-9}$ mol cm^{-2}. B, Variation of the electrocatalytic oxidation peak current for 1.5 mM ethanol as a function of ethanol/Γ_{Ni} ratio.

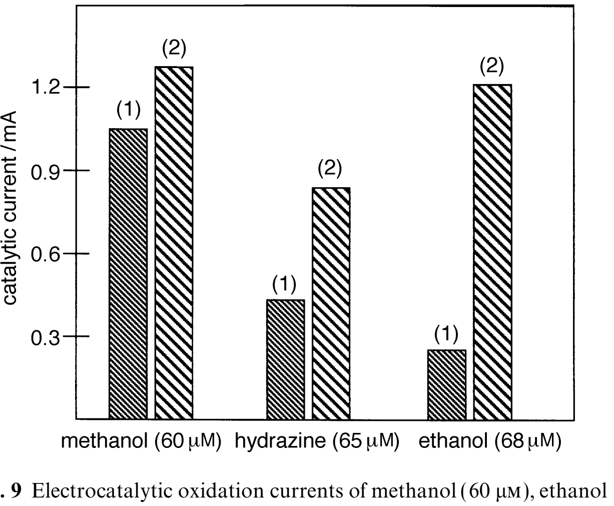

Fig. 9 Electrocatalytic oxidation currents of methanol (60 μM), ethanol (68 μM) and hydrazine (65 μM) at poly-NiTCTD films with (1) $\Gamma_{Ni} = 2.2 \times 10^{-8}$ mol cm^{-2} and (2) $\Gamma_{Ni} = 9.75 \times 10^{-8}$ mol cm^{-2}.

the film thickness. It should be noted that, even though the preliminary results presented here should be further examined, the electrocatalytic activity of nickel complex-based polymers seems to be promising. In addition, the films offer a very high stability after repeated use over several days and storage in air.

Conclusion

This study reports new examples of nickel macrocyclic-based film electrodes prepared by electrochemical polymerization in NaOH aqueous solution. It gives clear indications on the formation of nickel hydroxide like materials that show efficient electrocatalytic behaviour towards methanol, ethanol and hydrazine oxidation. Further studies are now under way to evaluate the strategy of using these electropolymerized complexes in the analytical determination of different kinds of phenol and alcohol pollutants.

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