

# Electrochemical Polymerization at an Electrode Surface: Film Formation of the Ni(II) Complex of Dibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene and the Ni(II) and Cu(II) Complexes of 5,7,12,14-Tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene: Copolymerization and Layered Polymerization

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## Abstract

The detailed mechanistic nature of the electropolymerization of metal complexes of 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene has been investigated at electrode surfaces. Polymerization was not observed if the second oxidation wave in the cyclic voltammogram was not scanned. The quantity of film deposition was shown to vary as a function of the percentage of the second oxidation wave scanned. An upper limit for deposition of film was reached at +1.4 V versus SCE. Copolymerization of both copper(II) and nickel(II) 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene showed no effect on the rate of polymerization due to the metal center. However, copolymerization of 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene copper(II) and dibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene nickel(II) showed that the methyl groups decreased the polymerization rate by a factor of ~6. Layered films of these complexes showed that the outer layer of film controls the redox properties at the electrode. Following the electrochemical features of ferrocyanide and 1,4-benzoquinone, it was possible to show that electrochemical activity through thinner films is possible but is inhibited by films that are at least 55 monolayers thick. Studies of effects on the electrochemical behavior of films due to the presence of fluoride, pyridine and cyanide were carried out.

## Introduction

The study of electropolymerized films on electrode surfaces has recently become an area of intense research [1]. Initial interest was focused on polymer films which were formed on an electrode surface. Later, transition elements were exchanged or complexed into films [2, 3]. More recently, this area

has been expanded with studies on metal containing complexes such as vinyl ferrocene which can electropolymerize directly onto the electrode [4–6]. A good deal of effort has been concerned with developing methods to both control and determine the amount of film deposited on the electrode [7, 8]. These metal/film modified electrodes have found use as catalysts [9–11], controlled ion release devices [12] and fuel cells [13].

A second area of recent research has focused on the electropolymerization of two or more metal containing complexes. Various ratios of two complexes have been polymerized at the same electrode to determine if copolymerization will occur and if rates of polymerization are comparable [14]. The formation of one polymer film on top of another has also been investigated [15]. Electrodes modified with different layers of film often have rectifying properties [16–18] and might be useful in mimicking electronic device behavior [19, 20]. The ability of unique complexes to polymerize on any conducting surface and exhibit properties of electronic devices could further revolutionize the semiconductor industry in forming molecular level circuits.

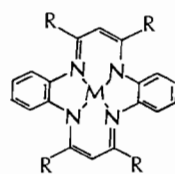
We have studied and reported the electropolymerization of nickel, palladium and platinum complexes of 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene [21, 22]. These films also catalyzed the reductions of CO<sub>2</sub> and O<sub>2</sub> [23, 24]. We report here the characteristics of layered polymerization and copolymerization of dibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene nickel(II), and the copper(II) and nickel(II) complexes of 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene (Fig. 1). We also report a study of these mixed films as possible oxidative catalysts.

## Experimental

### Materials

Tetraethylammonium perchlorate (TEAP) was purchased from Southwestern Analytical Chemicals,

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R = CH<sub>3</sub> & H  
M = Ni & Cu

Fig. 1. [M(R<sub>4</sub>Bzo<sub>2</sub>[14]tetraeneN<sub>4</sub>)].

Inc., dried and used without further purification. Methylene chloride was purchased from Fisher Scientific. Acetonitrile and all other chemicals were purchased from Aldrich Chemical Company. Argon, used for degassing solvents, was obtained from National Welders Supply Company.

#### Physical Measurements

Electrochemical properties were determined in methylene chloride or acetonitrile with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte in conventional three compartment 'H' cells. Cyclic voltammograms were obtained using a BAS CV 27 potentiostat and recorded with a YEW Model 3022 A4 X-Y recorder. The measurements were made at a Bioanalytical Systems platinum electrode. Electrochemical potentials were recorded versus a saturated calomel electrode (SCE). Before use, the disk electrode was polished sequentially with 3, 1 and 0.25  $\mu\text{m}$  diamond paste (Buehler) on a Buehler nylon disk followed by ultrasonic cleaning in deionized water (5 min) and in acetonitrile (5 min). Solutions were degassed for approximately 20 min with argon.

#### Syntheses

The nickel(II) and copper(II) complexes of 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene were prepared by a method described by Bailey *et al.* [21]. The nickel(II) complex of dibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene was prepared by a method described by Peng *et al.* [25]. Elemental analyses by Atlantic Microlabs, Atlanta, GA confirmed these preparations.

## Results and Discussion

#### Film Properties/Copolymerization

The polymerization of 5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza[14]annulene nickel(II) (abbreviated [Ni(Me<sub>4</sub>Bzo<sub>2</sub>[14]tetraeneN<sub>4</sub>))] has previously been reported [21]. Figure 2 displays cyclic voltammograms of the electropolymerization process and of the film in a pure solvent. The electropolymerization scheme [21] suggested that the monomer unit, [Ni(Me<sub>4</sub>Bzo<sub>2</sub>[14]tetraeneN<sub>4</sub>)], di-

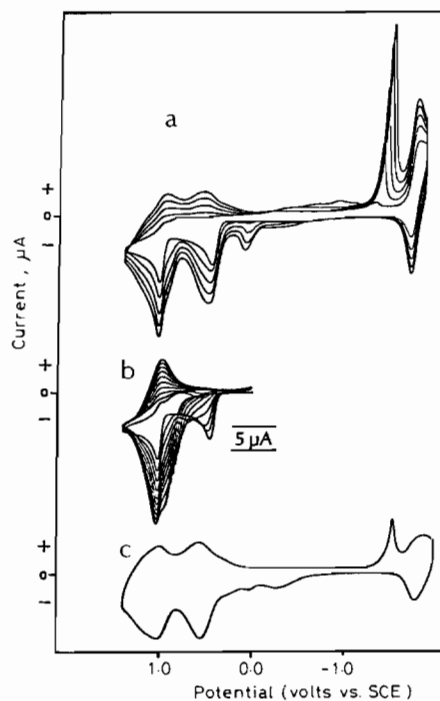


Fig. 2. Cyclic voltammograms of [Ni(Me<sub>4</sub>Bzo<sub>2</sub>[14]tetraeneN<sub>4</sub>)] in acetonitrile solutions containing 0.1 M TEAP (sweep rate 200 mV/s): (a)  $1.0 \times 10^{-3}$  M complex, +1.4 to -2.0 V vs. SCE; (b)  $1.0 \times 10^{-3}$  M complex, +1.4 to 0.0 V vs. SCE; (c) [Ni(Me<sub>4</sub>Bzo<sub>2</sub>[14]tetraeneN<sub>4</sub>)]<sub>n</sub>, +1.4 to -2.0 V vs. SCE.

merized through a radical mechanism at the carbon of the diiminate backbone. A second oxidation of the dimer leads to the polymer film. This polymerization scheme has been confirmed by studies on sterically hindered compounds which limit access to the diiminate carbon studies which showed that no polymerization took place when the methyl groups on the diiminate backbone were replaced with phenyl rings [26].

Since the suggested electropolymerization scheme of [Ni(Me<sub>4</sub>Bzo<sub>2</sub>[14]tetraeneN<sub>4</sub>)] hinges on the second oxidation wave, it was important to more fully understand the relationships between film formation and this potential. Initially, we varied the potential limit of scan into the second oxidation wave. As this limit was varied, an increase was observed in the amount of film formed (Fig. 3). An upper limit or plateau to the amount of film produced was observed at  $\sim 1.4$  V (versus SCE). Since the amount of film on the electrode can be controlled by varying the limit into which the second wave is scanned, for the first time we are able to deposit a monolayer onto the electrode surface.

Electropolymerizations of [Ni(Bzo<sub>2</sub>[14]tetraeneN<sub>4</sub>)] and a cyclic voltammogram of the film in a pure solvent are displayed in Fig. 4. One interesting and noteworthy difference between the cyclic voltammograms for this complex and the tetra-

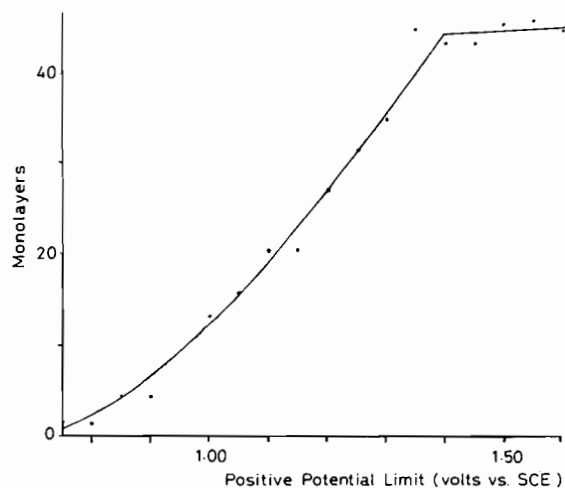


Fig. 3. Electrode surface coverage dependence of  $[\text{Ni}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]_n$  on scan range into the second oxidation wave of the complex, scan range  $-2.0$  V to various limits vs. SCE. The solvent was acetonitrile, the electrolyte was  $0.1$  M TEAP,  $1.0 \times 10^{-3}$  M complex and the scan rate  $200$  mV/s.

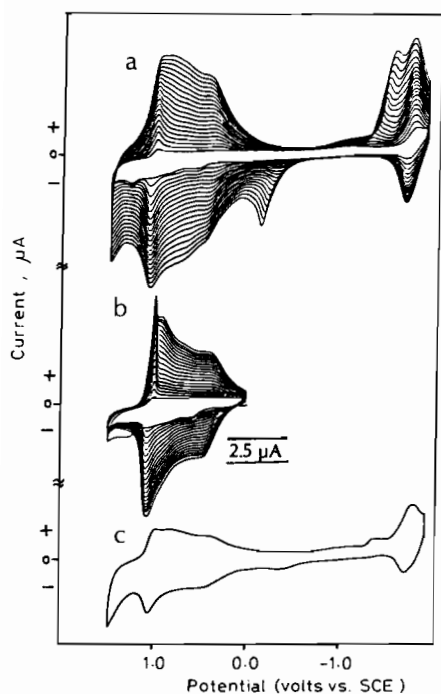


Fig. 4. Cyclic voltammograms of  $[\text{Ni}(\text{Bzo}_2[14]\text{tetraeneN}_4)]$  in acetonitrile solutions containing  $0.1$  M TEAP (sweep rate  $200$  mV/s): (a)  $1.0 \times 10^{-3}$  M complex,  $+1.4$  to  $-2.0$  V vs. SCE; (b)  $1.0 \times 10^{-3}$  M complex,  $+1.4$  to  $0.0$  V vs. SCE; (c)  $[\text{Ni}(\text{Bzo}_2[14]\text{tetraeneN}_4)]_n$ ,  $+1.4$  to  $-2.0$  V vs. SCE.

methyl analog is that no discrete oxidation waves exist for the oxidation of the individual diiminate backbones. The methyl groups must act as a small barrier to the electropolymerization.

In an effort to compare rates of polymerization, we attempted to polymerize two different complexes simultaneously. A copper and a nickel complex were chosen so that it was possible to monitor the film using the magnitude of the respective metal reduction waves. The current due to the reduction of each complex is proportional to the amount of complex polymerized onto the electrode [14]. The percentage of  $[\text{Cu}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$  reduction wave at  $-1.42$  V versus SCE) and  $[\text{Ni}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$  (reduction wave at  $-1.84$  V versus SCE) was varied (see Fig. 5). These two complexes were found to polymerize at approximately the same rate confirming our belief that the metal centers here have little effect on the rate of polymerization.

The rate of polymerization of  $[\text{Ni}(\text{Bzo}_2[14]\text{tetraeneN}_4)]$  was compared with  $[\text{Cu}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$  in an effort to determine the effect of the methyl groups on the rate or ease of polymerization. The tetrahydro macrocycle was found to polymerize twice as fast as the tetramethyl macrocycle (see Fig. 6). By comparing the current observed in this experiment for the copper tetramethyl macrocycle to that in the experiment above, it can further be suggested that it polymerized approximately 3 times faster in the presence of a tetrahydro macrocycle. The increase for the tetramethyl macrocycle

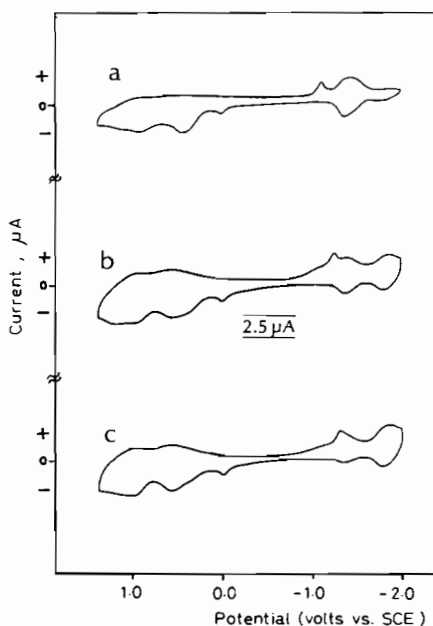


Fig. 5. Cyclic voltammograms of  $[\text{M}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]_n$  in acetonitrile solutions containing  $0.1$  M TEAP (sweep rate  $200$  mV/s,  $+1.4$  to  $-2.0$  V vs. SCE): (a)  $75\%$   $[\text{Cu}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ ,  $25\%$   $[\text{Ni}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ ; (b)  $50\%$   $[\text{Cu}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ ,  $50\%$   $[\text{Ni}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ ; (c)  $25\%$   $[\text{Cu}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ ,  $75\%$   $[\text{Ni}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$ .

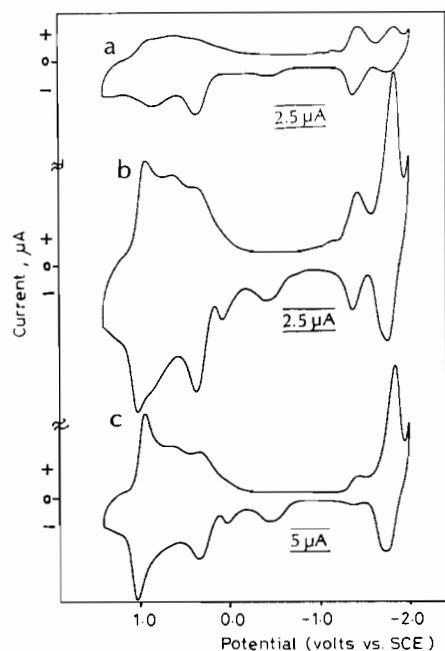


Fig. 6. Cyclic voltammograms of  $[M(R_4BzO_2[14]tetraene-N_4)]_n$  in acetonitrile solutions containing 0.1 M TEAP (sweep rate 200 mV/s, +1.4 to -2.0 V vs. SCE): (a) 75%  $[Cu(Me_4BzO_2[14]tetraeneN_4)]$ , 25%  $[Ni(BzO_2[14]tetraeneN_4)]$ ; (b) 50%  $[Cu(Me_4BzO_2[14]tetraeneN_4)]$ , 50%  $[Ni(BzO_2[14]tetraeneN_4)]$ ; (c) 25%  $[Cu(Me_4BzO_2[14]tetraeneN_4)]$ , 75%  $[Ni(BzO_2[14]tetraeneN_4)]$ .

polymerization could be attributed to polymerization with the less sterically hindered tetrahydro-macrocycle. Overall, this hinderance yields a six fold difference in the rate of polymerization.

#### Layered Polymerization

Since it is now known that one can copolymerize the various metal complexes and observe electrical activity for each species, it was of interest to determine the activity which would remain if layered polymers are deposited. It was also of interest to determine if any rectifying properties might exist in these layered materials. The unidirectional, or rectifying, flow of electrons across the interface between two substances, where one or both are semiconductor materials, is a familiar phenomenon highly exploited by current solid state electronics technology [17]. The interface here would be between the two layered films, each containing its own redox properties.

Initially, the nickel and copper tetramethyl macrocycles were studied. Eight scans of nickel tetramethyl macrocycle followed by two scans of copper tetramethyl macrocycle were carried out to produce film on the electrode. The layered film that resulted showed reduction waves for both complexes (see

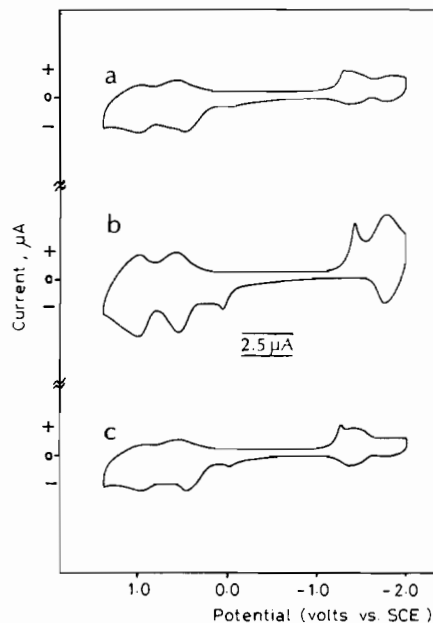


Fig. 7. Cyclic voltammograms of  $[M(Me_4BzO_2[14]tetraene-N_4)]_n$  in acetonitrile solutions containing 0.1 M TEAP (sweep rate 200 mV/s, +1.4 to -2.0 V vs. SCE): (a) 8 scans of  $[Ni(Me_4BzO_2[14]tetraeneN_4)]$  film followed by 2 scans of  $[Cu(Me_4BzO_2[14]tetraeneN_4)]$  film; (b) 2 scans of  $[Cu(Me_4BzO_2[14]tetraeneN_4)]$  film followed by 8 scans of  $[Ni(Me_4BzO_2[14]tetraeneN_4)]$  film; (c) 7 scans of  $[Ni(Me_4BzO_2[14]tetraeneN_4)]$  film followed by 3 scans of  $[Cu(Me_4BzO_2[14]tetraeneN_4)]$  film.

Fig. 7(a)). When this order was reversed, only the reduction wave for nickel tetramethyl macrocycle was observed (see Fig. 7(b)). The last complex polymerized on the electrode appears to control the observed electroactivity. As few as three scans of the second complex were needed to mask the reduction wave of the first complex (see Fig. 7(c)). When repeated scans of the electroactive layered film were carried out in pure solvent, the second layer appeared to erode away and the reduction wave of the first layer reappeared. The first complex is thus not removed during polymerization of the second complex. The electroactivity of layered modified electrode is thus inferred to be controlled by the outer layers even though the first layer is in immediate contact with the electrode surface.

Layered films of copper tetramethyl macrocycle and nickel tetrahydro macrocycle had different properties than the two tetramethyl layered films. If only one scan of nickel tetrahydro macrocycle, the reduction wave (at -1.83 V versus SCE) of the tetrahydro macrocycle was still apparent when the layered film was scanned in neat solvent (see Fig. 8(a)). Even after six scans of tetramethyl macrocycle on the one scan of tetrahydro macro-

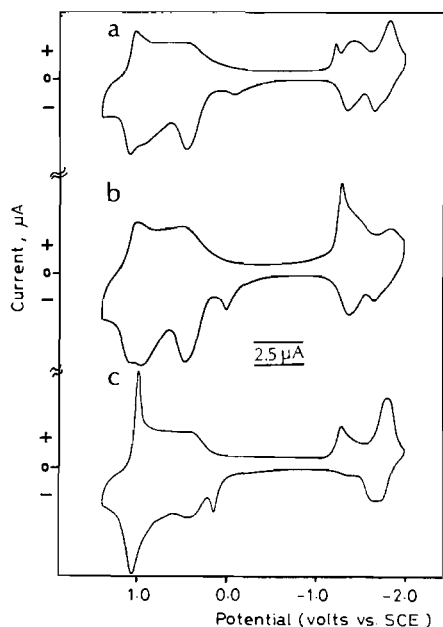


Fig. 8. Cyclic voltammograms of  $[M(R_4Bzo_2[14]tetraeneN_4)]_n$  in acetonitrile solutions containing 0.1 M TEAP (sweep rate 200 mV/s, +1.4 to -2.0 V vs. SCE): (a) 1 scan of  $[Ni(Bzo_2[14]tetraeneN_4)]$  film followed by 3 scans of  $[Cu(Me_4Bzo_2[14]tetraeneN_4)]$  film; (b) 1 scan of  $[Ni(Bzo_2[14]tetraeneN_4)]$  film followed by 6 scans of  $[Cu(Me_4Bzo_2[14]tetraeneN_4)]$  film; (c) 9 scans of  $[Cu(Me_4Bzo_2[14]tetraeneN_4)]$  film followed by 1 scan of  $[Ni(Bzo_2[14]tetraeneN_4)]$  film.

cycle, the reduction wave of the tetrahydro macrocycle was still observed (see Fig. 8(b)). Only one scan of tetrahydro macrocycle was needed to mask the reduction wave of the tetramethyl macrocycle (see Fig. 8(c)). This is not unexpected since one scan of tetrahydro macrocycle is approximately equal to six scans of tetramethyl macrocycle. The tetrahydro macrocycle must take a different form on the electrode than the tetramethyl macrocycle. These layered films appear not to have rectifying properties with respect to each other. However, as will be seen, non-layered films appear to have rectifying properties with respect to other electroactive species.

#### Electron Transfer

To determine the possible mode of electron transfer, electroactive species with well controlled redox waves were examined at film modified electrodes. Various thicknesses of nickel tetramethyl macrocycle were investigated. Redox waves of  $Fe(CN)_6^{4-}$  occur where none exist for the film. When film thicknesses on electrodes were four scans or less, little change in the redox waves of  $Fe(CN)_6^{4-}$  was observed. After the film became five scans thick, the redox wave of  $Fe(CN)_6^{4-}$  broadened and flat-

tened. Thicker films appeared to impede electron transfer. Electrons must be able to tunnel through thinner films. Soaking thicker films in  $Fe(CN)_6^{4-}$  solution had no effect on the observed change in redox waves which implies thicker films must not contain large defects which would allow penetration by  $Fe(CN)_6^{4-}$ .

Studies of 1,4-benzoquinone with various nickel tetramethyl macrocycle film thicknesses proved of interest. The second reduction wave of 1,4-benzoquinone lost electroactivity in the presence of two scans of film. Six scans of film caused the first reduction wave of 1,4-benzoquinone to broaden, flatten and become irreversible as observed for  $Fe(CN)_6^{4-}$ . These two studies help explain the loss of linearity observed for film growth [21, 22]. Poor electron transfer through thicker films from the unpolymerized complex slows film growth rate thus causing a break in linear relation between the number of scans and amount of film formed. After the electrode had been modified with eight scans of film, an increase in the reduction wave was observed with 1,4-benzoquinone in solution. A suggested explanation is a rectified charge transfer from the film to 1,4-benzoquinone [17].

#### Catalytic Properties

In order to understand mechanisms of film formation for tetramethyl macrocycles, a tetraphenyl macrocycle was studied [27]. Since tetraphenyl macrocycles do not form films, it was possible to explore their electrochemistry in the presence of small molecules such as fluoride, pyridine, cyanide and azide [28]. It was determined that tetraphenyl macrocycles bind some small molecules axially and are able to electrochemically catalyze oxidation. To check this property for various tetramethyl macrocyclic films, we investigated the reactivity of some film modified electrodes with respect to fluoride, pyridine and cyanide. Fluoride had no effect on film electrochemistry. Pyridine increased the current observed at the second oxidation wave by a small amount but not enough to warrant further investigation.

Cyanide, with an oxidation at  $\sim 0.85$  V (versus SCE), was quite different. In the presence of 5 scans of copper tetramethyl film, the oxidation of cyanide is shifted to a less positive value and observed as an increase in current at approximately the first oxidation wave of the film (see Fig. 9). A shift in oxidation occurred when only 1 scan of analogous nickel film was present. Ability to shift an oxidation to lower potential implies catalytic oxidation. Cyanide must bind to the film in order for its oxidation to coincide with an oxidation of the film. For completeness, effects of layered and copolymer films on cyanide oxidation were evaluated. Cyanide oxidation current

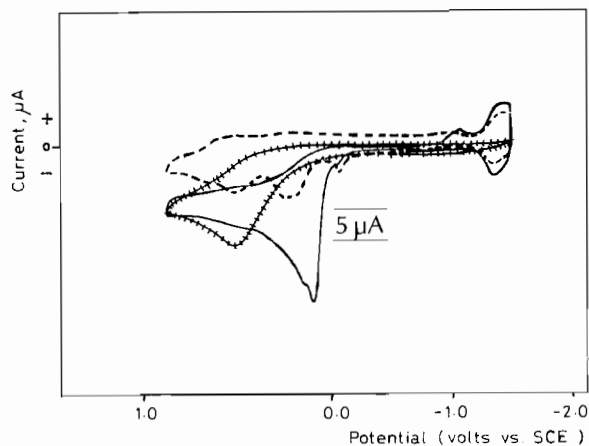


Fig. 9. Cyclic voltammograms in acetonitrile solutions containing 0.1 M TEAP (sweep rate 200 mV, +1.4 to -2.0 V vs. SCE): (---) 5 scans of  $[\text{Cu}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$  film; (+++) 1 mM tetraethylammonium cyanide; (—) 5 scans of  $[\text{Cu}(\text{Me}_4\text{Bzo}_2[14]\text{tetraeneN}_4)]$  film and 1 mM tetraethylammonium cyanide.

was less with layered films than non-layered films. However, with copolymer films, cyanide oxidation current was slightly greater.

## Conclusions

A study of film produced versus scan limit further supports the electropolymerization scheme for the tetramethyl tetraazaannulene macrocycles. Comparing reduction waves of simultaneously polymerized tetrahydro and tetramethyl macrocycles provided a measure of relative rates of polymerization with tetrahydro macrocycle polymerizing  $\sim 6$  times as fast as tetramethyl macrocycle. As scan number increased, a break in linear film growth rate had been observed and was attributed to poor electron transfer through thicker films. With a better understanding of how tetramethyl macrocycles polymerize, some other aspects of their films were explored. Bilayer films are not rectifiers, however, thicker films appear to rectify with 1,4-benzoquinone in solution. Other electropolymerizing complexes combined with these films could form rectifying devices. Shown to act possibly as both reductive and oxidative catalysis, films of mixed combinations should yield new varieties of catalytic modified electrodes.

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