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Electrochemical generation of a nickel–carbonyl complex, catalyst for the electroreductive coupling of organic halides and carbon monoxide into ketones

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Abstract

The nickel–carbonyl complex Ni(CO)bpy is involved in the nickel-catalysed electroreductive coupling of organic halides and carbon monoxide into ketones. The active species is obtained from a stoichiometric mixture of Ni^0, 2,2′-bipyridine and CO. The electrochemical method used to generate this complex allows a good tuning of Ni^0 production versus CO dissolution. We have shown that Ni(CO)bpy results from a CO equilibrium exchange between $Ni(CO)_2bpy$ and Nibpy. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Carbon monoxide; Nickel–bipyridine complexes; Electroreduction; Carbonylation catalysis

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1. Introduction

We recently reported [1] that symmetrical ketones are efficiently obtained by electroreductive coupling of organic halides and CO, according to the equation:

$$2RX + CO + 2e \rightarrow RCOR + 2X^-$$

This reaction involves a catalytic system generated by the electroreduction of the divalent nickel complex $Nibpy^{2+}$ (bpy = 2,2′-bipyridine) in a DMF solution fed with CO by bubbling at normal pressure.

For these electrosyntheses, we noted a crucial influence of the applied current intensity. Indeed, at too low current intensity the organic halide was not transformed, whereas at too high current intensity RR was formed along with the ketone RCOR. Then, we assumed that several zerovalent nickel complexes could be formed depending on the amount of CO dissolved versus the amount of electrogenerated Ni^0bpy. Thus, an excess of the strong ligand CO would yield a stable complex which is inactive towards RX, while lack of CO would lead to the formation of Ni^0bpy which is a well known catalyst for the conversion of RX into RR ([2]a,b).

The aim of this study was to evidence the various low-valent nickel complexes which can be formed when $Nibpy^{2+}$ is electroreduced in the presence of CO. We have found that the species which is active for the conversion of RX into RCOR is the non-saturated Ni(CO)bpy complex. It is mainly formed when the ratio of nickel–bpy and CO is 1:1. In relation with this, and from a preparative point of view, the electrochemical method has proved to be quite convenient to easily adjust the rate of production of Ni^0bpy versus the rate of dissolution of CO.

2. Results and discussion

As a preliminary remark, we can say that only few data on the binding of divalent nickel by CO have been

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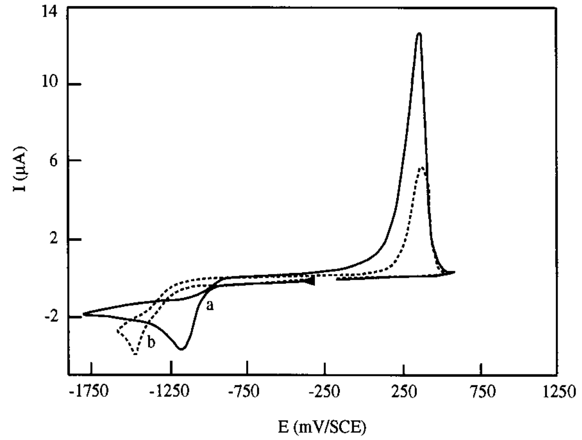

Fig. 1. Cyclic voltammograms of $Ni(CH_3SO_3)_2$ (4×10^{-3} M) in DMF + Bu_4NBF_4 (0.1 M). Au electrode. $v = 0.1$ V s^{-1}. (a) Under argon. (b) Under CO. $E_{initial} = -0.3$ V/SCE.

reported [3,4]. Notably, no divalent nickel complexes bound to both CO and bpy are either known, or to be postulated on the basis of the results of this study. On the contrary, we have obtained evidence for the formation of various CO-ligated low-valent nickel species according to the experimental conditions.

First we have examined the electrochemical behaviour of Ni^{2+} under CO and in the absence of other ligands. Fig. 1 presents cyclic voltammograms obtained at a gold microelectrode for a DMF solution of $Ni(CH_3SO_3)_2$ maintained under argon (Fig. 1, curve a) or CO (Fig. 1, curve b). Under argon, Ni^{2+} ions were irreversibly reduced at -1.2 V/SCE into metallic nickel, whose anodic redissolution was observed at 0.4 V/SCE. Double chronocoulometric experiments indicated that the same amount of electricity was engaged for both reduction and oxidation steps.

After CO bubbling, the Ni^{2+} electroreduction was shifted to more negative potential (-1.5 V/SCE) and double chronocoulometric measurements then indicated a lower amount of electricity for the anodic versus the cathodic process. In these conditions, the electroreduction of Ni^{2+} competitively leads to both metal and a low-valent carbonylated complex, possibly nickel tetracarbonyl $Ni(CO)_4$. We did not detect this complex, which is reportedly hardly reduced (-2.7 V/SCE in THF [5]) or oxidised (1.26 V/SCE in CH_3CN [5]). We did not further investigate this behaviour since no transformation of an organic halide occurred when Ni^{2+} was reduced in the presence of CO.

2.1. Electrochemical behaviour of $Nibpy_n^{2+}$ ($n = 1$ or 2) in the presence of CO

At normal pressure and room temperature, the concentration of CO in DMF solution does not exceed 2–4×10^{-3} M [6]. Nevertheless, a CO saturated DMF solution exhibits an oxidation signal at 1.5 V/SCE, whose intensity indicates that, possibly because of adsorption, the concentration of CO at the microelectrode is ca. 3×10^{-2} M. The concentration of Ni^{II} used in the analytical studies was therefore based on this value, to investigate the behaviour of solutions with various CO:Ni^{II} ratios, i.e. $[CO] > 2[Ni^{II}]$ and $[CO] < 2[Ni^{II}]$ corresponding, respectively, to an excess of CO or nickel.

2.1.1. Electrochemical behaviour when $[CO]:[Ni^{II}] > 2([Ni^{II}] < 1.5 \times 10^{-2}$ M)

The electrochemical behaviour of Ni–bpy complexes under an inert atmosphere has been previously described [2]. Fig. 2 (curve a) shows the well known, almost reversible, bielectronic process which corresponds to:

$$Nibpy^{2+} + 2e \rightleftharpoons Ni^0bpy$$

$$Ep(C_1) = -1.1 \text{ V/SCEEp}(A_1) = -0.93 \text{ V/SCE}$$

The A_2 peak, which did not appear at higher scan rate, arose from a partial decomposition of the unstable complex Ni^0bpy ([2]b).

After CO bubbling in the solution (Fig. 2, curve b), the electrochemical behaviour of $Nibpy^{2+}$ was radically modified. The bielectronic reduction occured at a slightly less negative potential (C_3 peak) with a total lack of reversibility and was followed by a one-electron reversible process (C_4/A_4 peaks). The reverse anodic A_3 peak, with a low intensity due to diffusion, is related to the C_3 step. Indeed, the relative intensity of A_3 peak versus C_3 peak increased at higher sweep rate. We propose that in these conditions, $Nibpy^{2+}$ undergoes an EC reduction mechanism, according to:

$$\left.\begin{array}{l} Nibpy^{2+} + 2e \rightleftharpoons Ni^0bpy \\ Ni^0bpy + 2CO \rightarrow Ni(CO)_2bpy \end{array}\right\} Ep(C_3) = 1.1 \text{ V/SCE}$$

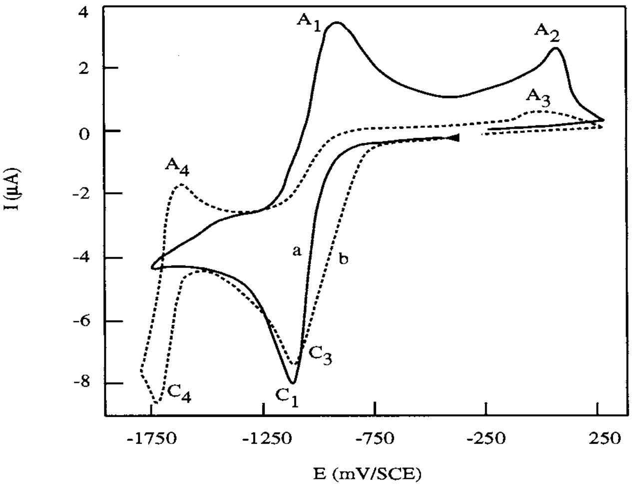

Fig. 2. Cyclic voltammograms of $Ni(CH_3SO_3)_2$ (10^{-2} M) + bpy (10^{-2} M) in DMF + Bu_4NBF_4 (0.1 M). Au electrode. $v = 0.1$ V s^{-1}. (a) Under argon. (b) Under CO. $E_{initial} = -0.3$ V/SCE.

The chemical step where Ni^0bpy associates CO should be very fast, since C_3 peak is more positive than C_1 peak [7]. In addition, no reverse oxidation of Ni^0bpy (A_1 peak) can be detected even at high scan rate (50 V s^{-1}).

We prepared $Ni^0(CO)_2bpy$ by exhaustive electrolysis of a $Ni(CH_3SO_3)_2$ + bpy (1:1 mol/mol) solution maintained under CO. The complete reduction of $Nibpy^{2+}$ involved 2 mol of electrons per nickel and yielded a red solution. The IR spectrum and the electrochemical behaviour of this electrolytic solution were consistent with previous data for $Ni(CO)_2bpy$ [8,9], which was obtained by ligand exchange reaction [10]:

$$Ni^0(CO)_4 + bpy \rightleftarrows Ni^0(CO)_2bpy + 2CO$$

As shown in Fig. 3, $Ni(CO)_2bpy$ is reversibly electroreduced:

$$Ni(CO)_2bpy + e \leftrightarrows Ni(CO)_2bpy^{\bullet -}$$

$$Ep(C_4) = -1.76\ V/SCE Ep(A_4) = -1.65\ V/SCE$$

and irreversibly electrooxidised:

$$Ni(CO)_2bpy - 2e \rightarrow Nibpy^{2+} + 2CO$$

$$Ep(A_3) = -0.16\ V/SCE$$

The cyclic voltammograms, as well as the electrolyses of divalent nickel were unaffected by addition of extra bpy to the solution ($[bpy]/[Ni^{II}] = 2$ to 15): as far as CO is in excess versus Ni^{2+} , the reduction of $Nibpy_2^{2+}$ only leads to $Ni^0(CO)_2bpy$:

$$Nibpy_2^{2+} + 2e + 2CO \rightarrow Ni^0(CO)_2bpy + bpy$$

Conversely, we added CO to a Ni^0bpy_2 solution obtained by electrolysis of $Nibpy^{2+} + 2bpy$: the dark green solution of Ni^0bpy_2 turned to red in a few seconds. Cyclic voltammetry showed similar peaks to those in Fig. 3 (C_4/A_4 and A_3). The rate of disappearance of Ni^0bpy_2 or the rate of formation of $Ni^0(CO)_2bpy$ can be measured by chronoamperometry, by setting the potential at the level of A_1 (−0.93 V/SCE) and C_4 (−1.76 V/SCE) peaks, respectively. The pseudo zero-order kinetic then observed only expresses the slow rate of dissolution of CO, which depends on the experimental device.

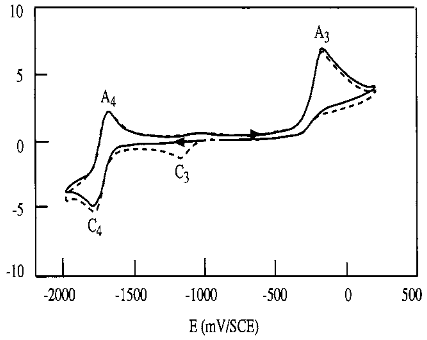

Fig. 3. Cyclic voltammograms of $Ni^0(CO)_2bpy$ (8×10^{-3} M) in DMF + Bu_4NBF_4 (0.1 M) under CO. Au electrode. $v = 0.1$ V s^{-1}. $E_{initial} = -0.8$ V/SCE. (a) (Full line): cathodic, then anodic scan. (b) (Dashed line): anodic, then cathodic scan.

This $Ni(CO)_2bpy$ complex is not, however, the species involved in the catalytic electroconversion of organic halides into ketones, since no reaction occurred after several hours when $PhCH_2Cl$ was added to a solution of $Ni(CO)_2bpy$, maintained under CO.

2.1.2. Electrochemical behaviour when $[CO]:[Ni^{II}] < 2$ ($[Ni^{II}] > 1.5 \times 10^{-2}$ M)

Fig. 4 shows the voltammograms obtained with increasing Ni^{2+}:CO ratio in a CO-saturated DMF solution, starting with the concentration of the case discussed above (Fig. 4, curve a). When the concentration of $Nibpy^{2+}$ was increased from 1.5×10^{-2} to 3×10^{-2} M (Fig. 4, curve b), the reduction of $Nibpy^{2+}$ remained irreversible and the intensity of the (C_4/A_4) signal assigned to the reversible reduction of $Ni(CO)_2bpy$ decreased progressively. In exchange, a new quite reversible process noted C_6/A_6 was detected at lower potentials. The reverse scan presented an ill-defined oxidation step at −0.1 V/SCE (A_5 peak). For concentrations of $Nibpy^{2+}$ $> 3 \times 10^{-2}$ M (Fig. 4, curve c), the A_1 peak related to the oxidation of Ni^0bpy was detected. We can explain this behaviour as follows: At low concentrations[1] of Ni^{II}, as discussed above, the only electrochemical reaction is:

$$Nibpy^{2+} + 2e + 2CO \rightarrow Ni^0(CO)_2bpy$$

When the concentration of Ni^{II} is between 1.5×10^{-2} and 3×10^{-2} M, CO is a limiting reagent at the level of the electrode and both complexes $Ni(CO)_2bpy$ and Ni^0bpy are formed[1]. This may indicate that a ligand exchange between these two complexes then yields a new species, presumably $Ni^0(CO)bpy$, according to Scheme 1. As detailed below, the processes C_6/A_6 and A_5 characterise the electrochemical properties of this new complex $Ni^0(CO)bpy$.

These conclusions are in good agreement with the observations made during the electrosyntheses of ketones from organic halides RX [1]. When the current was too low, RX was not transformed. This can now be explained by the formation of the inactive complex $Ni(CO)_2bpy$ due to slow generation of Ni^0 in the presence of excess of CO. On the other hand, at high current, a mixture of ketone RCOR and hydrocarbon RR was obtained. Owing to the low solubility of CO and its slow rate of dissolution, a mixture of

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[1] If the concentration of $Nibpy^{2+}$ is $> 3 \times 10^{-2}$ M, $Ni^0(CO)_2bpy$ disappears and the electroreduction generates a mixture of Ni^0CObpy and Ni^0bpy (Fig. 4, curve c).

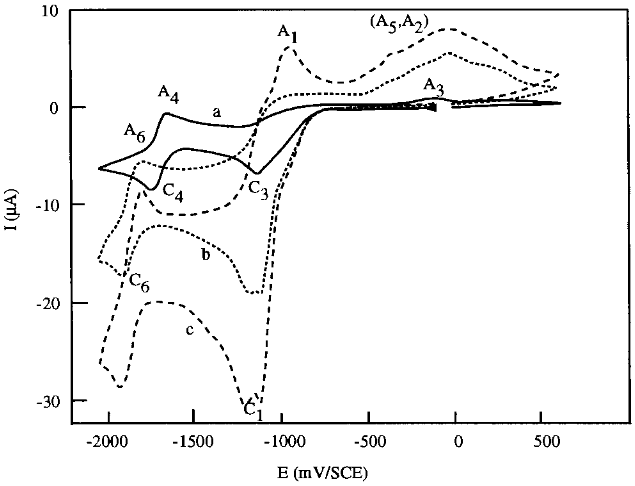


Fig. 4. Cyclic voltammograms of $Ni(CH_3SO_3)_2^+$ bpy (1:1 mol/mol) in DMF + Bu_4NBF_4 (0.1 M), under CO. Au electrode. $v = 0.1$ V s^{-1}. (a) $[Ni(CH_3SO_3)_2] = 10^{-2}$ M. (b) $[Ni(CH_3SO_3)_2] = 3 \times 10^{-2}$ M. (c) $[Ni(CH_3SO_3)_2] = 5 \times 10^{-2}$ M. $E_{initial} = -0.1$ V/SCE.

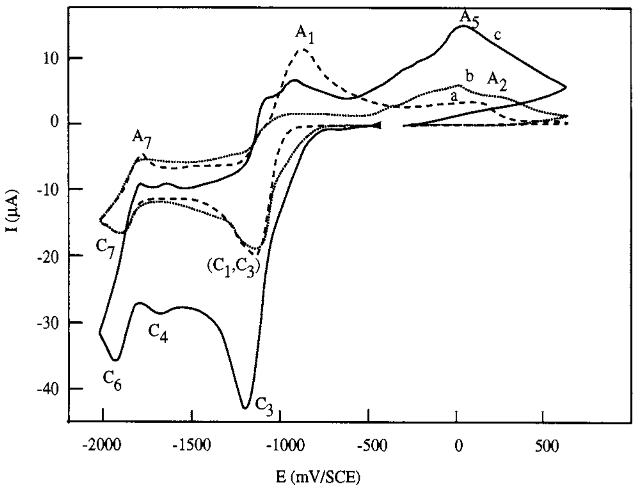


Fig. 5. Cyclic voltammograms of $Ni(CH_3SO_3)_2$ (3×10^{-2} M) + bpy (3×10^{-2} M) in DMF + Bu_4NBF_4 (0.1 M). Au electrode. (a) Under argon. $v = 0.1$ V s^{-1}. (b) Under CO. $v = 0.1$ V s^{-1}. (c) Under CO. $v = 0.5$ V s^{-1}. $E_{initial} = -0.3$ V/SCE.

$Ni^0(CO)bpy$ and Ni^0bpy could then be formed. The complex Ni^0bpy is well known to induce the catalytic electroreductive dimerisation of RX into RR ([2]a,b). The ketone is selectively obtained when the current intensity corresponds to the optimum in the formation of the active catalytic species $Ni^0(CO)bpy$.

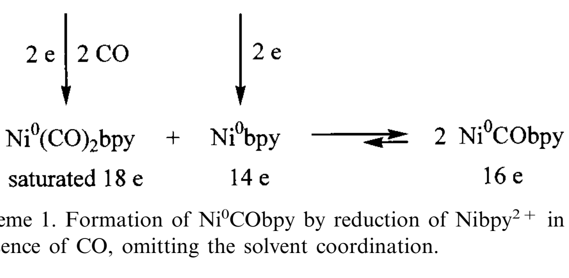
$Ni^0(CO)bpy$ is unstable and we were not able to determine its spectroscopic data. In order to obtain more information on its generation and redox properties, we have studied the influence of the voltage sweep rate (Fig. 5), for solutions where $Ni^0(CO)bpy$ can be the major electrogenerated species at the level of the electrode ($[Nibpy^{2+}] = 3 \times 10^{-2}$ M). We clearly detected a one-electron reversible step (C_6/A_6), which can be assigned to the following redox system:

$$Ni(CO)bpy + e \rightleftharpoons Ni(CO)bpy^{\bullet -}$$

$$Ep(C_6) = -1.93 \text{ V/SCE}$$

$$Ep(A_6) = -1.83 \text{ V/SCE}$$

The characteristic potential values of this C_6/A_6 transition were similar to those measured for $Ni^0(CO)_2bpy$ (C_4/A_4) or $Ni^0bpy_{1 \text{ or } 2}$ (C_7/A_7), which indicated that the one-electron transfer is presumably centred on the ligand and bpy. On the contrary, $Ni^0(CO)bpy$ was oxidised only at -0.1 V/SCE (A_5 peak), i.e. 0.8 V higher than the potential of the reversible transition $Ni^0bpy/Nibpy^{2+}$ (C_1/A_1). This behaviour is not surprising since for both $Ni^0(CO)bpy$ and $Ni^0(CO)_2bpy$, the two-electron transfer leading to Ni^{II} must be accompanied by the loss of CO.



Scheme 1. Formation of Ni^0CObpy by reduction of $Nibpy^{2+}$ in the presence of CO, omitting the solvent coordination.

Besides, at higher scan rate (Fig. 5, curve c), the C_4 peak (reduction of $Ni^0(CO)_2bpy$) and A_1 peak (oxidation of Ni^0bpy) became visible again. This could indicate that the reaction yielding $Ni^0(CO)bpy$:

$$Ni^0(CO)_2bpy + Ni^0bpy \rightleftharpoons 2Ni^0(CO)bpy$$

is moderately fast. This will be discussed in a coming paper, along with the comparative kinetics of the oxidative addition reaction of RX on Ni^0bpy or $Ni^0(CO)bpy$.

We also studied the influence of the amount of the ligand bpy on the formation of $Ni^0(CO)bpy$. The solutions were prepared from $Ni(BF_4)_2bpy_3$. In this case, the cyclic voltammetry indicated the formation of either only $Ni^0(CO)_2bpy$ when the nickel salt concentration was low, or a mixture of $Ni^0(CO)_2bpy$ and Ni^0bpy_2 when the Ni^{II} concentration was $> 1.5 \times 10^{-2}$ M. In keeping with the results presented above, no CO ligand-exchange occurred between the saturated complexes $Ni^0(CO)_2bpy$ and Ni^0bpy_2 to give the unsaturated 16e complex $Ni^0(CO)bpy$. Furthermore, the ketone RCOR was not obtained after addition of RX to a solution containing the mixture of $Ni^0(CO)_2bpy$ and Ni^0bpy_2. Only the dimer RR was obtained in that case.

3. Conclusion

This study has allowed us to show that several complexes are formed by electroreduction of divalent nickel–bpy complexes in the presence of CO. If CO is in excess, only the stable $Ni^0(CO)_2bpy$ complex, inactive towards organic halides, can be obtained. The active species which catalyses the electrochemical conversion of halides into ketones, is a transient, unsaturated $Ni^0(CO)bpy$ complex, resulting from a CO ligand exchange between $Ni^0(CO)_2bpy$ and Ni^0bpy simultaneously generated at the cathode. The reaction is efficient only if the rate of zero-valent nickel production is well fitted to the available amount of CO.

4. Experimental

DMF (Merck) and 2,2′-bipyridine (Aldrich) were used as received.

Tetrabutylammonium tetrafluoroborate was purchased from Fluka and further purified by recrystallisation from 1,1,1-trichloroethane/diethylether and dried in vacuo (30 mm Hg) at 70°C.

$Ni(BF_4)_2bpy_3$ [11] was prepared according to reported procedures.

$Ni(CH_3SO_3)_2$ was prepared from a $NiCO_3$, $Ni(OH)_2 \cdot 4H_2O$ (320 mmol) suspension in water (50 ml) and a methane sulphonic acid solution (640 mmol of $CH_3SO_3H + H_2O$ qsp 150 ml). The green solution was then evaporated when all the precipitate had disappeared. The solid obtained was washed with acetone, then diethylether and dried in vacuo at 120°C. The product colour was yellow–green. Yield: 75–90%

4.1. Preparation of Ni(CO)$_2$bpy in DMF solution

An exhaustive coulometric reduction at controlled current (0.2 A) of $Ni(CH_3SO_3)_2$ (8×10^{-3} M) + bpy (8×10^{-3} M) + Bu_4NBF_4 (0.1 M) in DMF solution was carried out under CO bubbling. The undivided cell was fitted with a magnesium rod as the anode, which was surrounded by a nickel grid as the cathode. The initial pale green solution turned to red during the electrolyses which involved 2 mol of electrons per mole of divalent nickel.

Alternatively, Ni^0bpy_2 complex was formed by electrolysing a $Ni(BF_4)_2bpy_3$ solution under argon and in the presence of excess bpy. The dark green solution then obtained lead to the red solution of $Ni(CO)_2bpy$ after CO bubbling. This complex was characterised by its IR spectrum (ν 1860, 1950 cm^{-1}) [8] and by its redox pattern (Fig. 3): reversible reduction (C_4/A_4 process at -1.76 V/SCE) and irreversible oxidation (A_3 peak) at -0.16 V/SCE [9].

Voltammetric experiments were carried out using a three-electrode configuration cell under argon or CO, in DMF solution + Bu_4NBF_4 (0.1 M). The working electrode was a gold disk electrode ($\varnothing = 0.5$ mm). A two-compartment system (saturated calomel reference electrode and DMF + 0.1 M Bu_4NBF_4 solution) separated by alumina-fritted disks was used to probe the working electrode potential.

The electrochemical experiments with ohmic drop compensations were performed with an EG&G PAR model 173 potentiostat interfaced with a microcomputer.

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