



Electrodes modified by electrodeposition of CoTAA complexes as selective oxygen cathodes in a direct methanol fuel cell

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Abstract

The oxygen reduction reaction (ORR) at cobalt tetraazaanulene (CoTAA) modified electrodes was investigated. As a first approach, modified electrodes were prepared by electrodeposition of CoTAA on glassy carbon (GC). The modification of the GC surface was monitored by u.v.–vis. differential reflectance spectroscopy (UVDRS). The recorded spectra (i.e., absorbance as a function of wavelength and time) showed that the electrodeposition of CoTAA at 0.8 V vs Ag|AgCl, that is, at a potential where the TAA ligand is oxidized to TAA⁺•, seems to produce a thin polymer film. Starting from these preliminary results, porous rotating disc electrodes (RDEs) were prepared by electrodeposition of CoTAA (0.8 V vs Ag|AgCl, 1 min) on graphite powder embedded in a recast Nafion[®] film. The use of a porous RDE allowed comparison of the activity and selectivity of Pt nanoparticles and CoTAA for the ORR under experimental conditions close to those of a fuel cell cathode, that is, at the catalyst|Nafion[®] interface. The activity towards the ORR of a porous electrode modified by electrodeposition of CoTAA is not affected when methanol is present in the electrolyte phase, whereas a noticeable decrease in the activity of Pt-based oxygen cathodes was observed under the same conditions. Half-cell life tests showed that CoTAA-modified electrodes and Pt-based electrodes have a comparable stability over a period of 90 min.

1. Introduction

The cross-over of methanol, from the anode to the oxygen cathode through the proton exchange membrane, is one of the major problem that hinders development of the direct methanol fuel cell (DMFC). This phenomenon causes a large decrease in fuel cell performance, because methanol is oxidized at the Pt-based cathode leading to a mixed potential [1–3].

Since the early 1970s, electrocatalysis of the ORR is known to proceed with some metal transition complexes of the N₄-type (i.e., phthalocyanines, porphyrins and tetraazaanulenes) [4, 5]. It was, however, soon recognized that these compounds are not completely stable in acidic and oxidizing environments [4]. Nevertheless, there is a continuing interest in the realization of stable electrodes based on metal transition complexes that catalyse the ORR. A possible approach is heat-treatment (up to 1000 °C) of carbon supported N₄-chelates containing iron and cobalt ions [6, 7], which greatly increases the catalytic activity and stability. The main problem is that heat-treatment probably modifies the ligand in a way that is not yet elucidated [6]. Another promising approach is the realization of modified

electrodes readily from electropolymerization of the metal macrocycle [8]. In this latter case, the ligand is not altered.

The cobalt tetraazaanulene (CoTAA) complex, which is the subject of this paper, has been used as an effective ORR catalyst in fuel cells [4, 5, 7]. It was also shown that a film of metallotetraazaanulene can be formed by oxidative electropolymerization and electrodeposition [9–11].

In the hope of developing active and selective catalysts, we therefore investigated the ORR in the presence of methanol at CoTAA-modified electrodes. As a first approach, modified electrodes were prepared by electrodeposition of CoTAA on glassy carbon (GC). The modification of the GC surface was monitored by u.v.–vis. differential reflectance spectroscopy. Starting from these preliminary results, porous rotating disk electrodes (RDEs) were prepared by electrodeposition of CoTAA on graphite powder embedded in a recast Nafion[®] film. The use of porous RDEs allowed comparison of the activity and the selectivity of Pt nanoparticles and CoTAA for the ORR under experimental conditions close to those of a fuel cell cathode, i.e. at the catalyst|Nafion[®] interface [12].

2. Experimental details

2.1. Materials

N,N'-dimethylformamide (Fisher), 1,2-phenylenediamine (Fluka), propargylic alcohol (Aldrich), CrO₃ (Fluka) and CoCl₂ · 6 H₂O (Fluka) were used as received. Acetonitrile (Aldrich, 99%) was distilled over P₂O₅ and dried over molecular sieves before use. Tetrabutylammonium perchlorate (Aldrich) was dried overnight at 50 °C and used without further purification. The 0.1 M HClO₄ solution was prepared from concentrated perchloric acid (Merk Suprapur, 70%) and ultrapure water (MilliQ, Millipore). All other chemicals were reagent grade and used without further purification.

Co(II)-dibenzotetraaza[14] annulene was synthesized according to Hiller's method [13]. The corresponding nonmetalled compound was obtained by reacting *o*-phenylene diamine with propargylic aldehyde. This latter was made by a method derived from that of Sauer [14]: the mechanical stirring system was replaced by a magnetic stirring system, and a single trap cooled with liquid nitrogen was used. The whole apparatus was purged with nitrogen gas before the reaction was started. After metallation of the H₂TAA ligand, the crude product was washed with methanol. u.v.–vis. spectra recorded in DMF agree well with those given in the literature [9].

2.2. Apparatus and procedures

A rapid scan spectrometer (Harrick RSS-C) equipped with two photomultipliers (Hamamatsu R955) was used for the u.v.–vis. differential reflectance spectroscopic measurements. The output signals were processed in a digital signal averager (Nicolet 370) and stored in a computer. Each spectrum was obtained after averaging 100 scans at 30 ms per scan between 162 and 730 nm. Details on the u.v.–vis. reflectance spectroscopy are given elsewhere [15].

The electrochemical measurements were performed with conventional instrumentation consisting of a potentiostat (Wenking LT87), a waveform generator (PPRI Hi-Tek Instruments), and a XYt-recorder (ABB). The electrochemical cells were three-electrode cells. The counter electrode was a platinum foil. The reference electrode was either a KCl saturated calomel electrode or a KCl saturated Ag|AgCl electrode separated from the working electrode compartment by a fine porosity glass frit and a Luggin capillary. In organic solvents the potential is referred versus the Ag|AgCl electrode, while in aqueous solutions the potential is referred to the reversible hydrogen electrode (RHE).

The glassy carbon (Carbone Lorraine) working electrodes (surface area 0.071 cm²) were prepared by polishing with 0.3 μm alumina (Escil) on a polishing cloth. To obtain roughened GC electrodes, the polishing was carried out with 600 grit SiC paper (Escil). After either polishing procedure the electrodes were sonicated

in pure water for several minutes, washed with acetone and dried.

The porous electrode was constructed by the following method. A mixture was prepared by sonicating 50 mg of graphite powder (HSAG 300, Lonza), 1000 mg of 5 wt % Nafion[®] solution (Aldrich) and 5 mL of purified water. A measured volume (~2 μL) of this mixture was deposited onto a polished GC disc electrode. Solvents were then evaporated at 80 °C yielding a porous electrode of controlled and reproducible geometry [12]. In the case of a Pt/C porous electrode, the procedure was the same, but 10% Pt/XC72-Vulcan (E-TEK) was used instead of graphite powder [12]. We have also previously shown [12] that for slow reactions, such as the ORR, the limitation by mass transport and ohmic loss in the porous electrode is negligible, when the recast Nafion[®] film containing the carbon supported catalyst (here CoTAA or Pt) is about 1 μm in thickness. Hence, it was possible to determine the activation overpotential characteristics after correction for the oxygen diffusion in solution using the RDE technique.

GC- and porous CoTAA-modified electrodes were prepared by electrodeposition (at 0.8 V vs Ag|AgCl for 1–5 min) from a N₂ purged and stirred 0.1 M Bu₄NClO₄ acetonitrile (ACN) solution saturated with CoTAA (~2 mM). The apparent surface concentration was calculated using the equation:

$$\Gamma_{\text{CoTAA}} = \frac{Q}{nFA}$$

where Q is the quantity of electricity associated with the electrodeposition process (i.e., the integral of the current against time response), n the number of electrons involved per molecule, F the faradaic constant, and A the apparent surface area of the electrode.

The real surface area A_{Pt} of the Pt-based electrodes was determined from the corresponding voltammetric peaks in the H upd region and assuming a theoretical charge density of 210 μC cm⁻². The surface concentration of Pt-based electrodes was thus calculated from the equation:

$$\Gamma_{\text{Pt}} = \frac{A_{\text{Pt}} \times 210 \times 10^{-6}}{AF}$$

Levich plots (i.e., plateau current density, j_L , against square root of the rotation rate, $\Omega^{1/2}$) allowed estimation of the number n of electrons involved in the reduction of O₂ at the CoTAA-modified electrodes. Theoretical Levich plots were calculated for $n = 2$ and $n = 4$ using the following equation [16]:

$$|j_L| = Bn\Omega^{1/2}$$

where $B = 0.62 F D_{\text{O}_2}^{2/3} \nu^{-1/6} [\text{O}_2] (2\pi/60)^{1/2}$, with $[\text{O}_2] = 1.4 \text{ mM}$ in oxygen-saturated solutions, $D_{\text{O}_2} = 1.7 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ is the diffusion coefficient of oxygen, and $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$ is the kinematic viscosity of aqueous

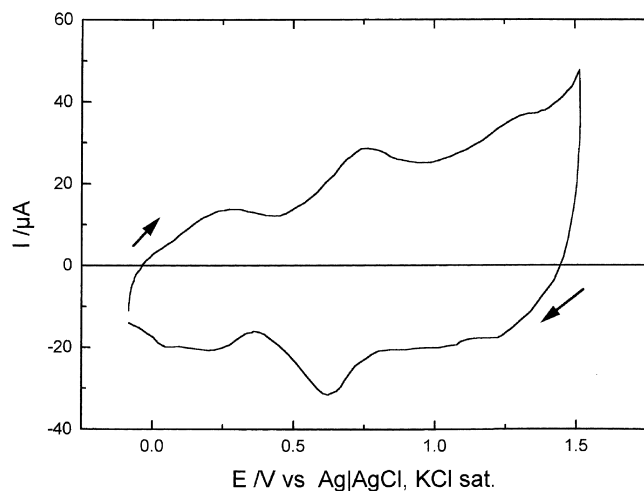


Fig. 1. Cyclic voltammogram (100 mV s^{-1}) at a GC electrode in a N_2 purged $0.1 \text{ M Bu}_4\text{NClO}_4$ acetonitrile solution saturated with CoTAA (2 mM).

solutions. This leads to $B \approx 0.0386 \text{ mA cm}^{-2} \text{ rpm}^{-1/2}$, when Ω is expressed in rpm.

Tafel plots (i.e., $E/\log|j_k|$) were obtained after correction for the kinetics of diffusion-convection of oxygen in solution using the equation:

$$j_k(E) = \frac{j(E, \Omega) \times j_L(\Omega)}{j_L(\Omega) - j(E, \Omega)}$$

where $j_k(E)$ is the current density for activation (charge transfer) control, $j(E, \Omega)$ the current density measured at potential E and rotation rate Ω , and $j_L(\Omega)$ the limiting current density at rotation rate Ω .

3. Results and discussion

3.1. Electrodeposition of CoTAA

CoTAA is only slightly soluble in acetonitrile (ACN), which is the reason why ACN solutions saturated with

CoTAA ($\sim 2 \text{ mM}$) were used.

Figure 1 shows the first cyclic voltammogram recorded at a smooth GC electrode in a N_2 purged and unstirred solution containing CoTAA. On the positive-going scan from -0.1 to 1.5 V vs Ag|AgCl, three peaks are observed at 0.3 , 0.7 and 1.25 V . On the negative-going scan, only two peaks are clearly discerned at 0.65 and 0.2 V , although a less pronounced peak may be observed at about 1.2 V . The peaks at $0.3/0.2 \text{ V}$ can be assigned to the Co(II)/Co(III) redox couple, while the peaks at 0.7 V and 1.25 V can be assigned to the oxidation of the TAA ligand to a π -cation radical ($\text{L}^{+\bullet}$), and to a π -dication diradical ($\text{L}^{2+\bullet}$), respectively [17]. According to Bailey et al. [9], $\text{L}^{+\bullet}$ radicals slowly couple to form dimers, while $\text{L}^{2+\bullet}$ rapidly form a polymer deposit on the electrode surface.

To gain additional understanding on the CoTAA electrodeposition process, u.v.-vis. differential reflectance spectra were recorded *in situ*. Spectra shown in Figures 2 and 3 were obtained after normalization and subtraction of a reference spectrum. As a result, a negative absorbance can be assigned to the removal (e.g., consumption by reaction) of species which were present at the electrode potential of the reference spectrum, while a positive absorbance can be assigned to the presence (e.g., formation by reaction) of new species at the electrode surface [18, 19].

Spectra recorded during the first cyclic voltammogram (-0.1 to 1.5 V vs Ag|AgCl, 5 mV s^{-1}) at a smooth GC electrode are shown in Figure 2. The reference spectrum was the spectrum recorded at -0.1 V before the potential scanning was started. Two peaks are observed in Figure 2: a large negative peak at about $450\text{--}475 \text{ nm}$ and a smaller positive peak at about 525 nm . During the positive-going scan (Figure 2(a)), the height of these two peaks significantly increases in absolute value. During the negative-going scan (Figure 2(b)), the height of these two peaks slightly decreases, so that the negative peak is still observed at -0.1 V . The spectrum recorded at -0.1 V after one scan

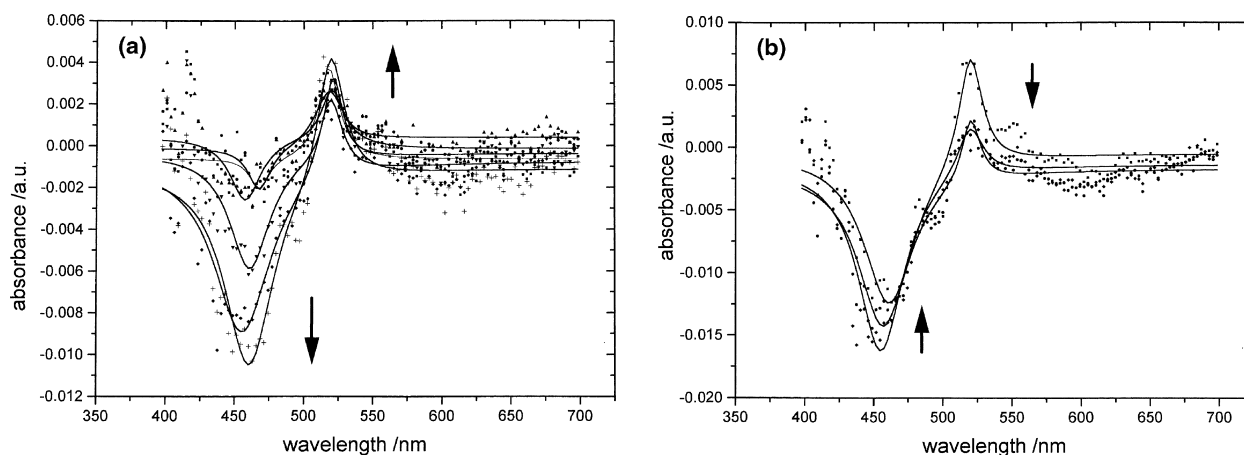


Fig. 2. U.v.-vis. differential reflectance spectra recorded *in situ* during the first cyclic voltammogram (5 mV s^{-1}) at a GC electrode in a N_2 purged $0.1 \text{ M Bu}_4\text{NClO}_4$ acetonitrile solution saturated with CoTAA (2 mM). (a) Positive-going scan. Key: (■) 0.15 , (●) 0.40 , (▲) 0.65 , (▼) 0.90 , (◆) 1.15 and (+) 1.40 V . (b) Negative going scan. Key: (■) 1.35 , (●) 0.85 and (◆) -0.10 V . Potentials are quoted to the Ag|AgCl reference electrode.

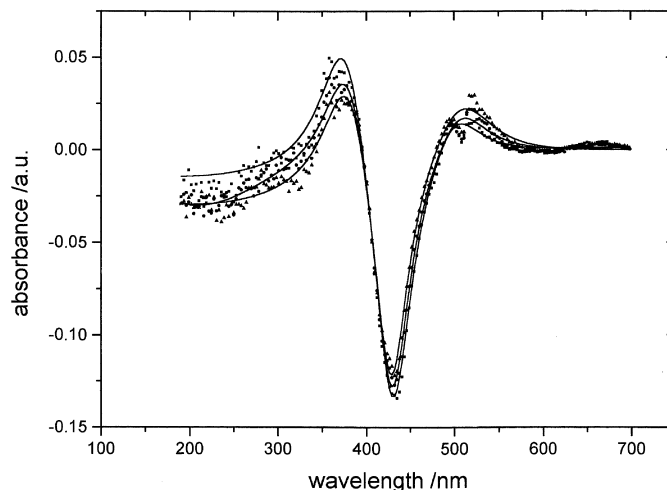


Fig. 3. U.v.-vis. differential reflectance spectra recorded at 0.8 V vs Ag|AgCl as a function of time at a GC electrode in a N_2 purged 0.1 M Bu_4NClO_4 acetonitrile solution saturated with CoTAA (2 mM). Key: (■) 10, (●) 150 and (▲) 300 s.

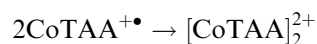
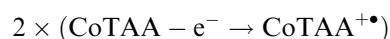
up to 1.5 V is thus very different from the reference spectrum, which provides evidence that the electrode surface was irreversibly modified by the CV treatment. The most likely assumption is that CoTAA was electrodeposited on the GC electrode, because CV treatment should not significantly modify the absorbance response of a bare GC electrode. As a result, the large negative peak at about 450–475 nm is likely due to the consumption of the CoTAA monomer which was initially adsorbed at the electrode surface, because the peak appears at $E > 0.65$ V, that is, at a potential where the TAA ligand is oxidized. However, the positive peak at about 525 nm can likely be attributed to the formation of CoTAA dimers and/or to the formation of a polymer at the electrode surface. An other possibility to explain this positive absorbance, is the detection of $CoTAA^{+\bullet}$, because this cation radical is stable on the CV time scale [9].

Polymerization by CV is not a convenient method to prepare large scale electrodes required in fuel cell systems. Therefore we investigated the possibility of preparing modified electrodes by electrodeposition of CoTAA at a constant potential. U.v.-vis. differential reflectance spectra were recorded each 10 s during 5 min at a GC electrode held at 0.8 V vs Ag|AgCl, i.e. at a potential where the CoTAA monomer is oxidized to a $CoTAA^{+\bullet}$ cation radical. The reference spectrum was recorded at the same electrode at 0.3 V, that is, at a potential where the TAA ligand is not oxidized. Absorbance versus time responses recorded at a constant potential of 0.8 V (Figure 3) exhibit a large negative peak at 435 nm and a smaller positive peak at 520 nm, and are similar to those obtained after one potential scan between -0.1 and 1.5 V (Figure 2). It is therefore likely that the two absorbance peaks in Figure 3 are due to the electrochemical oxidation of the CoTAA monomer leading to the formation of CoTAA dimers and/or to the formation of a polymer at the electrode surface. The height of the two peaks in Figure 3 also varies

slightly over a period of 5 min (the negative peak decreases, while the positive peak increases in absolute value), which indicates that the structure of the electrode surface varies slowly with time. These results provide evidence that a potential step from 0.3 to 0.8 V leads to the electropolymerization of CoTAA at the electrode surface and that the growth of the polymer film is slow.

According to these previous results, roughened GC and porous modified electrodes were prepared by electrodeposition of CoTAA at 0.8 V vs Ag|AgCl. The electrodeposition was performed in a N_2 purged and stirred ACN solution containing CoTAA. Contact time between the electrode surface and the CoTAA ACN solution was about 15 min before the potential was stepped to 0.8 V for 1 min. In all recorded current versus time transient responses (not shown here) a plateau current is rapidly attained likely due to the finite rate of CoTAA diffusion in solution.

Apparent surface concentration can be calculated using the equation $\Gamma = Q/(nFA)$, where Q is the quantity of electricity associated with the electrodeposition process (i.e., the integral of the current against time response corrected from the contribution of the double layer charging). The number n of electrons involved was estimated from the EC mechanism proposed by Bailey et al. [9]:



which implies that 2 electrons per mole of CoTAA are involved in the electropolymerization process. Typical Γ values, calculated over four different experiments, are about 2.5×10^{-9} and 2.2×10^{-8} mol cm^{-2} for the roughened GC electrode and the porous electrode,

respectively. Assuming that a monolayer corresponds to $2.43 \times 10^{-11} \text{ mol cm}^{-2}$ of CoTAA complexes [9], the calculated Γ values indicate that about 100 and 900 CoTAA monolayers were electrodeposited at the roughened GC electrode and the porous electrode, respectively. The apparent surface concentration of the porous modified electrode is about one order of magnitude greater than that of the roughened GC modified electrode. In addition, the roughness factor of the porous electrode is at least one order of magnitude greater than that of the roughened GC electrode. The apparent surface concentration therefore increases as the roughness factor of the electrode increases, which indicates that effective electrodeposition of CoTAA inside the porous electrode constructed from graphite powder and recast Nafion[®] did occur.

3.2. Oxygen reduction reaction (ORR)

The catalytic reduction of oxygen in a 0.1 M HClO₄ solution was examined at CoTAA modified RDEs prepared from smooth, roughened GC electrodes and porous electrodes, respectively. The voltammetric responses recorded at a rotation rate of 500 rpm are shown in Figure 4(a). At CoTAA modified electrodes, significant cathodic currents are observed for potentials

more negative than 0.8 V vs RHE, and below 0.6 V the cathodic currents are diffusion-limited. This likely indicates that CoTAA modified electrodes are active towards the oxygen reduction, because a bare GC electrode does not exhibit this voltammetric behaviour. In the case of the porous modified electrode, a superimposed cathodic peak at 0.45–0.5 V is observed during the first positive-going scan (not shown here) and tends to disappear in the following scans. This voltammetric response is probably related to the porous structure of the electrode, because it is not observed at smooth and roughened GC modified electrodes, but has already been observed at a slurry electrode prepared from CoTAA monomers adsorbed on acetylenic black [5].

The Tafel plots obtained after correction for the oxygen diffusion in solution are shown in Figure 4(b). Tafel like behavior was observed over nearly 2 decades. Tafel slopes of 65–75 mV (decade)⁻¹ were calculated for potentials ranging from 0.8 to 0.65 V vs RHE. These values of $dE/d[\log |j_k|]$ agree well with those previously reported in the literature [5].

The intensities of the plateau current measured for rotation rates between 500 and 2500 rpm were used to determine the number of electrons involved in the ORR. The slopes of the Levich plots shown in Figure 4(c) give a number of electrons between $n = 2$ and 4, which means that oxygen is reduced to both H₂O₂ and H₂O at

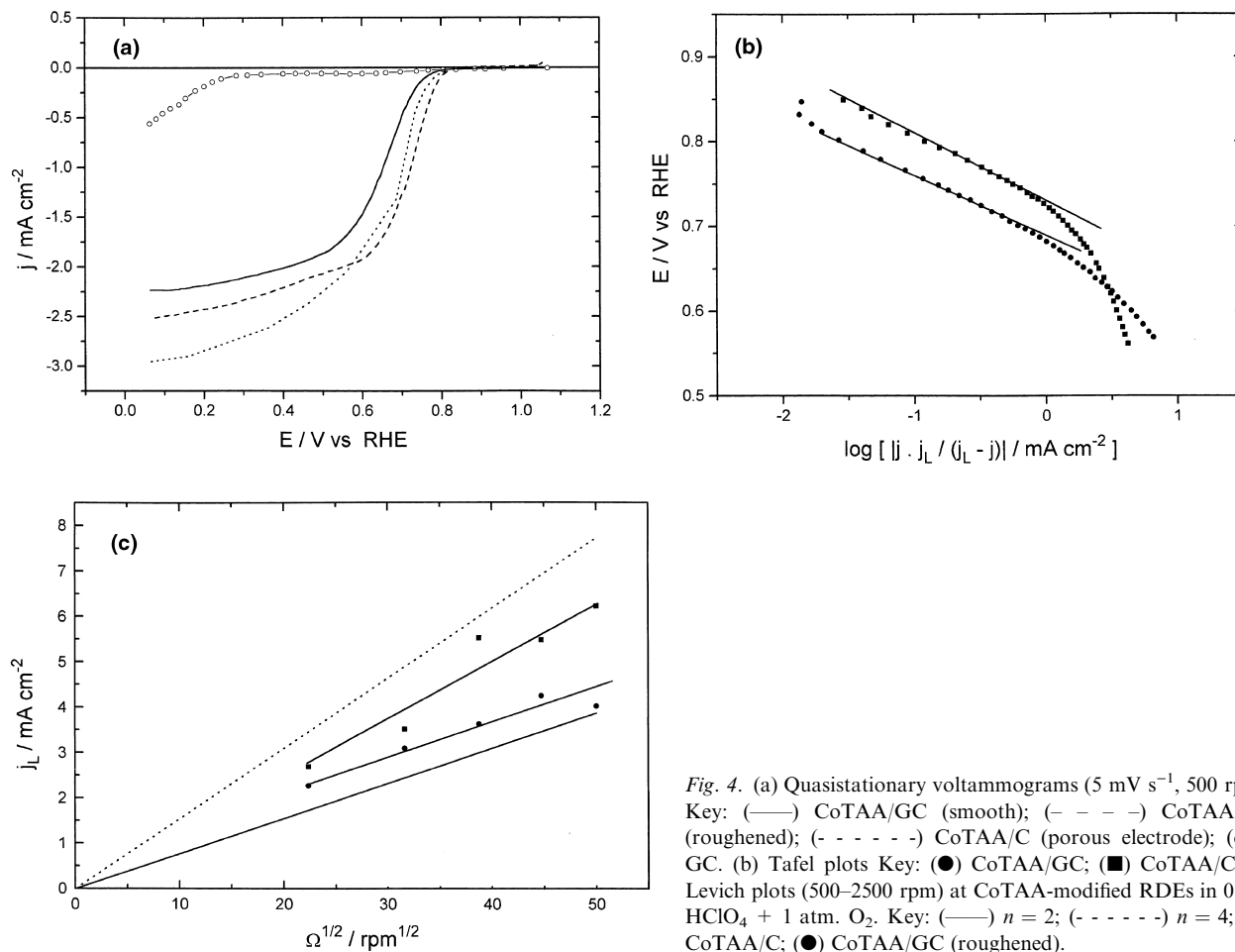


Fig. 4. (a) Quasistationary voltammograms (5 mV s^{-1} , 500 rpm). Key: (—) CoTAA/GC (smooth); (---) CoTAA/GC (roughened); (· · · · ·) CoTAA/C (porous electrode); (o-o) GC. (b) Tafel plots Key: (●) CoTAA/GC; (■) CoTAA/C. (c) Levich plots (500–2500 rpm) at CoTAA-modified RDEs in 0.1 M HClO₄ + 1 atm. O₂. Key: (—) $n = 2$; (· · · · ·) $n = 4$; (■) CoTAA/C; (●) CoTAA/GC (roughened).

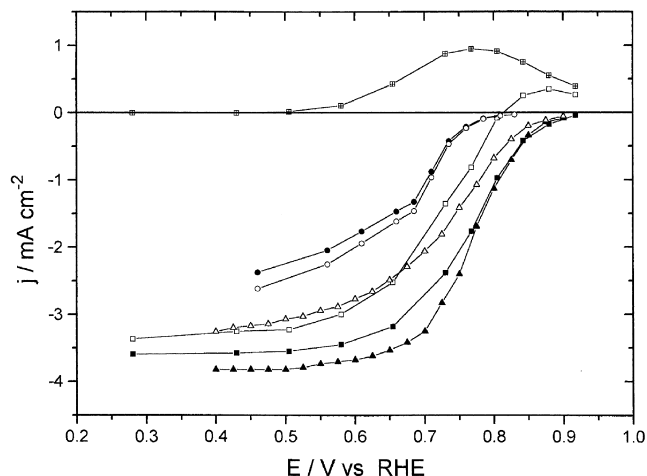


Fig. 5. Quasistationary voltammograms (5 mV s^{-1} , 500 rpm) at Pt-based and CoTAA modified RDEs in $0.1 \text{ M HClO}_4 + 1 \text{ atm. O}_2$ and $0.1 \text{ M HClO}_4 + 1 \text{ atm. O}_2 + 123 \text{ mM CH}_3\text{OH}$. Key: (\boxplus) Pt: $0.12 \text{ M CH}_3\text{OH}$; (\blacksquare) Pt: O_2 ; (\square) Pt: $\text{O}_2 + 0.12 \text{ M CH}_3\text{OH}$; (\bullet) CoTAA/C: O_2 ; (\circ) CoTAA/C: $\text{O}_2 + 0.12 \text{ M CH}_3\text{OH}$; (\blacktriangle) Pt/C: O_2 ; (\triangle) Pt/C: $\text{O}_2 + 0.12 \text{ M CH}_3\text{OH}$.

CoTAA modified electrodes. Slightly higher values of n were obtained at the porous modified electrode.

The goal of this preliminary work was not to determine the ORR mechanism at CoTAA modified electrodes. However, it must be emphasized that the number of electrons involved in the ORR at electrodes modified by CoTAA electrodeposition is significantly greater than 2, whereas Co complexes of the N_4 type usually reduce O_2 to H_2O_2 when physically adsorbed at the electrode surface [8, 16]. This probably means that electrodeposition of CoTAA yields a catalyst in which some of the Co centres may cooperate during the ORR, that is, some of the catalyst–oxygen adducts could be Co-O-O-Co [20]. Additional experiments, in particular concerning the activity towards the reduction and

Table 1. Activity of Pt-based and CoTAA-modified electrodes for the ORR in methanol-free and methanol-containing solutions. Values of current density per surface area (j_k), current density per mole of catalyst (j^*) are calculated from corresponding Tafel plots.

| | Bulk Pt | Pt/C | CoTAA/C |
|--|---------|-------|---------|
| $-j_k(\text{O}_2)$ at 0.85 V $/\mu\text{A cm}^{-2}$ | 478* | 372* | |
| $-j_k(\text{O}_2)$ at 0.7 V $/\text{mA cm}^{-2}$ | 10.8* | 25.1* | 2.2* |
| $-j^*(\text{O}_2)$ at $0.7 \text{ V} \times 10^5$ $/\text{A mol}^{-1}$ | 6.3 | 4.6 | 1.0 |
| $-j_k(\text{O}_2 + \text{CH}_3\text{OH})$ at 0.7 V $/\text{mA cm}^{-2}$ | 3.8* | 5.8* | 2.3* |
| $-j^*(\text{O}_2 + \text{CH}_3\text{OH})$ at $0.7 \text{ V} \times 10^5$ $/\text{A mol}^{-1}$ | 2.2 | 1.1 | 1.0 |

* current density per geometric surface area.

† current densities per real Pt surface area. Surface area of Pt is 7.9 and $24.8 \text{ cm}^2 \text{ cm}^{-2}$ for the bulk Pt and the Pt/C electrode, respectively.

oxidation of H_2O_2 , are currently being performed in our laboratory and should provide a better understanding of the ORR mechanism at CoTAA modified electrodes.

3.3. ORR in electrolyte containing CH_3OH : comparison with Pt-based cathodes

Voltammograms recorded at Pt-based and CoTAA modified rotating disc electrodes in an oxygen atmosphere are shown in Figure 5. When no methanol was added to the electrolyte, oxygen reduction current at Pt-based cathodes is observed for $E < 0.95 \text{ V}$ vs RHE and the plateau current measured at $E < 0.6 \text{ V}$ indicates that four electrons are involved in the ORR, that is, oxygen is mainly reduced to water. When $0.123 \text{ M CH}_3\text{OH}$ were added, oxygen reduction currents at Pt-based cathodes were significantly shifted to the more

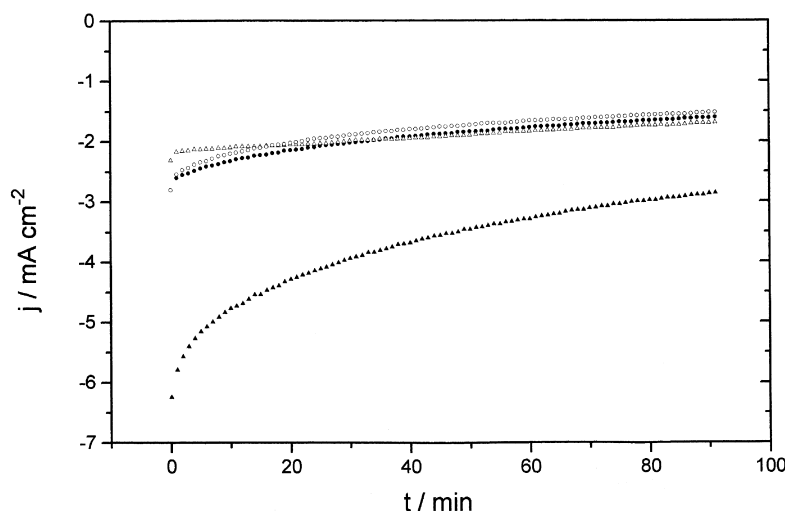


Fig. 6. Potentiostatic responses at Pt/C ($E = 0.8 \text{ V}$ vs RHE) and porous CoTAA-modified ($E = 0.65 \text{ V}$ vs RHE) RDEs rotating at 2000 rpm in $0.1 \text{ M HClO}_4 + 1 \text{ atm. O}_2$ and $0.1 \text{ M HClO}_4 + 1 \text{ atm. O}_2 + 123 \text{ mM CH}_3\text{OH}$. Key: (\blacktriangle) Pt/C: O_2 ; (\bullet) CoTAA/C: O_2 ; (\triangle) Pt/C: $\text{O}_2 + \text{CH}_3\text{OH}$; (\circ) CoTAA/C: $\text{O}_2 + \text{CH}_3\text{OH}$.

negative values. The observed effect of methanol on the ORR at the bulk Pt electrode agrees well with previously reported results [2]. In particular, at $E \geq 0.8$ V, the polarization curve in the presence of O_2 and CH_3OH appears to be the algebraic sum of the polarization curve for neat O_2 and that for the oxidation of neat CH_3OH . Unlike the case of Pt-based cathodes, the presence of methanol did not alter the kinetics of oxygen reduction at the CoTAA-modified electrodes. The voltammograms in Figure 5 hence demonstrates that CoTAA selectively catalyses the ORR, that is, there is no mixed potential between oxygen reduction and methanol oxidation.

Tafel plots were drawn from the voltammograms presented in Figure 5. The current density values calculated at 0.85 and 0.7 V vs RHE are listed in Table 1. Under neat oxygen atmosphere and at a potential of 0.85 V vs RHE, the activity (i.e. the current density per real Pt surface area) of the bulk Pt electrode is about four times greater than that of the Pt/C (10 wt % E-TEK) electrode, which is in good agreement with previously reported data concerning the particle size effect on the ORR at Pt-based electrodes [21]. For a better evaluation of the respective cathode performances, current per mole of catalyst at the electrode surface was also calculated (Table 1). When no methanol was added, the bulk Pt electrode exhibits the greater activity for the ORR, the activity of the Pt/C electrode at 0.7 V is about 1.4 times lower (because of the particle size effect [21]), and that of the CoTAA modified electrode is about six times lower. Nevertheless, when methanol is added, the Pt/C electrode and the CoTAA-modified electrode have almost similar activities, while the bulk Pt electrode is still the most efficient oxygen cathode at 0.7 V. It is however to be emphasized that Pt/C is the catalyst actually used in fuel cell cathode.

To check the stability of the CoTAA-modified electrode for the ORR, potentiostatic experiments were achieved. Current against time responses were recorded at Pt/C and CoTAA/C RDEs (2000 rpm). The curves shown in Figure 6 suggest that the porous CoTAA-modified electrode is as stable as the Pt/C electrode over a period of 90 min, because a similar decrease of activity with time is observed for both electrodes. It is therefore very likely that the electrodeposition of CoTAA in a porous structure of graphite powder and recast Nafion[®] enhances the stability of this N_4 -chelate catalyst under acidic and oxidizing environments. Nevertheless, life-tests at higher temperatures ($T > 70$ °C) and over a much longer period of time ($t > 100$ h) are required to evaluate the stability of the CoTAA-modified electrodes under fuel cell operating conditions.

4. Conclusion

U.v.-vis. differential reflectance spectroscopy suggests that the electrodeposition of CoTAA at a potential where

the TAA ligand is oxidized to a π -radical cation follows an EC mechanism, as initially assumed by Bailey et al. [9].

We thus prepared porous modified electrodes by electrodeposition of CoTAA on graphite powder inside a recast Nafion[®] film, which is to our knowledge the first time that electrodeposition of CoTAA inside recast ionomer film is reported. This allowed investigation of the ORR kinetics under experimental conditions close to those of a fuel cell cathode, while controlling the oxygen mass transport through the RDE technique [12].

Under neat oxygen atmosphere, CoTAA-modified porous electrodes reduce oxygen to hydrogen peroxide and water, because it was found that the number of electrons involved in the electrochemical reaction is comprised between 2 and 4. This promising result likely indicates that electrodeposition of CoTAA yields modified electrodes in which some of the cobalt centres can cooperate during the oxygen reduction reaction [20].

The activity of CoTAA-modified cathode towards ORR is independent of the presence of methanol, while addition of 0.1 M CH_3OH to the electrolyte leads to a pronounced decrease in activity of the Pt-based electrodes.

Although the performances of the CoTAA-based electrodes investigated in this work are lower than those of a Pt-based electrode, we prepared by this method porous oxygen cathodes that are not affected by the presence of methanol, which is an important result for the development of an efficient cathode for DMFCs.

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