JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 1139–1146

Oxygen electrocatalysis under fuel cell conditions: behaviour of cobalt porphyrins and tetraazaannulene analogues

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Received 5 June 1995; revised 7 May 1996

Under fuel cell conditions, using a protonic conductor Nafion® electrolyte, active cobalt porphyrins ($TpOCH_3PPCo$ or CoTMPP and derivatives) and cobalt tetraazaannulene (CoTAA) supported on an active charcoal were investigated towards oxygen reduction to test their activity and stability. Over a 200 h period, performances were found almost constant with CoTAA after an 800 °C heat treatment (HT 800), whereas performances with different substituted phenyl porphyrins declined. XPS analyses were also carried out on these electrodes. On all samples they displayed a complete loss of cobalt within the measurement accuracy. Heat treatment temperature effects were visible on the N1s spectra for the CoTAA samples, the most stable and active samples presenting the lowest oxidation state after current drain application.

1. Introduction

To reduce the cost of fuel cells using solid polymer protonic electrolytes the substitution of platinum for the oxygen liberating cathode by less expensive catalysts is still a matter of interest [1–3]. Data collected from H_2SO_4 solutions under fuel cell conditions were previously presented by Yeager [4] using cobalt tetramethoxyphenylporphyrin (CoTMPP or $TpOCH_3PPCo$) and hydrogen or cobalt dibenzotetraazaannulene (H_2 or CoTAA) supported on carbon blacks or active charcoals. In these experiments high activities were displayed by Co chelates (CoTMPP and CoTAA) (e.g., 0.7 V vs RHE at $100\,mA\,cm^{-2}$ for CoTAA samples) though life test performances were not given. Stability was previously investigated using gas diffusion electrodes with thermally treated CoTAA [5]. Stability was achieved, but under lower current densities (0.7 V vs RHE at $5\,mA\,cm^{-2}$).

It is known that thermal treatment enhances the catalytic properties of both CoTMPP and CoTAA dispersed on carbon support. Optimal temperatures were found to be about 600 °C [4, 6].

In two previous [7, 8] papers we investigated both CoTMPP and CoTAA supported on an active charcoal (Norit SX Ultra selected for its low Fe content). The effects of the heat treatment on the activity and stability were explored using a rotating disc electrode and spectroscopic techniques such as XPS and ToF–SIMS. Bonding between the cobalt chelate and the support through the chelate nitrogens seemed to occur during heat treatment.

From EXAFS investigations several configurations of active site were proposed in which cobalt ions are present in all cases [4]. This process has also been well documented in the literature [4, 9, 10]. The protonation of the nitrogen atoms bound to the surface is a prerequisite for further oxygen reduction [11].

Tests with a duration over 100 h were recently carried out by our group [8] using the rotating disc technique on CoTAA impregnations (13% w/w loadings) on a SX Ultra active charcoal from Norit. After these duration tests the Co content present fell below the XPS detection threshold, though relatively fair activities were still displayed.

The aim of the present paper is, under fuel cell conditions using the Nafion® solid polymer electrolyte, to scrutinize the differences in the behaviour for oxygen reduction of $TpOCH_3PPCo$, $TpCF_3PPCo$ and CoTAA supported on a preselected active charcoal as a function of heat treatment and loading effects. To determine the correlation between structural configurations and the electrochemical behaviour, the Nafion® coated electrodes were analysed by XPS before and after the assays.

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2. Experimental details

2.1. *Catalyst processing*

The synthesis and characterization of $TpOCH_3PPCo$ and $TpCF_3PPCo$ were previously described [7] and for CoTAA the experimental protocol published by Hiller [12] was used. The oxygen electrochemical catalysts were processed by vacuum deposition of $TpOCH_3PPCo$, $TpCF_3PPCo$ and CoTAA on a Printex XE2 carbon black (BET area $1000\,m^2\,g^{-1}$) or on a Norit SX ultra active charcoal (BET area $1200\,m^2\,g^{-1}$) with a low Fe content and a 13% w/w loading unless otherwise specified [13].

Thermal treatments were performed at 500 (HT 500), 600 (HT 600) and 800 °C (HT 800) for 2 h under nitrogen or argon atmosphere. Thermal treatment had previously been found to improve the electrochemical performance using the rotating disc electrode (RDE) techniques [7, 13].

2.2. *Test conditions*

Single cell test fixtures of $5\,cm^2$ were purchased from Globe Tech Inc. (USA). Their main components were two graphite blocks, enclosing the membrane–electrode assembly, with the gas inlet and outlet and ribbed channels for the distribution of reactant gases behind the porous gas diffusion electrodes. This $5\,cm^2$ single cell was equipped with a reference electrode (small piece of fuel cell electrode), embedded in the graphite plate on the anode side. Current collection from the cell and compression of the overall assembly were achieved using two 15 mm thick copper plates. The single cell was incorporated in a test station with temperature controllers, humidification, flow meters and pressure regulator. During the performance evaluation, the fuel cells were connected in series with an electronic load; cell voltages, and half-cell potentials were recorded versus current densities. Measurements were made at 80 °C and under 3 atm H_2 at the anode and 5 atm Air/O_2 at the cathode.

Before these measurements the elemental cell under investigation was prepolarized at 0.55 V vs RHE and the current variation with time was recorded with dry gases and without water evacuation. This procedure allows membrane moistening and therefore minimizes the membrane resistance.

2.2.1. Electrode and M.E.A manufacturing. The double layer electrodes were made of carbon cloth, catalyst dispersed carbon blacks, PTFE as a binder and hydrophobic component and at least one protonic conductor, Nafion®, in order to improve ionic contact with the electrolyte membrane.

2.2.2. Electrode manufacture. The diffusion layer was obtained by filling the carbon cloth with a mixture of carbon powder (Vulcan XC72-Cabot Corporation) and PTFE 30 N (Dupont de Nemours). The C/PTFE proportion was approximately 70/30 at the oxygen liberating electrode. The PTFE was then sintered by heat treatment under a reducing atmosphere. The active layer–catalyst deposited on carbon, a mixture of PTFE 30 N and 5% w/w of Nafion® 1100 solution (Sigma–Aldrich) was then sprayed onto one side of the diffusion layer. The spraying method allowed an easy control of the catalyst loading on the electrodes. In our tests, it corresponded to approximately $0.8\,mg\,cm^{-2}$ of catalyst (chelate and support).

Characterizations were performed previously by STM and mercury porosimetry. These data showed [15] two types of pores in the active layer, macropores and micropores, with 80–200 nm and 10 nm average size, respectively.

The electrochemical reaction takes place in the macropores where there is a simultaneous access of the gases and presence of the polymer film. The respective proportions of Nafion® and PTFE were optimized in the case of Pt [16]. The values determined correspond to an optimization for the catalyst activity and for its rate of utilization. Therefore the defined structure allows an accurate characterization of the catalyst activity.

In the case of platinum [16] it was concluded that the wetting characteristics were independent of the elapsed time. Reacting gases were saturated with water at the cell entrance and the water produced by the reaction was removed by the gas circulation on the oxygen side. The rate of humidity in the electrodes and the membrane was held constant during the test duration.

2.2.3. Electrodes and membrane assembly. For the performance evaluation an anode E-TEK Inc. electrode was used with $0.35\,mg\,cm^{-2}$ platinum loading. The two electrodes were reimpregnated with an electrolyte Nafion® solution in order to obtain loadings of approximately $0.5\,mg\,cm^{-2}$. They were then hot-pressed on each side of the proton exchange membrane (Nafion® 117- Dupont de Nemours).

2.3. *XPS analysis*

X-ray photoelectron spectra were recorded on a Scienta ESCA 300 spectrometer using a high power rotating anode (4000 rpm) and monochromatized $AlK_\alpha(1,2)$ X-ray ($h\nu = 1486.7\,eV$). The samples were analysed at a take off angle of 80° to collect the photoelectrons coming from a depth of 10 nm. The core level spectra were calibrated by setting up the C1s peak due to carbon atoms in a CH_X environment at 284.5 eV.

The catalysts were deposited on a double-sided silver conductive adhesive tape purchased from SPI supplies Division of Structure Probe Inc. (USA). The pressure in the analysis chamber was in the low 10^{-10} torr range.

The samples were investigated both on the active (covered with the Nafion® film) and inactive side of the electrode before and after the electrochemical tests under fuel cell conditions. Before the assays the XPS spectrum was measured on the active side of the electrode in the presence of the Nafion® film before the fuel cell was completed. After the assays the counter electrode was peeled off, leaving the investigated electrode covered with its Nafion® film. After the electrochemical tests the elemental electrode with its Nafion® membrane was thoroughly washed with distilled water. Cobalt ions were found with the IPC (inductive plasma coupling) method. Their amount was equal to 90–95% of the initial value.

3. Discussion and results

Figure 1(a) depicts the effects of the support on TpOCH$_3$PPCo activities at a typical heat treatment temperature (500 °C). Fuel cell electrodes were prepared as previously described. Significant differences are visible under current drain in favour of the Norit SX supported preparations.

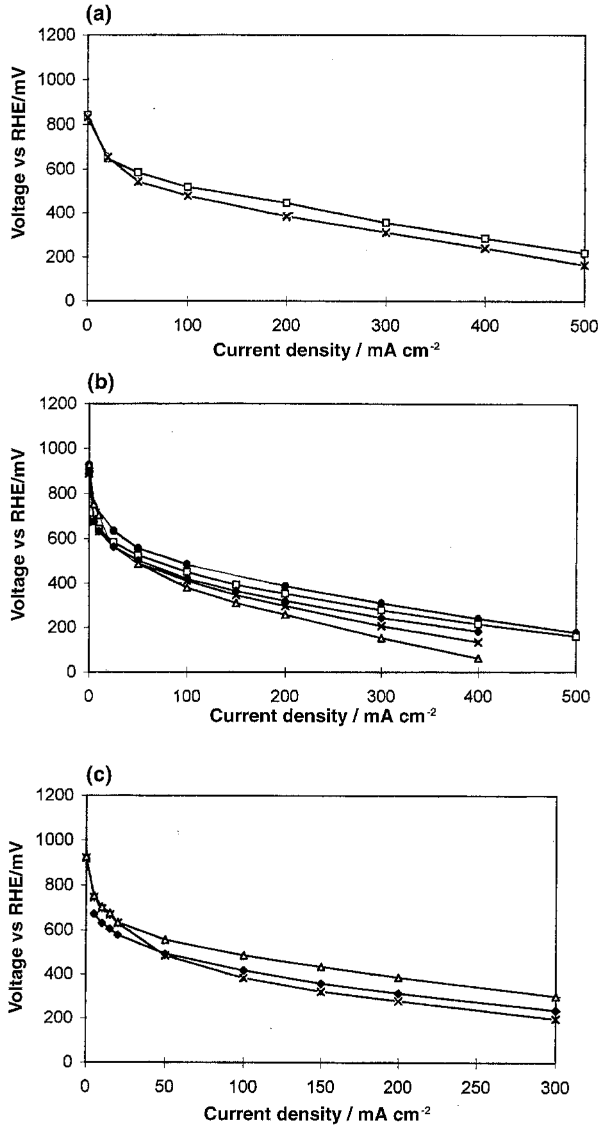

Fig. 1. (a) Effect of the support on the activities of TpOCH$_3$PPCo HT 500 under nitrogen (fuel cell conditions: $p(H_2) = 3$ atm, $p(O_2) = 5$ atm.). Key: (□) : Norit SX Ultra, (×) Printex XE2. (b) Effect of the impregnation loadings on the i/E curves in the case of CoTAA HT 800 preparations. Key: (◆) 5%, (□) 8%, (●) 13%, (Δ) 18%, (×) 23%. (c) Effect of loading on the activities of CoTAA/SX Ultra HT 800. Key: (Δ) 13%, (×) 18.4%, (◆) 23%.

In the following experiments only Norit SX Ultra supported samples were examined. Figure 1(b) shows (i/E) curves for CoTAA/SX Ultra impregnations (HT 800) at different loadings from 5 to 23% w/w. The catalyst charge was varied from 0.5 to 1 mg cm^{-2}.

From these data best performances were found for samples with about 13% w/w loading (0.9 mg cm^{-2} charge). At a constant charge the performance against the loading drop is more pronounced for higher than for lower loadings.

To check the optimal loading effect on the electrochemical performances for CoTAA/SX Ultra at a charge of 0.9–1.0 mg cm^{-2}, three loadings were examined for the HT 800 samples (Fig. 1(c)). Best performances were also found for the 13% w/w loading in agreement with the earlier literature [14]. For the highest loadings the performances were independent of the charge, whereas for the lowest ones reproducibility effects were encountered.

For the same loading (13% w/w and 0.9–1.0 mg cm^{-2} charge) chosen on the basis provided in [17], i/E curves for TpOCH$_3$PPCo samples at different heat treatment temperatures are shown in Fig. 2(a). Best performances are found for the HT 800. Figure 2(b) yields similar effects on TpCF$_3$PPCo within the same conditions.

These data are in contrast with those obtained with RDE techniques [7], where better performances were realized with the 500–600 °C heat treated preparation. In the present experiments the applied current

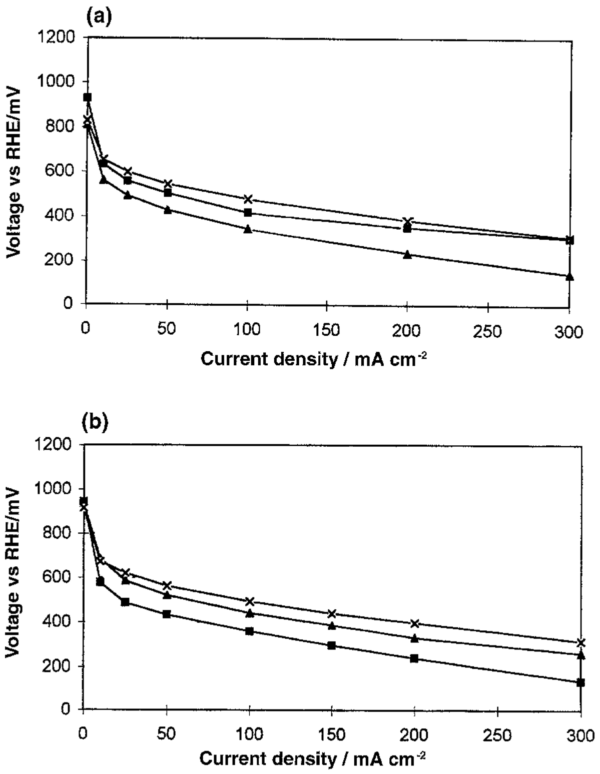

Fig. 2. (a) Influence of the heat treatment temperatures on the activities of TpOCH$_3$PPCo/SX Ultra at 13% w/w loading Key: (▲) HT 500, (■) HT 600, (×) HT 800. (b) As (a) for TpCF$_3$PPCo. Key: (■) HT 500, (▲) HT 600, (×) HT 800.

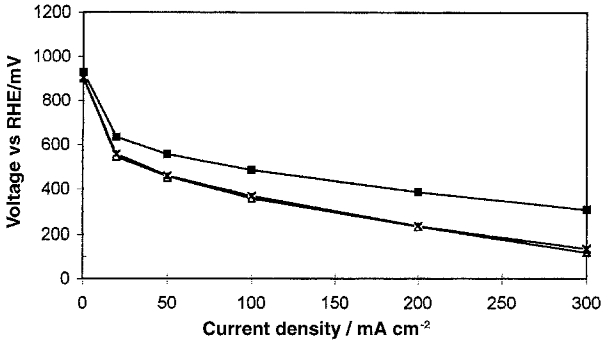

Fig. 3. As for Fig. 2(a) for CoTAA. Key: (Δ) nontreated, (×) HT 600, (■) HT 800.

densities are well above those used in [7]. This result could be explained in terms of reaction cycles involving remaining cobalt ions which would yield fast turn over. Their content must be lower under fuel cell conditions than with RDE techniques for a given time of operation (see below).

The same investigations were carried out in the case of CoTAA with the same loading (0.8–1.0 mg cm^{-2} charge) (Fig. 3). Similar conclusions as in the previous case can be deduced.

To compare CoTAA, TpOCH$_3$PPCo and TpCF$_3$PPCo supported on SX Ultra at 13% w/w and HT 800, *i*/*E* curves are displayed in Fig. 4. They yielded similar activities. Compared to the activities reported in [2] with CoTAA supported on carbon blacks a special attention has to be paid to the charge. In this reference with a catalyst charge of 15 mg cm^{-2} (20% w/w CoTAA loading) for 100 mA cm^{-2} the resulting voltage was about 0.7 V vs RHE. In Fig. 4 at the same potential (0.7 V vs RHE) the current density is about 8 mA cm^{-2} (for 0.8 mg cm^{-2}) yielding a better activity for an equivalent charge.

To discriminate between these samples, longevity tests were undertaken and data recorded for CoTAA, TpOCH$_3$PPCo and TpCF$_3$PPCo supported on SX Ultra HT 800. The same current of 100 mA cm^{-2} was applied and the resulting voltages were recorded versus the elapsed time (Fig. 5).

The relatively low decline in activity with the CoTAA preparations is clear. The worst performances for the porphyrin preparations were found with TpCF$_3$PPCo. This is in agreement with data obtained by the RDE techniques reported in [7].

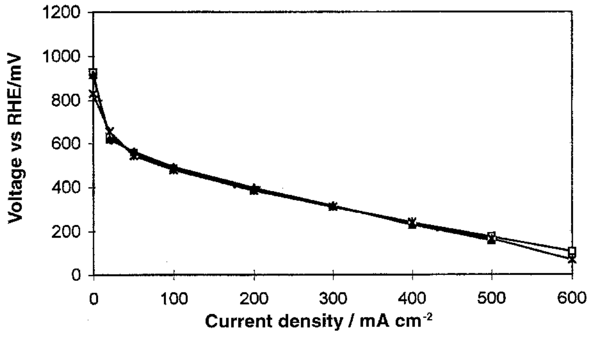

Fig. 4. Comparison between activities of TpOCH$_3$PPCo (×), TpCF$_3$PPCo (▲) and CoTAA (□) supported on SX Ultra at the same loading (13% w/w) and HT 800.

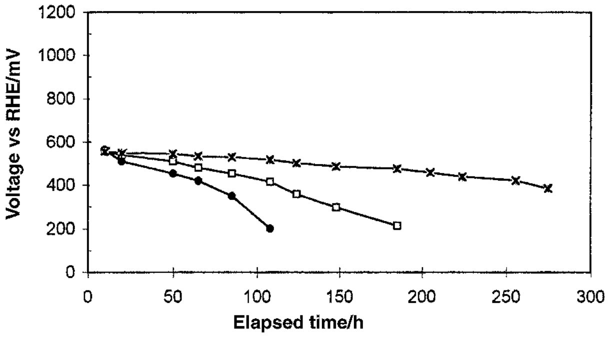

Fig. 5. Electrochemical life test under fuel cell conditions on TpOCH$_3$PPCo (□), TpCF$_3$PPCo (●) and CoTAA (×) supported on SX Ultra at the same loading (13% w/w) and HT 800. (0.8–1.0 mg cm^{-2} charge).

In the case of the CoTAA preparations, after a 280 h current drain application, performances remained better than those presented in Fig. 3 concerning the HT 600 samples. These findings are encouraging compared to literature data [5], which were not performed under fuel cell conditions as done here.

The XPS spectra of TpOCH$_3$PPCo or CoTAA, preparations before current drain application, are exhibited in Fig. 6(a) and 6(b), respectively for the Co2p$_{3/2}$ and N1s spectra. These were realized by examination of the active side covered with the thin Nafion® film. (See electrode preparation above.)

In Fig. 6(a) a mixture of Co(II) and Co(III) valencies is clearly visible with the satellite charateristics of Co(II) which features the existence of CoO [8]. The Co(II)-Co(III) proportion was found to be about 68–32%.

Figure 6(b) displays the N1s spectrum with two components located at 398.1 eV and 401.4 eV in the 61–39% range, respectively. The difference in binding energy can be ascribed to a protonation process [8].

After the electrochemical test the Co2p$_{3/2}$ peak intensity vanished below the detection threshold (on all samples). This phenomenon was also observed in [8] in which the longevity tests (RDE experiments) were performed over 100 h. In the present experiments after 100 h current drain the voltage drop displayed on Fig. 5 is small for the CoTAA HT 800 samples (28.5 mV). As operating conditions with fuel cell are more drastic for the electrode stability than with RDE the cobalt ion disappearance seen by XPS must also be assumed after 100 h operation. Thus the further decay of the performances for the HT 800 samples cannot be correlated to the cobalt ion disappearance from our XPS measurements.

In contrast N1s corresponding spectra after the duration test (HT 800) are displayed in Fig. 7(a). On this figure two nitrogen components are clearly visible at 401.4 and 400.0 eV with a 40–60 intensity ratio. The difference in the peak positions cannot fit a protonation process. The same conclusion can be made for the other HT 800 or no heat treated samples

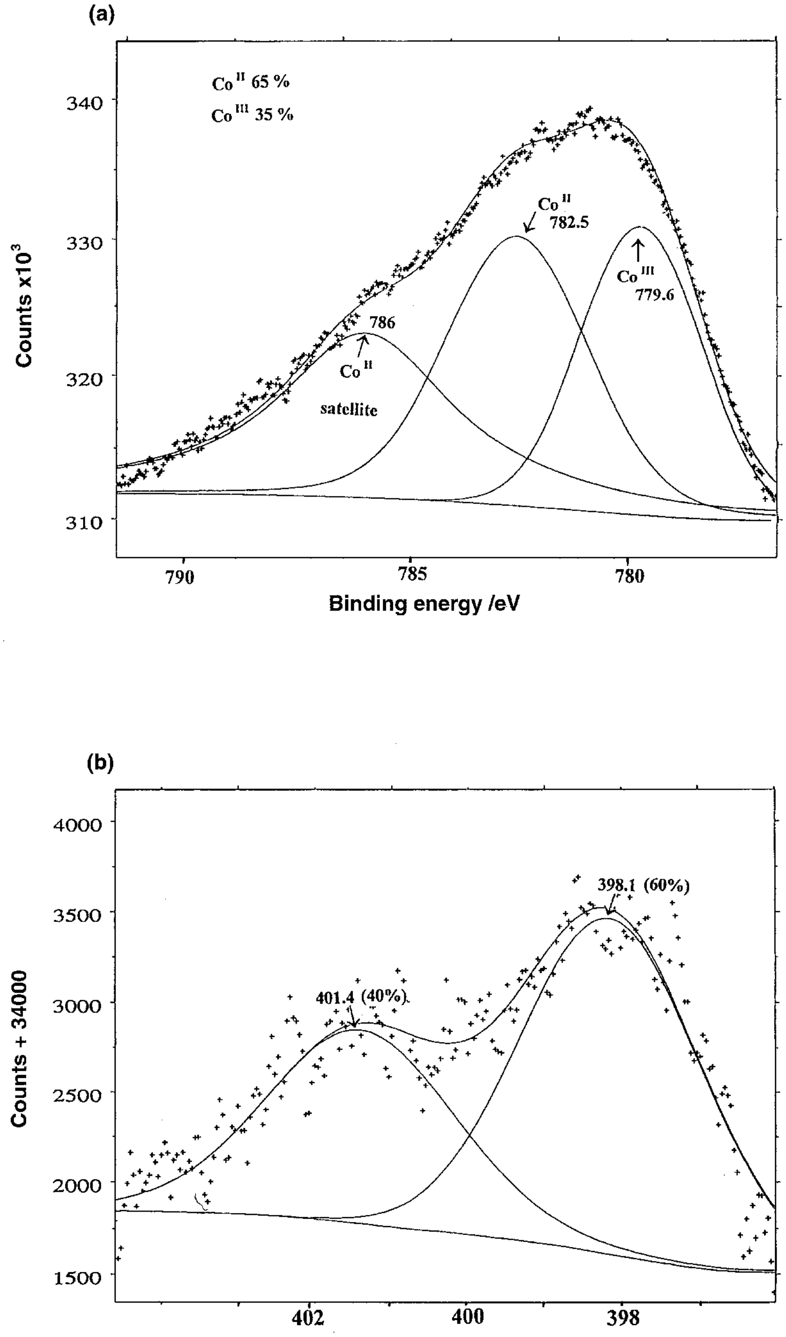

Fig. 6. (a) $Co2p_{3/2}$ spectrum for CoTAA/SX Ultra 13% w/w HT 800 under nitrogen or argon (0.9 mg cm^{-2} charge) before the electrochemical test. (b) As for (a) but for N1s spectrum.

where the binding energy separation between the two remaining N1s peak does not exceed 2.2 eV. (See Fig. 7(b) for nonheat treated CoTAA/SX Ultra samples.)

The observation of these two nitrogen peaks in the 40–60% range focuses on a strong modification of the initial precursor molecule. In all cases the protonation of the nitrogen cannot be detected by XPS techniques after the test duration. In the reduction of dioxygen to water a proton transfer process must be involved [11] and the underlying phenomenon of proton transfer must be understood. In [18] it is suggested that the nitrogen analogue of the chinone couple is involved in the oxygen reduction process on heat treated Co macrocycles. The above data may be interpreted on the same basis. According to this view the most reactive sites after heat treatment for the protonation process correspond with CoTAA preparations to the less oxidized N1s (398.1 eV component) as found by XPS. Therefore the configuration of the nitrogen atoms in the macrocyle play an important role in the oxygen reduction stability under fuel cell conditions.

After the chinone couple (formation of NH groups due to the protonation of the nitrogens linked to the support) oxygen adsorption should be the next step on these sites. It must be followed by nitrogen oxidation because the reduction of oximes is taking place at relatively low potentials compared to those observed in the above described systems. As a matter of fact NO_3^- were detected by ToF-SIMS on similar systems investigated [8].

The free energy oxidation state diagram for the nitrogen oxidation states in acid and basic solutions has been displayed in [19]. Species corresponding to minima are

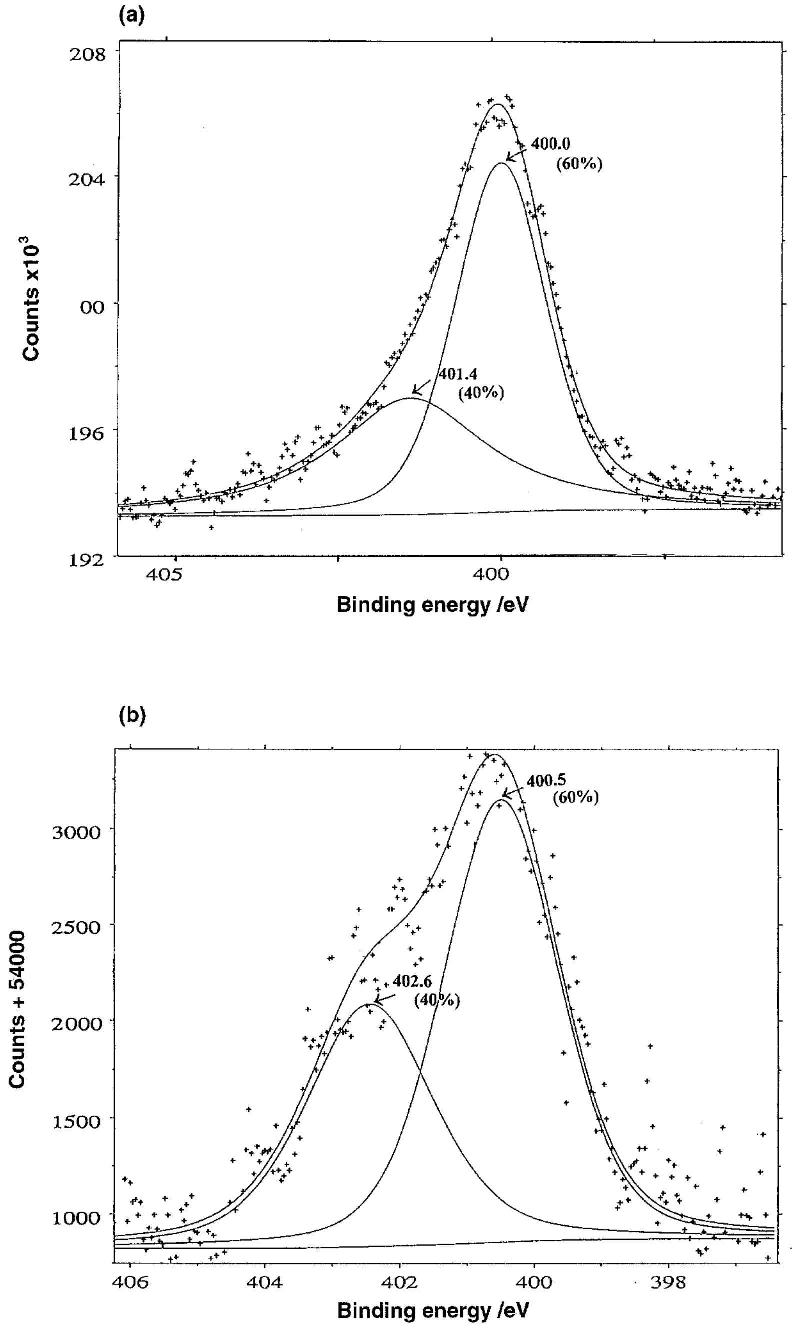

Fig. 7. (a) N1s spectrum as for Fig. 6(b) but after the electrochemical test. (b) N1s spectrum as for (a) but for nonheat treated samples.

expected to be thermodynamically stable. Conversely, points that lie at maxima are expected to be unstable. From this diagram it can be inferred that lower nitrogen oxidation states such as NH_3OH^+ or $N_2H_5^+$ are highly favourable to a protonation reaction such as

$$R\text{-}NH_2OH^+ + H^+ + e^- \longrightarrow RNH_2^+ + H_2O \text{ (fast)}$$

To yield a catalytic cycle this protonation should be followed by the reoxidation of RNH_2^+ by oxygen via a chemical step which should not be rate limiting from the shape of the (i/E) curves:

$$2\,RNH_2^+ + (x+\tfrac{1}{2})O_2 \longrightarrow 2\,RNO_x + 2H^+ + H_2O$$

The rate determining step would consist in an electrochemical reduction of $R\text{–}NO_x$ stable into $R\text{–}NH_2OH^+$ unstable according to

$$R\text{–}NO_x + (2x+1)H^+ + 2xe^- \longrightarrow RNH_2OH^+ + (x-1)\,H_2O$$

An alternative explanation could be the role of the remaining cobalt ions. Their content is at least 30 fold lower after operation than the initial values according to the XPS detection threshold. They could act in very tiny amounts. In this respect the bonding of these cobalt ions must be different after the 800 °C heat treatment from the 600 °C ones as already shown by the N1s spectra.

As a function of the heat treatment temperatures, the O1 s spectra remained unaffected and a typical curve is shown in Fig. 8. The peak maximum occurs at 532.6 eV and is charateristic of weakly bonded

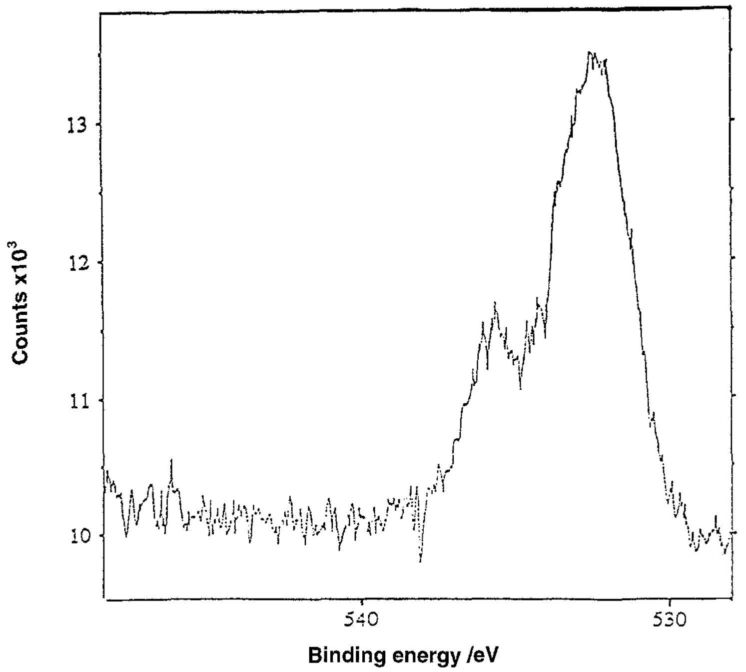

Fig. 8. Typical O1s spectra obtained on CoTAA/SX Ultra (13% w/w) HT 600 under nitrogen.

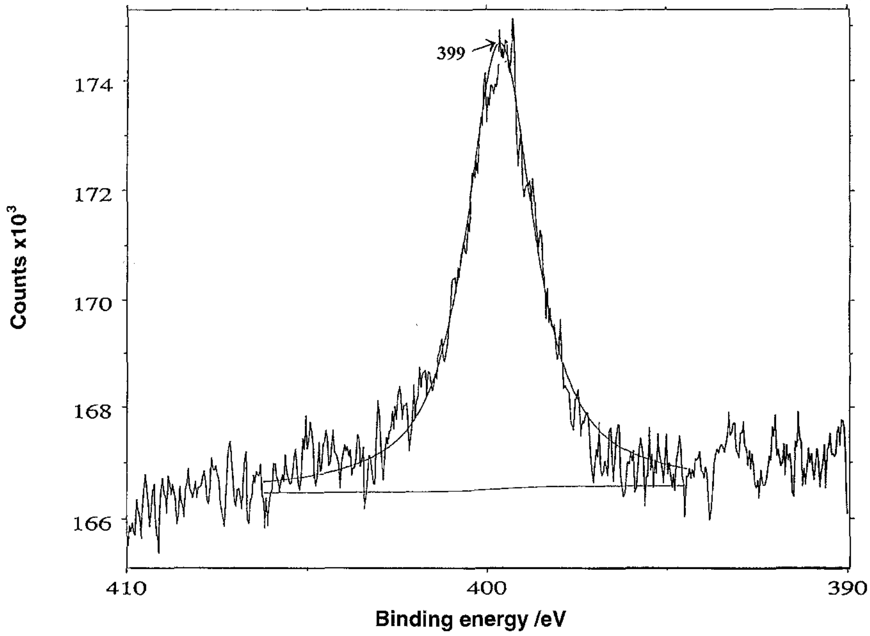

Fig. 9. N1s spectra after electrochemical life test for TpOCH$_3$PPCo/SX Ultra (13% w/w) HT 800 under nitrogen or argon.

oxygen. The presence of attached water is displayed by the shoulder. The width of the O1 s spectra suggests the existence of various bonded oxygen species.

N1s spectra for TpOCH$_3$PPCo/SX Ultra HT 800 are shown in Fig. 9 after the duration test. No major differences are displayed with the CoTAA samples. The above differences in the electrochemical performances between the investigated porphyrins and the most stable and active CoTAA samples cannot be explained on the basis of XPS data alone. In a previous paper using EPR techniques [7], the differences between the stabilities of these porphyrins were related to the cobalt superoxo oxygen bond formation. As the central cobalt ion vanishes the decline in the performances can be easily understood.

4. Conclusions

Using a solid polymer acid electrolyte as protonic conductor, TpOCH$_3$PPCo, some of its derivatives and cobalt tetraazaannulene catalysts supported on a carbon blacks and an active charcoal were assayed for oxygen reduction versus duration time under fuel cell conditions. At a constant current density of 100 mA cm^{-2} over a 200 h period, an almost constant voltage was realized with CoTAA impregnations after the 800 °C heat treatment though the TpO CH$_3$PPCo and TpCF$_3$PPCo analogues yielded poor performances. XPS analyses were carried out on both the active covered with the Nafion® film and inactive sides of the working electrodes before and after the duration tests. They displayed a complete loss of cobalt even for the most active and stable samples (CoTAA/Norit SX Ultra HT 800).

As a function of the heat treatment temperatures on CoTAA samples, the oxidation of nitrogen ions decreases as seen by the position of the N1s spectra. This feature suggests an interpretation of heat treatment effects in terms of the kinetics of protonation of the nitrogen sites followed by their chemical oxidation. Therefore the above data suggest, for active electrodes, a reaction mechanism taking place on nitrogen atoms containing fragments, the precursor molecule being completely overturned. However taking into account the accuracy of the measurements the activity of small amounts of remaining cobalt ions cannot be ruled out. In this case their bonding with the support must be different after the 800 °C heat treatment from that existing after lower temperature applications.

Acknowlegements

The authors are grateful to Prof. R. Guilard and his group for the TpOCH$_3$PPCo and TpCF$_3$PPCo syntheses and characterizations. Ecotech, Gie Psa Renault and Ademe are gratefully acknowledged for their financial support.

References

[1] G. Tamizhmami and GA. Capuano, *J. Eletrochem. Soc.* **141** (1994) 132

[2] G. Tamizhmani, G. A. Capuano, J. P. Dodelet, D. Guay, G. Lalande, *ibid.* **141** (1994) 41.

[3] L. Dignard-Bailey, M. L. Trudeau, A. Joly, R. Schullz, G. Lalande, D. Guay and J. P. Dodelet, *J. Mat. Res.* **9** (1994) 3203.

[4] E. Yeager, *Final report, Lawrence Berkeley Laboratory, LBL.*, 26054 (Sept. 1988).

[5] K. Wiesener, *Electrochim. Acta* **31** (1986) 1073.

[6] J. C. Huang, *Proc. Electrochem. Soc.* **89** (1989) 268.

[7] P. Gouérec, A. Biloul, O. Contamin, G. Scarbeck, M. Savy, J. M. Barbe and R. Guilard, *J. Electroanal. Chem.* **398** (1995) 67.

[8] P. Gouérec, A. Biloul, O. Contamin, G. Scarbeck M. Savy, J. Riga, L. T. Weng and P. Bertrand, *J. Electroanal. Chem.* submitted.

[9] A. Biloul, O. Contamin, M. Savy, G. Scarbeck, J. Riga and J. Verbist, *J. Electroanal. Chem.* **365** (1994) 239.

[10] B. van Wingerden, J. A. R. van Veen and C. T. J. Mensch, *J. Chem. Soc. Faraday Trans. I* **84** (1988) 65.

[11] A. J Appleby, *J. Electroanal. Chem.* **357** (1993) 117.

[12] H. Hiller, P. Dimroth and H. Pfitzner, *Justus Liebigs Ann. Chem.* **717** (1968) 137.

[13] M. Savy, A. Biloul, O. Contamin, P. Gouérec and G. Scarbeck, *Proceedings of the 'First International Symposium on New Materials for Fuel Cells Systems'*, (edited by O. Savadogo, PR. Roberge and N. Veziroglu) 9–13 July Montreal, Canada. (1995) p. 665.

[14] A. Biloul, F. Coowar, O. Contamin, G. Scarbeck and M. Savy, *J. Electroanal. Chem.* **350** (1993) 89.

[15] A. Tounsi, PhD thesis, Université de Paris VI (1994).

[16] S. Besse, G. Bronoel, N. Tassin, Y. Naimi and A. Tounsi, *Proceedings op. cit.* [13] (1995) 144.

[17] A. Biloul, F. Coowar, O. Contamin, G. Scarbeck and M. Savy, *J. Electroanal. Chem.* **350** (1993) 89.

[18] A. L. Wijnoltz, PhD thesis, University of Eindhoven (1995).

[19] P. H. Rieger, 'Electrochemistry', 2nd ed, Chapman & Hall, (1994) p. 20.