

# A new method for electrochemical screening based on the rotating ring disc electrode and its application to oxygen reduction catalysts

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A new method for electrochemical characterization of composite electrode materials is reported. A paste of the catalytic material in Nafion<sup>®</sup> is coated on a rotating ring disc electrode (RRDE) to partially simulate the working environment of a proton exchange membrane (PEM)/electrode composite as used in, for example, water electrolysis or PEM fuel cell operation. This allows direct comparison of a wide range of candidate electrocatalysts in a reproducible manner. Problems specific to these volumic electrodes are accommodated satisfactorily by rational modification of the standard expressions used in RRDE analysis. The value of the method is illustrated in studies of various cobalt complexes which show promise in dioxygen reduction; namely, cobalt tetramethoxyphenylporphyrin (CoTMPP), cobalt phthalocyanine (CoPC), and cobalt cyclam (CoCy), supported on a range of particulate carbons BP2000, Printex XE 2 and Vulcan XC-72. Typical electrochemical parameters have been measured or estimated, including half-wave potentials ( $E_{1/2}$ ), Tafel slopes ( $b$ ), 'activation currents' ( $I_a$ ) and the average number of electrons transferred ( $n$ ). The nature of the complex itself and the carbon support have a strong influence on electrode behaviour. Ligands with more aromatic character give better performance. Dramatic improvements in performance result from heat pre-treatment, which is tentatively attributed to the formation of dimeric cobalt species via thermally-induced aggregation. In terms of the four electron reduction (to water), the best result was obtained for CoTMPP on Printex XE2 and rationalized on the basis of popular current views on the mechanism and catalyst functionality. CoPC on BP2000 is unusual in showing a strong change in  $n$  with reduction potential. Product selectivity ranges between mainly hydrogen peroxide ( $n = 2$ ) and water ( $n = 4$ ) with increasing overpotential.

Keywords: *composite electrodes, electrochemical screening, oxygen reduction catalysts*

## 1. Introduction

The main impetus to industrial development of polymer electrolyte membrane fuel cells (PEMFC) as the technological basis of future energy systems is the prospect of compact power sources utilizing renewable hydrogen, operating at high efficiency and with negligible environmental pollution. A primary application would be as propulsion units in the next generation of electric vehicles, in which the driving range offered by high energy density chemical fuel(s) stored on-board would be superior to conventional battery power [1]. Other advantages of the H<sub>2</sub>/O<sub>2</sub> PEMFC are its low temperature operating conditions and its high power density [2]. However, the electrochemical processes of hydrogen oxidation and oxygen reduction traditionally require a precious metal catalyst. Platinum is ideal in the former reaction but is only of modest performance in oxygen reduction in acid

medium [3–6]. When coupled with its high cost and rarity, these detrimental factors seriously hamper the development of the Pt-based PEMFC for commercial purposes.

Serious attention is presently being given to the possibility of replacing platinum by cheaper alternatives with better oxygen reduction properties, while not sacrificing long-term stability. It can be argued that this constitutes one of the greatest challenges of modern catalysis, i.e., the activation of small molecules like O<sub>2</sub> for simultaneous multielectron transfer.

To be a viable candidate as cathode electrocatalyst in PEMFCs, the material must fulfill the following criteria. It must reduce oxygen with high activity at high current densities and at low overpotential. It must also reduce oxygen directly to water, which involves a complex four-electron transfer. The 2e<sup>-</sup> reduction to hydrogen peroxide is unsatisfactory in this context. Finally, it must have good electrocatalytic stability. Most success to date has been achieved with transition metal complexes, particularly those

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based on cobalt [7–14]. Many methods of catalyst preparation and incorporation into the fuel cell cathode have been tried and no standard electrochemical testing method has yet been established for catalyst screening purposes [15–28]. As a consequence, the reported literature data have been obtained over such a wide range of conditions that they cannot be usefully compared.

In this paper, a method is described which allows valid comparison of many types of catalytic materials by testing under closely similar conditions pertinent to operation in a PEMFC. In essence, the catalyst complex is adsorbed up to fixed loading on a particulate carbon support. A paste of this material is then made in fixed proportions with Nafion® and carefully applied to the surface of a rotating ring disc electrode (RRDE). Thus, although the catalyst is *ex-situ* tested, it exists as a volumic electrode which resembles closely the active layer of the cathode in PEMFC. By coupling this condition with the known value of the RRDE in allowing *in situ* detection of intermediates (hydrogen peroxide in this case), a powerful method of electrochemical analysis is created. Experiments were conducted in an oxygen-saturated aqueous acid medium and electrochemical parameters were determined, including half-wave reduction potential ( $E_{1/2}$ ), ‘activation current’ ( $I_a$ , as defined below), Tafel slope ( $b$ ), and the number ( $n$ ) of electrons transferred as a function of applied potential. Since it was difficult to simulate conditions of gas pressure and temperature in a working PEMFC in conjunction with the RRDE setup, no realistic assessment of catalyst stability can be made with this method. Stability testing is best done at a later stage of development in a real fuel cell device.

Preparative details of the catalytic material and its coating on the electrode surface are given. The examination of nonplanar and volumic electrodes in RRDE experiments requires a nonclassical data treatment. As such, method development represents a substantial part of this work and its inherent assumptions are described and justified. To illustrate the power of the method, three different cobalt complexes supported on various commercial particulate carbons (BP 2000, Printex XE 2 and Vulcan XC-72) have been examined, along with the effect on these of heat pretreatment at temperatures ranging between 200 and 1100 °C. The complexes were chosen for their well-documented activity in oxygen reduction, but differ in the extent of conjugation of the organic ligands. In cobalt tetramethoxyphenylporphyrin (CoTMPP) and cobalt phthalocyanine

(CoPC), it is suggested that the ligands present a fully delocalized system which may assist electron transfer by the cobalt ion. This is not possible in the cyclam complex Co(Cy).

## 2. Experimental details

### 2.1. Materials

The complexes cobalt tetramethoxyphenylporphyrin (CoTMPP) and cobalt phthalocyanine (CoPc) were obtained from Aldrich. Cobalt cyclam (CoCy) was kindly supplied by Professor Guilard (University of Dijon, France) for which the last step of the preparation was realized following the method of Bosnish [29, 30]. The carbon supports were obtained commercially, and their physico-chemical properties are summarized in Table 1.

### 2.2. Complex adsorption on carbon

For the TMPP and PC complexes, the carbon support (typically 1 g of Vulcan XC-72, Black Pearl 2000 or Printex XE 2) was dispersed into 200 ml dimethylformamide (DMF). The complex was then added in an amount corresponding to roughly 1 wt % as cobalt assuming total adsorption, that is, ~125 mg CoTMPP, ~100 mg CoPC.

The suspension was sonicated under stirring for 30 min and left under magnetic stirring at 70 °C overnight. The complex was then precipitated by adding 500 ml of cold distilled water, filtered and washed successively with cold and hot distilled water. The resulting filtrate was colourless, indicating that the complex was entirely adsorbed on the carbon. The solid was dried under vacuum at 70 °C overnight. This black powder is termed the ‘untreated’ catalytic material.

For cobalt cyclam, the adsorption was possible directly in distilled water (~250 mg CoCy and 4 g carbon BP 2000 suspended in 60 ml H<sub>2</sub>O). The suspension was sonicated for 30 min and then magnetically stirred. After four hours, the liquid was no longer green, indicating that the complex was fully adsorbed on the carbon. The suspension was then filtered and the solid dried under vacuum at 70 °C overnight. The nominal Co loading was about 1.4 wt %.

### 2.3. Heat treatment of the catalytic materials

The catalytic material was placed in a quartz tube and oxygen was purged with argon for 30 min. The

Table 1. Physicochemical properties of carbon supports

Carbon	Specific surface area /m <sup>2</sup> g <sup>-1</sup>	Particles diameter /nm	pH	Ashes /wt %	Volatiles materials /wt %
Printex XE 2	950	30	8.0	< 1	–
Black Pearl 2000	1475	15	8.6	2	2.0
Vulcan XC 72	254	30	8.5	2	1.5

furnace was first preheated to the desired temperature (i.e., between 200 and 1100 °C), the tube and contents were then inserted into the furnace and left for 2 h under argon. This flow was maintained while the tube was allowed to cool and the sample was finally discharged at room temperature. To obtain a perfectly homogenous powder suitable for incorporation into the polymer electrolyte, the catalytic material was ground under liquid nitrogen.

#### 2.4. Catalytic paste electrode

10 mg of Nafion® (H<sup>+</sup> form) was dissolved in 1 ml of acetonitrile. 50 μl of 11 wt % PTFE in water (obtained by dilution of the commercial suspension GP2 from ICI) was added to the Nafion® solution, followed by 20 mg of the cryoground catalytic material. The mixture was stirred for 15 min in an ultrasonic bath for homogenization. 14 μl of this suspension was carefully deposited to cover the whole disc surface of the RRDE. The solvent evaporated within a few minutes and the electrode bearing the catalytic paste was then ready for electrochemical studies.

#### 2.5. Electrochemical measurements

The measurements were performed with a RRDE (mod. AFDT 21, Pine Instruments). This comprised a vitreous carbon disc (2.5 mm diam.) separated from a platinum ring (0.82 mm wide) by an insulating Teflon ring (0.26 mm wide). The theoretical collection efficiency ( $N_0$ ) is 0.3940. The RRDE was driven by a rotator system (model AFASR, Pine Instruments), and the electrode was regularly polished between experiments. The disc electrode was connected to an EG&G PAR 362 potentiostat and the ring electrode to the disc channel of a Tacussel bipotentiostat. The utilization of two different potentiostats necessitated the use of two counter electrodes (platinum grids) and two reference electrodes (Tacussel saturated calomel TR100). Test measurements with the RRDE were made in aqueous 0.3 M HClO<sub>4</sub> at room temperature after oxygen sparging of the solution and with oxygen flow maintained over the solution during the experiment. Blank measurements were made under nitrogen for correction (subtraction) purposes. During the measurement the ring potential was fixed at +1.1 V vs SCE which is sufficient to oxidize to O<sub>2</sub> any hydrogen peroxide diffusing from the disc. The ring current ( $I_r$ ) was recorded simultaneously with the disc current ( $I_d$ ).

### 3. Results

#### 3.1. Method development and blank tests

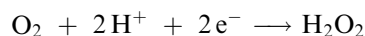
Because of the irregular and volumic nature of these electrocatalysts as mounted specimens, the collection efficiency of the RRDE must be established at any

particular rotation speed  $\omega$ . The latter was found to be optimum at 100 rpm, giving both well-defined diffusion plateaux and acceptable currents. At higher values of  $\omega$ , convective effects result in an increased oxygen flow into the electrode such that significant contributions to the measured current result from the internal part of the electrode, that is, volumic effects are more serious. Such phenomena were seen to cause serious distortion of the diffusion plateaux at the disc and loss of collection efficiency at the ring. The optimum scan rate of the potential was found to be 5 mV s<sup>-1</sup>, that is, the highest possible rate still representative of quasi steady state conditions, as confirmed by reproducing identical curves at lower scan rates.

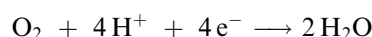
Before the electrochemical studies proper, the integrity of the RRDE setup was checked against various blank conditions. Voltamperograms of the uncoated glassy carbon disc produced curves exhibiting a small reversible wave at the disc but nothing at the ring. The behaviour of the Nafion®/PTFE coated disc was almost identical. When a carbon support (Vulcan XC 72) was included in the paste, either untreated or pre-treated at 600 °C, a similar (small) reversible wave but now with a significant capacitive current were observed, while no current was detected at the ring. As expected, the commercial platinum on carbon sample (E-tek) gave a strong oxygen reduction wave and capacitive current on the disc, but nothing at the ring.

#### 3.2. Fundamental considerations: a working scale for $n$

In addition to standard electrochemical parameters determined in this work (e.g., Tafel slope, half-wave potential, etc.) relating only to catalyst *activity*, a vital additional marker of the overall performance of the electrocatalyst in this work (and by implication in a real fuel cell application) is the *selectivity*, as expressed by the value of  $n$ , the average number of electrons transferred. Intermediate peroxide formation,  $n = 2$ , according to



is a highly-undesirable situation in an operating fuel cell, carrying the risks of corrosion and loss in energy efficiency. The optimum value for  $n$  is 4, that is, full reduction to water:



Under ideal circumstances (i.e., on a smooth RD electrode) the value of  $n$  is readily obtained from the slope of the Levich expression (1), which relates the diffusion plateau current to rotation speed:

$$I_1 = 0.2 n F A D^{2/3} \nu^{-1/6} C_\infty \omega^{1/2} \quad (1)$$

where  $I_1$  is the diffusion plateau current (A),  $A$  is the electrode surface area (cm<sup>2</sup>),  $D$  is the diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $\nu$  is the solvent viscosity (cm<sup>2</sup> s<sup>-1</sup>),  $C_\infty$  is concentration (mol cm<sup>-3</sup>), and  $\omega$  is the electrode rotation speed (rpm).

Unfortunately, for the volumic electrodes under study here, the assumptions underlying its derivation are almost certainly not valid. The flow pattern near the real electrode surface will likely be turbulent. Furthermore, the effective surface area of the electrode,  $A$ , is unknown and variable such that the RDE can yield at best only the product  $nA$ . This problem has been observed in related studies in the laboratory of Prof. M. Savy at the University of Versailles, France. Plateau current values are strongly dependent on the mass or thickness of the catalytic deposit and its presumed effect on  $A$ . In addition, plots of  $I_1$  against  $\omega^{1/2}$  at different loadings, albeit quite linear, show different slopes.

To obtain at least some working estimate of  $n$  the well-known advantage of the rotating ring disc electrode (RRDE) is exploited here [31]. Using an appropriately selective oxidizing potential at the ring, any intermediate peroxide species escaping from the disc yields a reoxidation current,  $I_r$ , specific for this two-electron reduction product. If the collection efficiency,  $N$ , is known, the contribution to the total reduction current,  $I_d$ , at the disc from peroxide formation alone,  $I_d(\text{H}_2\text{O}_2)$ , is simply  $N \times I_r$ . Thus, the contributions from the two mechanistic pathways for oxygen reduction can be distinguished and evaluated.

It can be shown by simple algebra that  $n$  is readily expressible as a function of  $I_d$ ,  $I_r$  and  $N$  as follows:

$$n = 4I_d / (I_d + I_r/N) \quad (2)$$

where  $I_d = I_d(\text{H}_2\text{O}) + I_d(\text{H}_2\text{O}_2)$  and  $I_r = I_r(\text{H}_2\text{O}_2) = NI_d(\text{H}_2\text{O}_2)$ . Inspection shows that it immediately satisfies the extreme cases. For 100% selectivity to water,  $I_r = I_d(\text{H}_2\text{O}_2) = 0$ , so that  $n = 4 I_d(\text{H}_2\text{O})/I_d(\text{H}_2\text{O}) = 4$ . For 100% selectivity to peroxide,  $I_d = I_d(\text{H}_2\text{O}_2) = I_r/N$ , so that  $n = 4 I_d(\text{H}_2\text{O}_2)/2I_d(\text{H}_2\text{O}_2) = 2$ .

Attempts were made to determine  $N$  using various quinones as catalysts known to be selective for hydrogen peroxide generation from oxygen. Unfortunately, these samples were all found to be inactive or unstable as mounted in the standard way, that is, supported on carbon and applied as a paste in Nafion<sup>®</sup>. The next best approach was to identify which of the Co complexes under study gave the highest  $I_r/I_d$  ratio and to assume 100% selectivity to peroxide, thus equating  $I_r/I_d$  with  $N$  for all practical purposes. Unfortunately, the amounts of peroxide produced in this case were too small for independent verification for example, by wet chemical methods. In preliminary work, the highest  $I_r/I_d$  measured was a value of 0.22 for a sample of CoTMPP on Vulcan XC-72, heat treated at 1093 °C. By setting  $N = 0.22$ , a relative scale is established in which  $n$  is always underestimated. However, inspection of Equation 2 reveals that the relative error in  $n$  ( $\Delta n/\Delta N \propto I_r$ ) rapidly decreases at higher  $n$  (lower  $I_r$ ), ultimately becoming negligible when  $I_r/N \ll I_d$ . Thus, the method is 'fail safe' in the sense that it is impossible to identify falsely a mediocre catalyst as a good catalyst, that is, one for which  $n > 3.5$ . In fact, as the true  $N$  must

lie somewhere between 0.22 and 0.39 (the nominal collection efficiency for smooth electrodes: see Section 2.5), a provisional estimate of the error introduced can be made for any apparent value of  $n$  ( $n_{\text{app}}$ ). For example, on the reasonable supposition that  $N_{\text{true}}$  is around 0.3, then  $n_{\text{app}}$  will be underestimated by  $\sim 20\%$ ,  $10\%$  and  $5\%$ , at  $n_{\text{true}} = 2, 3$  and  $3.5$ , respectively. Thus, a workable scale for  $n$  is established for screening purposes.

### 3.3. Electrochemical studies of Co complexes supported on carbons

3.3.1. Activity. Representative voltammograms at both the disc (overall reduction current) and the ring (intermediate  $\text{H}_2\text{O}_2$  reoxidation), along with the effect of heat pretreatment, are shown in Figs 1 and 2 for CoTMPP adsorbed on particulate carbons BP 2000 and Printex XE 2, respectively. Table 2 summarizes the major trends in activity of all the Co complexes on various supports. The listed parameters are the half-wave potential of oxygen reduction ( $E_{1/2}/\text{mV}$  vs SCE), the Tafel slope ( $b/\text{mV dec}^{-1}$ ), and the 'activation current' at 500 mV vs SCE ( $i_A$ ; both in apparent surface-specific units/ $\mu\text{A cm}^{-2}$ , and complex-specific/ $\text{A mol}^{-1} \text{Co}$ ). The effects of carbon support (Vulcan XC-72, Black Pearls 2000 and Printex XE 2) on the most active complex (CoTMPP), all complexes compared on the same carbon (Black Pearls 2000), and the effects of heat pretreatment (from 300 to 1093 °C) in most cases is included.

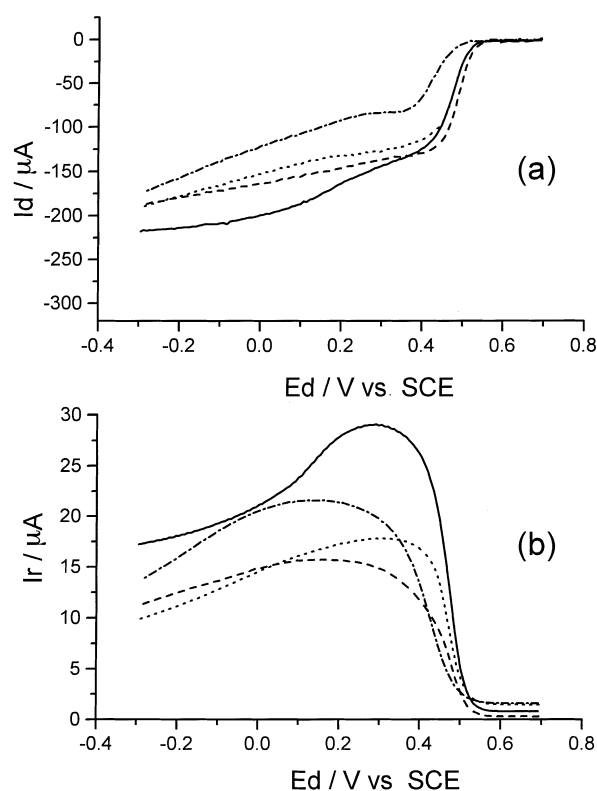


Fig. 1. Voltammograms obtained at (a) the disc, (b) the ring with CoTMPP adsorbed on BP 2000; treated at: (—) 300 °C; (---) 600 °C; (· · · ·) 800 °C; (- · - · -) 1093 °C.

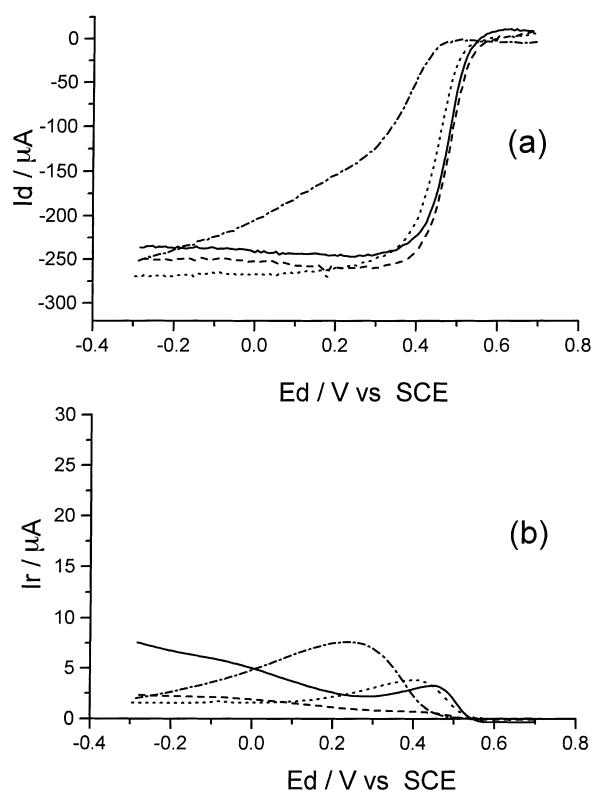


Fig. 2. Voltammograms obtained at (a) the disc (b) the ring with CoTMPP adsorbed on Printex XE2; treated at: (—) 300 °C; (---) 600 °C; (· · · ·) 800 °C; (- · - · -) 1093 °C.

CoTMPP gave the best results of all the complexes, with the activities dropping in the order: CoTMPP > CoPC > CoCyclam. The effect of the carbon support was also significant, as illustrated for CoTMPP, giving an order: Printex XE 2 > Black Pearls 2000 > Vulcan XC-72. The trend in activity with heat pretreatment is arguably the most universal feature of the data. Virtually without exception, samples gave their best performance, (i.e., the highest  $E_{1/2}$ )  $i_A$ , and lowest  $b$  values, when previously heated at around 600 °C.

3.3.2. *Selectivity.* In terms of selectivity to water or peroxide, CoTMPP on Printex XE 2 gave the best result, that is, the lowest ring current (see Fig. 2). Hence, this combination of complex and support is clearly superior in terms of both activity and selectivity ( $4e^-$  reduction to water). Reflecting activity trends, a beneficial effect of heat treatment on selectivity (increasing  $n_{app}$ ) is also evident regardless of the complex and support material. The most impressive result,  $n_{app} \geq 3.8$ , was obtained for CoTMPP on Printex XE 2 pretreated at 800 °C. However, good selectivity was not observed for the same complex on other carbons. The wide range of performance for CoTMPP is well illustrated in the plots of  $n_{app}$  against overpotential as shown in Fig. 3, where the data for Printex XE 2 and BP 2000 appear as two distinct sets

Table 2. Comparison of the electrocatalytic activities of the catalytic materials: half wave potential ( $E_{1/2}$ ), Tafel slope ( $b$ ) and current of charge transfer ( $i_A$ ) at +500 mV vs SCE obtained with CoTMPP (on Vulcan XC72, BP 2000 and Printex XE2), CoPc (on BP 2000) and CoCyclam (on BP 2000) heat treated at various temperatures

Compounds and parameters	Temperature of heat treatment				
	Untreated	300 °C	600 °C	800 °C	1093 °C
<i>CoTMPP on Vulcan XC72</i>					
$E_{1/2}/\text{mV vs SCE}$	+370	+410	+460	+440	+370
$b/\text{mV dec}^{-1}$	96	—	59	—	77
$i_A/\mu\text{A cm}^{-2}$	693	—	305	—	20
$i_A/\text{A mol}^{-1}$	3050	—	1345	—	90
<i>CoTMPP on BP 2000</i>					
$E_{1/2}/\text{mV vs SCE}$	+400	+440	+470	+450	+420
$b/\text{mV dec}^{-1}$	53	56	57	—	131
$i_A/\mu\text{A cm}^{-2}$	66	122	198	—	46
$i_A/\text{A mol}^{-1}$	335	619	1005	—	232
<i>CoTMPP on Printex XE2</i>					
$E_{1/2}/\text{mV vs SCE}$	+260	+480	+480	+450	+320
$b/\text{mV dec}^{-1}$	162	52	61	—	85
$i_A(\mu\text{A cm}^{-2})$	107	336	331	—	25
$i_A/\text{A mol}^{-1}$	471	1479	1457	—	112
<i>CoCyclam on BP 2000</i>					
$E_{1/2}/\text{mV vs SCE}$	—	+330	+380	+270	+210
$b/\text{mV dec}^{-1}$	—	110	141	—	217
$i_A/\mu\text{A cm}^{-2}$	—	10	36	—	15
$i_A(\text{A mol}^{-1})$	—	45	157	—	67
<i>CoPc on BP 2000</i>					
$E_{1/2}/\text{mV vs SCE}$	+150	+170	+420	+400	+420
$b/\text{mV dec}^{-1}$	190	149	70	—	103
$i_A/\mu\text{A cm}^{-2}$	4.6	2.0	117	—	76
$i_A/\text{A mol}^{-1}$	20	9.0	516	—	336

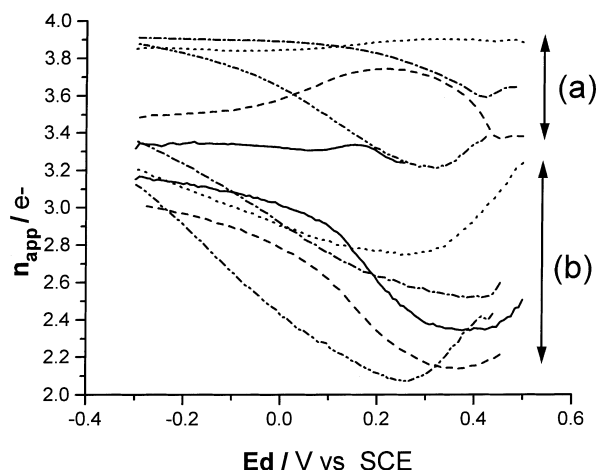


Fig. 3. Plots of  $n_{app}$  against potential with CoTMPP adsorbed on (a) Printex XE2 and (b) BP 2000; (—) untreated and treated at: (---) 300 °C; (····) 600 °C; (-·-·-) 800 °C; (-·-·-·-) 1093 °C.

of curves with  $n_{app}$  averaging  $\sim 3.7$  and  $\sim 2.5$ , respectively. The trend of  $n_{app}$  slowly increasing with overpotential is representative of virtually all samples tested but its significance is not yet clear. The dominant role of the carbon support can be seen more clearly in Fig. 4, a graphical plot of  $n_{app}$  at high (fixed) overpotential against heat treatment temperature for CoTMPP on all three carbons. CoCy gave the worst performance with  $n_{app}$  values less than 3 regardless of support and heat treatment. On supports other than Printex XE 2, CoPC was generally superior to CoTMPP, as illustrated in Fig. 5. CoPC on BP 2000 was also unique in showing a very strong dependence of selectivity on overpotential. As shown in Fig. 6, instead of the relatively stable plateau response for currents at the disc and ring typically observed, there are distinct steps in  $i_d$  and a maximum in  $i_r$  which are maintained even after heat treatment.

#### 4. Discussion

The principal objective of this work is to demonstrate a new electrochemical method for rapid and conve-

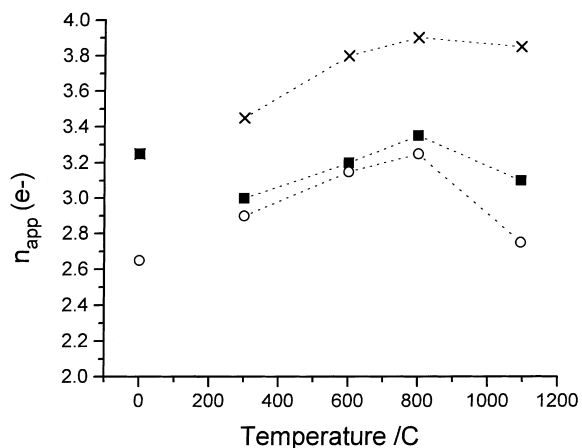


Fig. 4. Comparison of  $n_{app}$  at  $-300$  mV vs SCE against heat treatment temperature obtained with CoTMPP adsorbed on (■) BP 2000; (○) Vulcan XC72; (×) Printex XE2.

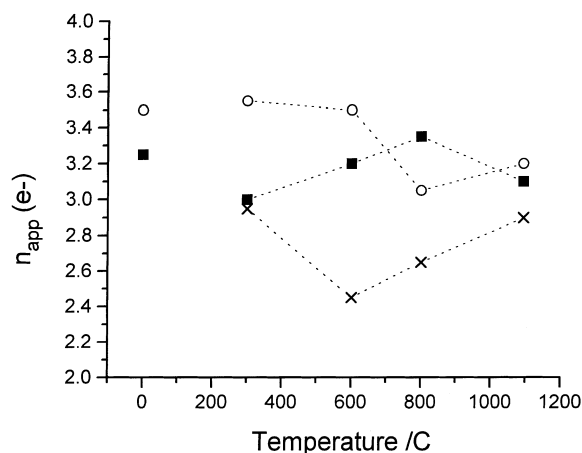


Fig. 5. Comparison of  $n_{app}$  at  $-300$  mV vs. SCE against heat treatment temperature obtained with (■) CoTMPP; (○) CoPc; (×) CoCyclam, each adsorbed on BP 2000.

nient screening, under simulated 'in situ' conditions, of candidate cathode materials as electrocatalysts for dioxygen reduction in the PEM fuel cell. The major findings, viz., the wide range of performance shown by the model Co complexes, the dramatic effect of heat treatment, and the important role of the particulate carbon support, all testify that the method has excellent discriminatory power.

The electrocatalytic properties of cobalt macrocycles for dioxygen reduction have been extensively studied. Regarding the mechanism, Collman has shown that the four-electron reduction to water proceeds efficiently only over *binuclear* complexes

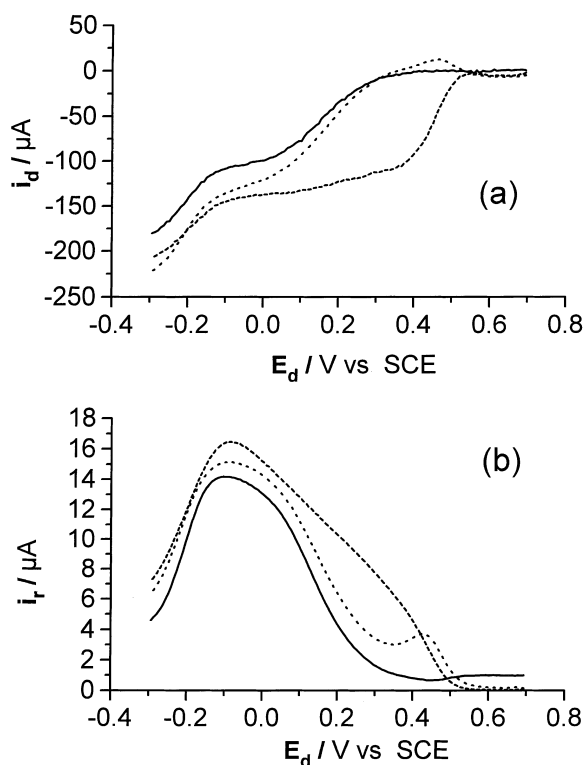


Fig. 6. Voltammograms obtained at (a) the disc, (b) the ring, for CoPc adsorbed on BP 2000; (—) untreated and treated at: (---) 300 °C; (····) 600 °C.

[32–38]. Cooperative assistance from the second metallic site is evidently required to go beyond the facile two-electron reduction promoted readily by mononuclear species, including cobalt porphyrins and macrocycles. Dimers with a *cofacial* geometry, such as those prepared by Collman and Chang [39, 40], appear the most efficient to date but these do not possess the necessary long-term stability for use in practical fuel cell devices.

In light of the above, it seems at first sight surprising that some of the samples under study here are able to reduce dioxygen selectively to water as the complexes involved are mononuclear. The observation of numbers of electrons transferred, being close to four suggests that the deposition and/or the annealing process brings about the formation of pairs of catalytic centres able to function as ‘Collman and Chang dimers’. The practical outcome is that the valuable properties of expensively produced binuclear complexes can apparently be reproduced by starting from cheaper mononuclear complexes and subjecting them to a simple heat treatment to (presumably) induce surface aggregation. The optimum temperature range for thermal activation found here, (i.e., 600–800 °C) seems remarkably high, but is consistent with many published results. Van der Putten [41] argues that complex migration to create the active dimer form probably occurs at lower temperature but that the high-temperature treatment is useful to stabilize the dimer by improving its bonding to the support. Consistent with this view, Sawaguchi [42] has shown that when a porphyrin dimer is adsorbed directly and heated to 800 °C, there is both an enhancement of performance with the preservation of the dimer structure. Savy [24] has shown that a double layer of a cobalt phthalocyanine favours the four-electron transfer after thermal treatment, and also demonstrated a strong influence of the support.

Regarding the electrocatalytic stability, a correlation with selectivity has been reported, that is, materials treated at temperatures which maximize  $n$  are also more stable [18, 43]. This indicates that instability may be linked to the presence of  $\text{H}_2\text{O}_2$ , which is not unreasonable as it is a powerful oxidant. If correct, the good selectivity of the CoTMPP/Printex XE2 system augers well for its prospects in stability testing.

The role of the carbon support is obviously important but not yet understood. Printex XE2 appears to give the best results in general but correlations with any single property, such as surface area (see Table 1), are not evident. Adsorption processes are strongly affected by the chemical nature of the surface, especially by the presence of impurities such as oxygen and sulfur compounds, metallic traces, etc. As this information is not available, no definitive conclusion can be made.

In terms of relative performance, the best samples exhibit half-wave potentials that compare favourably with those of platinized carbons in similar conditions [44]. Other workers have also reported optimal ac-

tivities in their complexes after treatment at about this temperature [19, 28].

CoTMPP and CoPC show good performance in many cases and are far superior to CoCy. This is perhaps not surprising as the first two ligands have aromatic character whereas the cyclam ring is aliphatic. It is generally considered that the former can better serve as an ‘electronic well’ for intermediate charge storage, and to increase charge transfer efficiency. These molecules are also known to aggregate quite easily [23, 24], which may lead preferentially to the formation of ‘pseudodimers’ instrumental in the four-electron reduction of oxygen to water. However, a detailed interpretation is beyond the scope of this work.

The unusual behaviour of the CoPC/BP 2000 system is particularly interesting because this is the clearest evidence of potential-dependent selectivity. The rapid drop in the ring current in the potential region where the disc current increases sharply (see Fig. 6) can only be interpreted reasonably in terms of a sudden switch in selectivity from peroxide to water formation. A similar phenomenon has already been reported by Collman and L’Her for dimers of cobalt porphyrin [45, 46]. If this can be better understood and controlled, it has intriguing implications for electrocatalytic syntheses in general, that is, the option of ‘tuning’ the potential to optimize the selectivity to a desired product among a number of possibilities.

## 5. Conclusion

A versatile method based on the RRDE has been established which allows rapid electrochemical screening, under close to *in situ* conditions, of candidate materials as electrodes in practical (volumic) form for polymer electrolyte membrane fuel cells. It provides information on activity ( $E_{1/2}$ , Tafel slope, etc.) and selectivity (the average number of electrons transferred), with quite high precision.

The power of the method has been illustrated in studies of some Co complexes of interest as potential cathode electrocatalysts for dioxygen reduction. The results reaffirm much of the literature in terms of the nature of the complex, carbon support, heat treatment, etc., and their influence on performance. A preliminary indication of likely stability *in situ* can be gained from the observed selectivity to water, which is very high for CoTMPP on Printex XE2. However, only long-term testing under working conditions can provide a definitive answer. Evidence for potential-dependent selectivity has been observed, with implications for electroorganic synthesis.

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