

## Cobalt and cobalt-based macrocycle blacks as oxygen-reduction catalysts in alkaline fuel cells

Y. Kiros\*, O. Lindström and T. Kaimakis

*Royal Institute of Technology, Department of Chemical Technology, 100 44 Stockholm (Sweden)*

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### Abstract

The electrochemical reduction of oxygen on high surface area carbons catalyzed by cobalt and pyrolyzed macrocycles has been studied in alkaline fuel cells. Tests were also carried out with 'green black', i.e., pyrolyzed phyto-biomass. Galvanostatic polarization curves show that cobalt from cobalt acetate and fine cobalt metal powder exhibit a high catalytic activity. The activity of pyrolyzed cobalt tetraphenylporphyrin (CoTPP) is due to the combined effects of the cobalt additive and the charred residue of the macrocycle. 'Green black', with chlorophyll as macrocycle black precursor, has a similar effect. The dissolution of cobalt from the electrode surface has been established. Life tests with these electrodes are reported.

### Introduction

The reduction of oxygen by pyrolyzed macrocycles such as porphyrins and phthalocyanins has been investigated in alkaline electrolytes by many authors [1–8]. 'Green black', i.e., pyrolyzed phyto-biomass of green leaves, shows a similar effect. The present study was carried out to obtain effective alternates to the noble metals, which are affected by corrosion in both alkaline and acidic solutions [9], agglomeration problems [10, 11] and high cost.

The initial activity of pyrolyzed transition metal macrocycles supported on carbons for the reduction of oxygen is high. However, the performance degradation shown by these catalysts is still a problem. Mössbauer, ESCA (electron spectroscopy for chemical analysis) and EELS (electron energy loss spectroscopy) studies of cobalt-based macrocycles, treated at high temperatures, indicate loss of the nitrogen–metal bond [12], and that cobalt oxide is present along with the pyrolysis product [13, 14].

In this paper, factors influencing the long-term operation of cobalt-based gas diffusion electrodes for the reduction of oxygen in alkaline fuel cells are presented. The role of cobalt as electrocatalyst is assessed. The dissolution of cobalt in the electrolyte is examined. Cobalt metal powder, of powder metallurgy grade, shows promise as an electrocatalyst for the reduction of oxygen.

### Experimental

Details of the preparation of catalysts based on cobalt tetraphenylporphyrin (CoTPP) and on 'green black' have been described in previous papers [14, 15]. These catalysts

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\*Author to whom correspondence should be addressed.

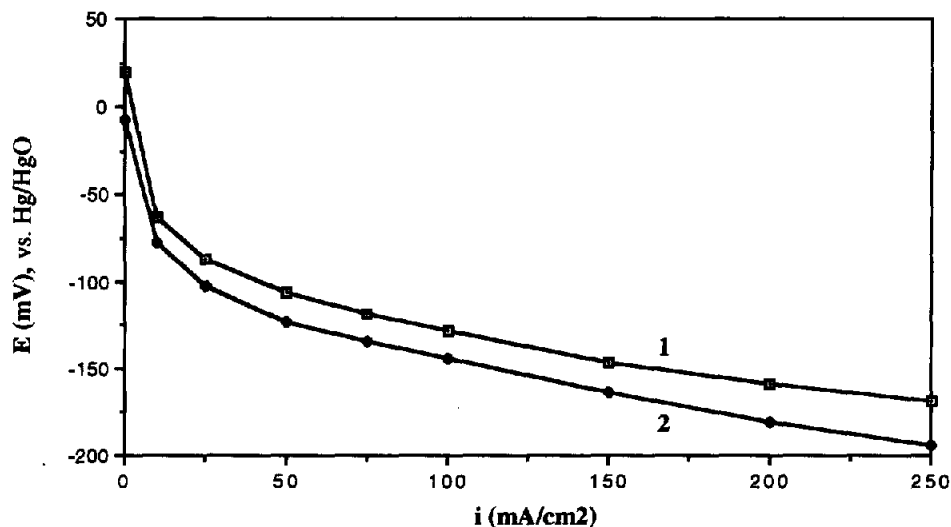


Fig. 1. Comparison of polarization performance of oxygen-reduction electrodes: (1) 1% cobalt acetate, and (2) Ketjen black + Vulcan XC-72.

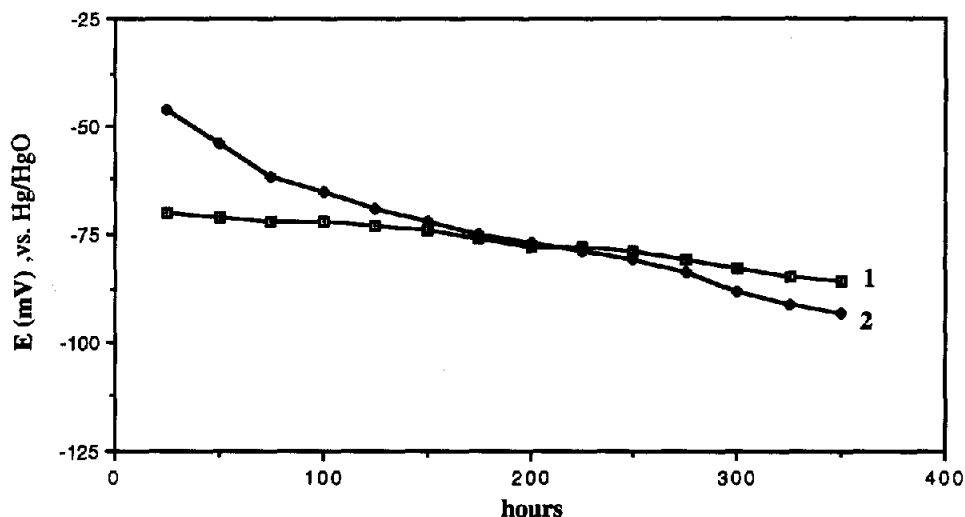
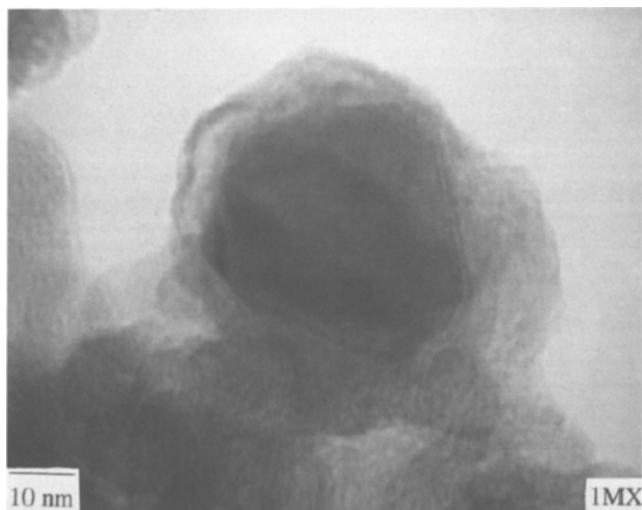
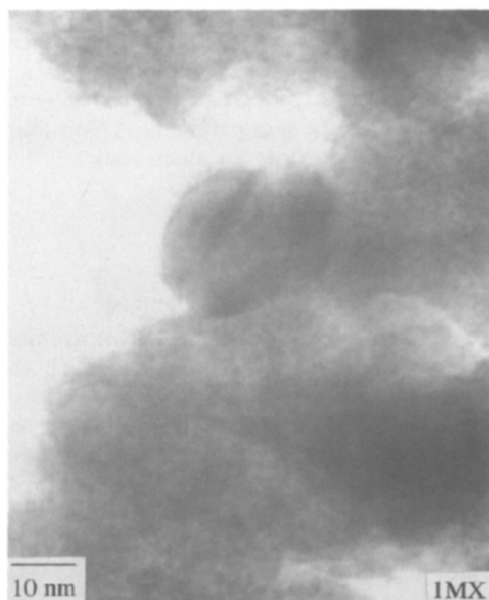


Fig. 2. Time vs. potential characteristics of a CoTPP-based electrode at (1) 20 °C, (2) 60 °C.

were impregnated on high surface area carbons with a weight ratio of 1:1 mixtures of Vulcan XC-72 to Ketjen black EC. Electrodes with metallic cobalt powder and cobalt acetate were prepared in the same way. The cobalt powder was homogenized with the carbons in a mixer, while cobalt acetate was dissolved in methanol and then dried at 60 °C. Concentrated formic acid was then added dropwise to the mixture under ultrasonic agitation, followed by drying in an oven at 90 °C. The carbon materials with cobalt were then heat treated at 700 °C and for a period of 5 h in a stream of 3:1 mixture of nitrogen and hydrogen.



(a)



(b)

Fig. 3. SEM micrographs of the Teflon-bonded electrodes (a) fresh electrode, and (b) after 100 h of electrochemical operation.

The electrodes were prepared by the rolling method. The catalyst and diffusion layers were separately rolled to 0.5 and 0.7 mm thickness, respectively. The sheets were then rolled together on a nickel screen (100 mesh) and pressed at  $150 \text{ kg/cm}^2$ . The polytetrafluoroethylene (PTFE) content of the catalyst layer was 12% and of the

TABLE 1

Elemental analysis of a CoTPP-based electrode by energy dispersive spectroscopy

New electrode			Used electrode (1680 h at 60 °C)	
Element	At. %	At. ratio C:F×100	At. %	At. ratio C:F×100
Carbon and fluorine	99.709	100.000	98.849	100.000
Cobalt	0.204	0.205	0.030	0.030
Sulfur	0.065	0.065	0.053	0.054
Nickel	0.018	0.018	0.078	0.079
Silicon			0.036	0.036
Potassium			0.872	0.882
iron			0.049	0.049

diffusion layer 60%. The electrodes were finally dried and sintered at 320 °C in hydrogen for 1 h.

Rectangular 4 cm<sup>2</sup> specimens were mounted in holders for the half-cell tests. The reduction of oxygen was performed in 6 M KOH, prepared from KOH pellets (EKA Nobel, analytical grade) and distilled water. Air or oxygen was fed at the rear face of the electrode. The reference electrode was a Hg/HgO electrode in the same electrolyte solution. A nickel screen served as counter electrode. The electrodes were tested galvanostatically for the evaluation of performance comparisons. A constant current density of 50 mA/cm<sup>2</sup> was applied in the life tests of the electrodes.

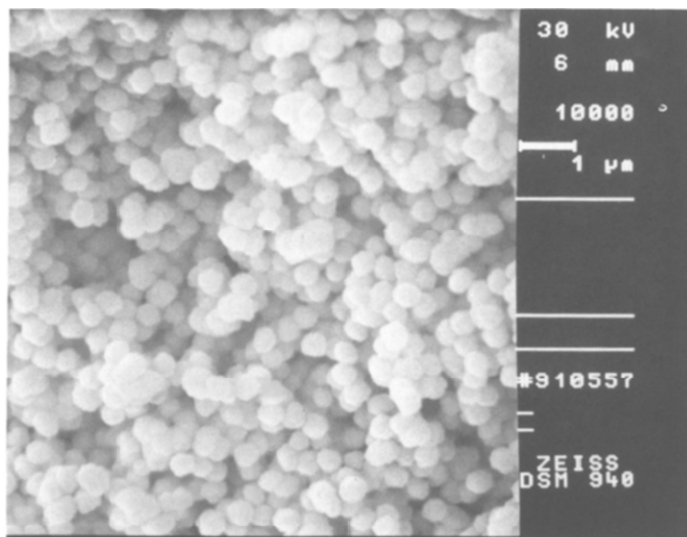
## Results and discussions

### *Cobalt and CoTPP-based electrodes*

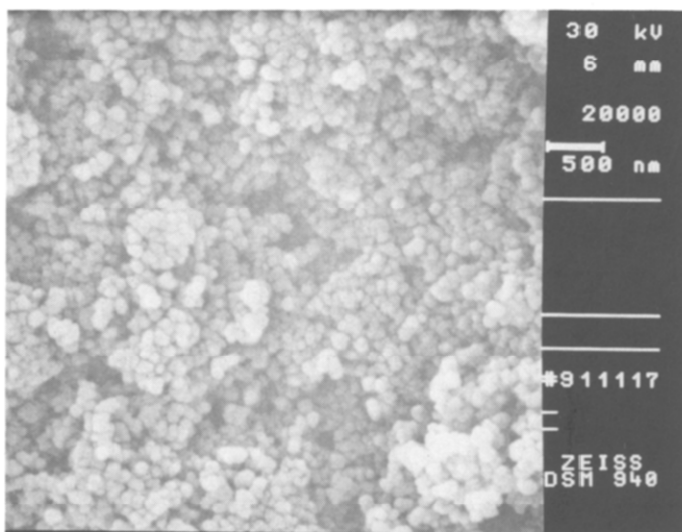
The electrochemical activity of Teflon-bonded electrodes with 1% cobalt acetate and the carbon mixtures (Vulcan XC-72 and Ketjen black EC) is compared in Fig. 1. The curves run essentially parallel with almost 25 mV gain at 250 mA/cm<sup>2</sup> for the electrode with the cobalt acetate additive.

Figure 2 shows activity versus time of a pyrolyzed CoTPP-based electrode in 6 M KOH at 21 and 60 °C. The high initial performance is due to the combined effect of cobalt and the pyrolyzed macrocycle. After a few hours the activity declines, which may be ascribed to the loss of cobalt.

Jiang and Tseung [16] have studied the dissolution of cobalt oxide catalysts supported on graphite during oxygen reduction in 7 N KOH and at 20 °C. The dissolution of cobalt oxide from a fresh electrode was relatively fast during the first 150 h. The cobalt loss is clearly shown in Fig. 3 by the scanning electron microscope (SEM) images of a new electrode and an electrode, which has been operated for about 100 h. Energy dispersive spectroscopy (EDS) results for the elemental analysis of cobalt are given in Table 1 for both new and used electrodes. They indicate that the cobalt content in the electrode surfaces has greatly decreased. Thus, extraction or dissolution of cobalt particles from the support materials seems to be a major cause of the degradation of catalyst activity. Other impurities such as silicon, iron and nickel were also leached from various parts of the cell compartment during the test procedure.



(a)



(b)

Fig. 4. SEM micrographs of morphologies of (a) cobalt powder, and (b) electrode with carbon, Teflon and cobalt powder.

An SEM photo of the surface of the precursor fine cobalt powder is given in Fig. 4(a). This Figure shows aggregation of cobalt with a clear distinction of the fine particles. Figure 4(b) displays an SEM photo of the catalyst layer of the electrode. The distribution of the catalyst is uniform throughout the whole electrode area. Cobalt-based electrodes prepared, as described above, exhibit very fine particles intimately interwoven with the carbon support leading to a good conductivity [17].

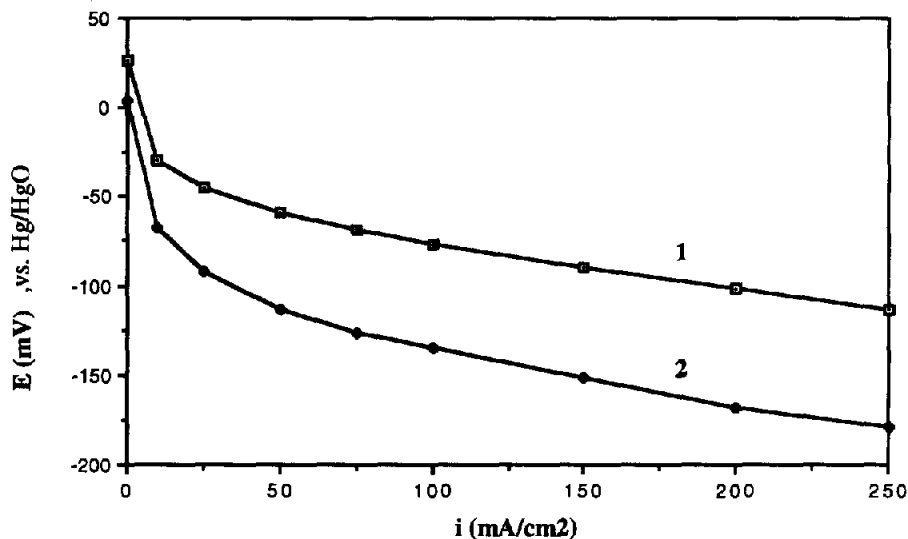


Fig. 5. Polarization curves of cobalt powder-based oxygen reduction electrodes at 60 °C: (1) pretreated, and (2) untreated electrodes.

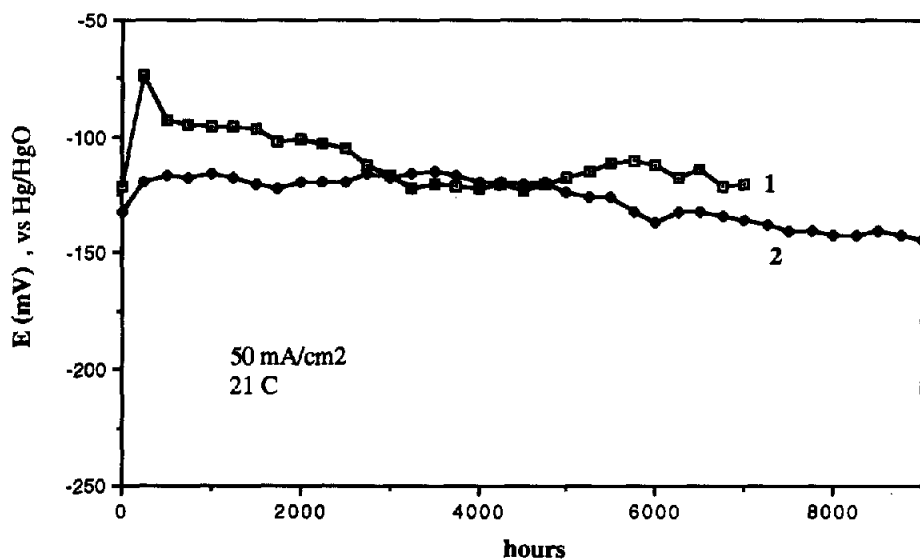


Fig. 6. Potential variation vs. time of oxygen electrodes with catalysts (1) CoTPP, and (2) fine cobalt powder.

Figure 5 shows the effect of pretreatment of the fine cobalt metal powder. The amount of cobalt present in these electrodes was 2.25 wt.%. The pretreated cobalt powder, according to the experimental procedures described, was more active than the addition of cobalt powder, the steps of pretreatment being totally excluded. The existence of cobalt oxides in the pretreated ones was confirmed by X-ray diffractometry and in the case of pyrolyzed CoTPP-based electrodes also by EELS [14].

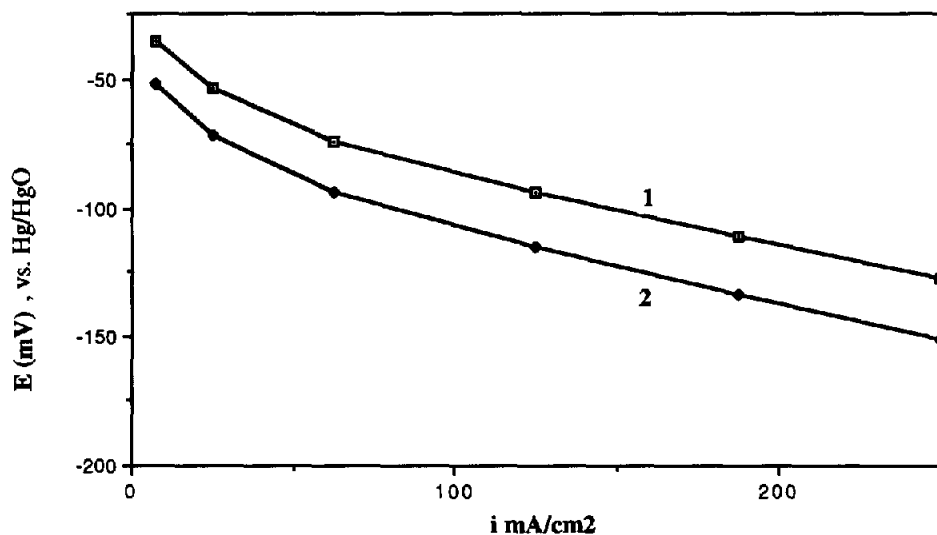


Fig. 7. Polarization curves of green black-based electrodes with cobalt additives: (1) chlorophyll black, and (2) phyto-black.

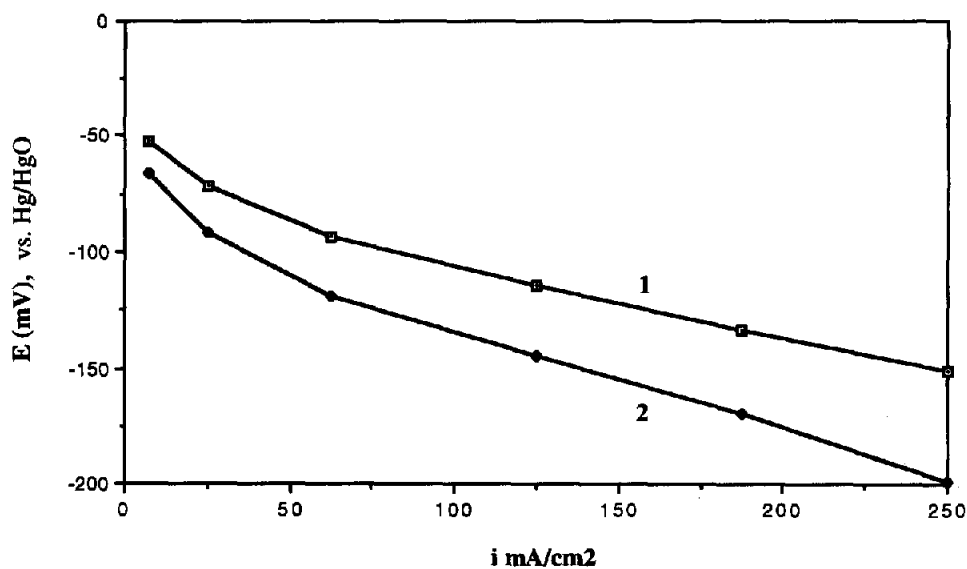


Fig. 8. Polarization curves of phyto-black with cobalt, heat treated at (1) 800 °C, and (2) 400 °C.

Figure 6 shows a life test for cobalt and CoTPP-based electrodes under constant current loads of 50 mA/cm<sup>2</sup> and 21 °C. The degradation of the CoTPP-based electrode was high during the first 500 h, after which the electrode became stable. The average decay rate is 6.6  $\mu$ V/h during 7000 h of operation. The cobalt powder-based electrode has so far been quite stable with a decay rate of 1.2  $\mu$ V/h for more than 9000 h.

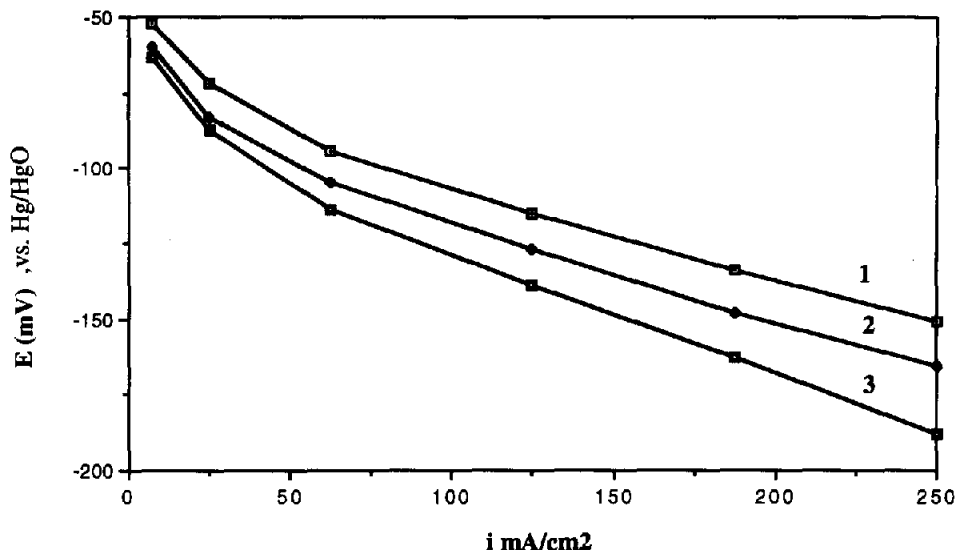


Fig. 9. Polarization curves of phyto-black with cobalt at 800 °C and different pyrolysis times: (1) 5 h; (2) 1 h, and (3) 1 h.

These results indicate that pyrolyzed CoTPP and metal cobalt powder are satisfactory cathode catalysts at low operating temperatures. They have a low decay rate for long operating times. The high initial activity seems to be due to the combined effect of the active cobalt oxides and the cobalt macrocycles blacks. With dissolution of the cobalt oxides into the electrolyte, the activity decreases at higher temperatures.

#### 'Green black' electrodes

Figure 7 shows polarization characteristics of electrodes based on chlorophyll and phyto-black catalysts with cobalt additive. The chlorophyll extracts was obtained commercially, while the raw material of the phyto-black was nettle leaves. The catalyst precursors were pyrolyzed on Vulcan XC-72 (220 m<sup>2</sup>/g). The catalytic activity of these materials, as depicted in the Figure, are quite high.

The effect of the pyrolysis temperature in the creation of an active material is shown in Fig. 8. The phyto-black on the carbon support was pyrolyzed at 400 and 800 °C, respectively. Pyrolysis at high temperatures gives a higher catalytic activity, which according to Okabayashi *et al.* [18] is ascribed to changes in the bulk properties of the material, such as lower resistivity and magnetic susceptibility. The influence of the pyrolysis time on the activity of the phyto-black is shown in Fig. 9. Longer pyrolysis time gives enhancement on the performance characteristics of the material. This effect may be attributed to the change of the surface properties of the phyto-black. The BET surface area increased from 39.5 m<sup>2</sup>/g at 1 h treatment to 47.5 m<sup>2</sup>/g at 5 h treatment.

The performance obtained by 'green black' electrodes at low concentrations (3 mg/cm<sup>2</sup>) has shown that lower cost materials instead of speciality chemicals may be used for the electrochemical oxygen reduction.



## Conclusions

The experimental results obtained in this study enable us to draw the following conclusions:

- (i) the observed enhanced cathodic reduction of oxygen is attributed to the combined effect of the macrocyclic black and cobalt additive;
- (ii) there are many causes of electrode performance deterioration, but loss of cobalt seems to be an important factor;
- (iii) at low temperatures, the electrodes are quite stable with minor decay rates over a prolonged time, and
- (iv) 'green black' electrodes, the charred residues of chlorophyll extract and nettle leaves with cobalt additive, prove to be cost-efficient cathode catalysts.

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