Pyrolyzed macrocycles on high surface area carbons for the reduction of oxygen in alkaline fuel cells

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Abstract

Polarization characteristics and preparation methods of double-layer porous gas diffusion electrodes on various carbon materials in alkaline fuel cells were investigated The electrodes with active carbon carriers were catalyzed with cobalt/iron tetraphonylporphyrin or silver These electrodes show a potential of -186 mV (versus Hg/HgO) at 1 0 A/cm^2 when operated with oxygen at 40 °C and 5 M KOH Various techniques such as surface area measurements, scanning (SEM) and transmission (TEM) electron microscopy in combination with energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) were used to characterize the structure and morphology of the catalyst layer

Introduction

Electrocatalysis of oxygen reduction by organic metal complexes, particularly the metalloporphyrins and phthalocyanines in aqueous solutions, has been the subject of extensive study in the past [1–4] The metalloporphyrins, which are essential for life in nature, have major effects in the transport, storage and activation of oxygen as well as redox processes [5] These metal chelates have attracted much attention as potential catalysts in electrochemistry, especially in the reduction of oxygen in porous gas diffusion electrodes These macrocycles, which can be either synthesized or naturally obtained from crude oil products [6] or green plants [7] are now considered as main alternatives to the costly noble metal catalysts

Metalloporphyrins in their original state are not very active and are also unstable in aqueous solutions The poor activity and stability in these chemical environments have been overcome by heat treatment between 400–1000 °C in inert gases At these temperatures profound changes in the porphyrin structure are expected to take place [8, 9] The pyrolysis product of tetraphenylporphyrin with transition metals on high surface area carbons exhibits excellent catalytic properties in the reduction of oxygen when incorporated into a porous teflon-bonded electrode

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As is well known, the reactivity of a porous electrode not only depends on the catalytic activity but also on the establishment of the three-phase interface, i e between the gaseous reactant, the electrolyte and the catalyst in contact with the electronically conducting support material The selection of carbon blacks for the dispersion of catalyst particles is therefore of prime importance in creating this three-phase interface [10] The carbon material with its specific physical, chemical and surface properties, both as electro-catalyst and/or electrocatalyst support, strongly affects the stability and performance characteristics in the reduction of oxygen in porous electrodes [11–13] Thus, further chemical and heat treatment of these microporous structures has been carried out by many fuel cell researchers both as a state of the art technique and as a scientific approach to improving electrode capacities

The aim of this study is to assess and compare the electrochemical performance of some carbon materials promoted with catalysts in double-layered PTFE-bonded electrodes in alkaline solutions The report is based on experimental evidence to substantiate the relationships between electrode performance of the catalyst on the one hand, and the physiochemical nature of the support material on the other

Experimental

Catalyst preparation

Cobalt tetraphenylporphyrin (CoTPP) or iron tetraphenylporphyrin (FeTPP) was prepared by the following procedure Anhydrous cobalt acetate or iron acetate was dissolved in methanol Then the carbon support (with the specifications given in Table 1) was added to the solution in small amounts under continuous agitation After all the carbon was added, the paste was dried at 60 °C and homogenized in a mixer The mixture was gradually blended under ultrasonic agitation with a solution of concentrated formic acid containing the dissolved products of meso-tetraphenylporphyrin (H_2TPP) The slurry obtained was then dried overnight at 90 °C and ho-mogenized again in a mixer Following this step the resulting powder was heat treated at 700 °C in a horizontal quartz tube under continuous flow of inert gas for a period of 5 h

TABLE 1

Physical properties of the carbon supports

Type of carbon	Surface area (m^2/g)	DBP absorption ($cm^3/100$ g)	Delivered by (Co)
Flamruss 101	20	112	Degussa Norden AB
Vulcan XC-72	254	178	CABOT
ketjenblack EC	950	350	AKZO Chemie

Preparation of electrodes

Double-layer teflon-bonded gas diffusion electrodes were prepared by the rolling method described by Schautz [14] The electrodes are composed of a nickel screen serving as a current collector and structural support for the electrode, the gas diffusion layer with its hydrophobic structure as an oxygen/air supplying zone and an active (catalyst) layer as a reaction zone The materials included in the construction of the electrodes were composed as follows

active (catalyst) layer	catalyst on carbon	10–15%
	PTFE	10–20%
	carbon (unactivated)	20–30%
diffusion layer	carbon	30–50%
	PTFE	50–70%
current collector	nickel screen	80–100 mesh

The gas diffusion layer consists of a highly wet-proofed carbon which provides a gas-supplying channel, prevents electrolyte penetration and supports the active layer Carbon together with teflon suspension (60% by weight) was milled in a colloidal mill and filtered The filtrate was then dried and a hydrocarbon solvent was added to the mixture in order to get a rollable dough This layer was rolled first on a nickel screen to a thickness of 0 7 mm The active layer, which was wet-proofed by teflon and prepared by the same method as above, was double rolled to a total electrode thickness of 1 0 mm The electrode was then pressed (150–200 kg/cm^2), dried at 100 °C and sintered at 320 ° C for 1 h in a hydrogen atmosphere The electrode was spot welded with a nickel wire and tested in a half-cell configuration

Test electrodes

A schematic of the electrochemical cell and associated equipment is shown in Fig 1 The half cell was used to obtain the electrochemical measurements on the gas-fed porous cathode, where the electrode was placed between two pieces of plexiglass cell which were then clamped together with bolts The frontal view of the cell was exposed to the electrolyte solution,
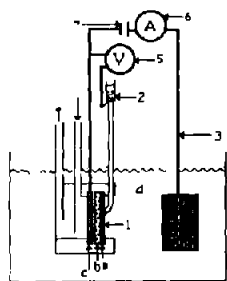

Fig 1 Electrochemical cell 1, working electrode consisting of (a) active layer, (b) diffusion layer and (c) nickel screen, 2, reference electrode, 3, counter electrode, 4, electrolyte (5 M KOH) 5, volt meter, 6, ampere meter, 7 current supply

while at the rear side of the electrode air/oxygen flowed downward through the gas inlet port and out of the cell through the gas outlet The incoming air was scrubbed with a 5 M KOH solution

Steady-state current–potential curves of the double-layered teflon-bonded electrodes were obtained in 5 M KOH and at 40 °C without iR correction The electrode potentials were measured using the Hg/HgO (5 M KOH) reference electrode, attached with a Luggin capillary to the working electrode having an area of 10 cm^2 The counter electrode was a nickel wire mesh placed in the same electrolyte solution

Results and discussion

SEM photographs of the 0 15 mm thick active (catalyst) layer composed of the activated and unactivated carbon, catalyst (CoTPP) and PTFE are shown in Fig 2(a) and (b) Figure 2(a) shows a freshly prepared electrode with a polished and interwoven surface structure, while Fig 2(b) shows the same electrode displaying the aggregation of fine particles of the electrode with higher magnification. Figure 3(a) shows TEM images with well-defined particle structures of the cobalt and carbon support TEM in conjunction with EDS (Fig 3(b)) and EELS (Fig. 3(c)) gives the characteristic features of the morphology and structure of this layer The image shows cobalt particles surrounded by carbon substrate, often having a rectangular shape, indicating a well-developed crystalline structure The particle size of the
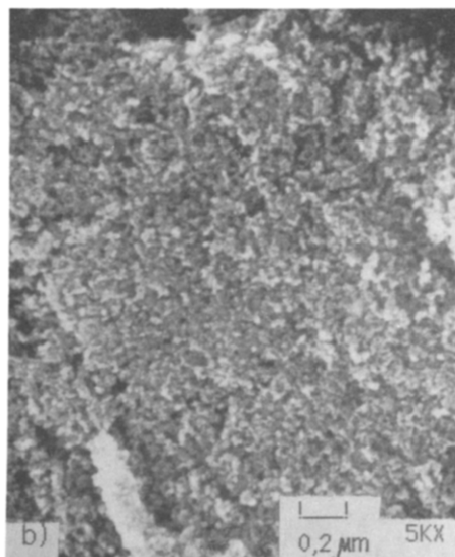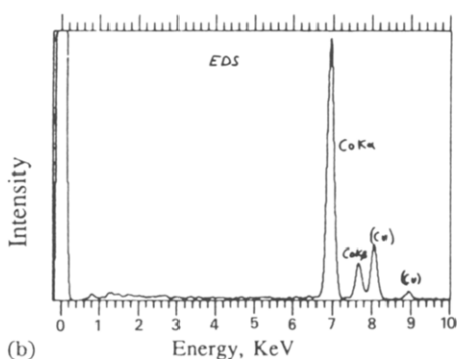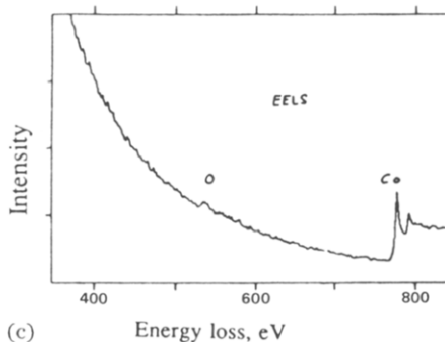

(a)   (b)

Fig 2 SEM micrographs of the active layer of the porous gas diffusion electrode on Vulcan XC-72

(a)

(b)   Energy, KeV   (c)   Energy loss, eV
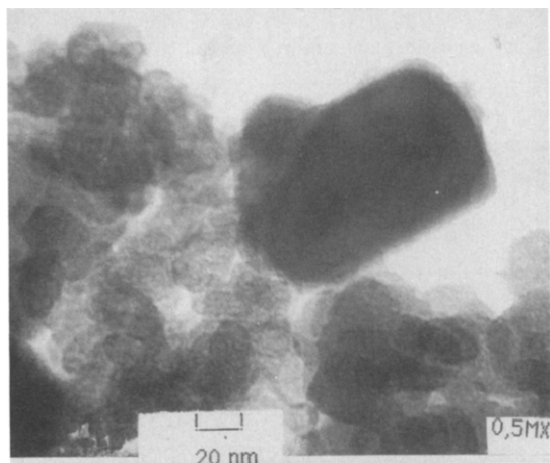
Fig 3 Structural and morphological analyses by TEM (a), EDS (b) and EELS (c) of the active layer on Vulcan XC-72

cobalt ranges from 10–80 nm The EEL spectrum shown in Fig 3(c) shows the characteristic edge at 786 eV arising from Co, while the peak at 532 eV corresponds to oxygen, implying that the cobalt particles are most likely oxidized

The surface areas of the pyrolysis products of the carbons with CoTPP were determined by the BET method using nitrogen as the adsorbing gas at −196 °C It is evident from Table 2 that the initial surface areas of the carbons given in Table 1 decrease considerably with the catalyst present, except for Flamruss, which has a graphite-like structure This effect is attributed primarily to the heat and chemical treatment which alters the physiochemical and surface properties of the carbon materials used These electrode structures, which are characterized by a high surface area and high porosity, provide low resistance to electrolyte flow and a high interfacial area for electrode reactions [15]

TABLE 2

Surface areas of the pyrolysis products of the catalyst and carbon material

Carbon	BET (m^2/g)
Flamruss	18 6
Vulcan XC-72	76 7
Ketjenblack EC	327 6

TABLE 3

Surface areas of the active layer on the electrodes

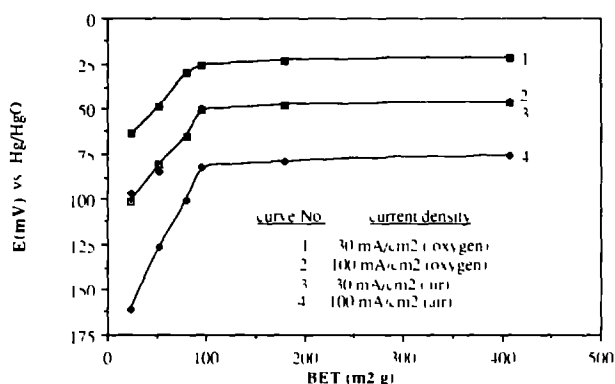| Mixtures of unactivated carbon, carbon + CoTPP and PTFE	Weight ratio (wt /wt)	BET (m^2/g)	Catalyst loading (mg/cm^2)
Flamruss/Vulcan	1 0/0	24 3	2 24
Flamruss/Vulcan	1 5/1 0	52 2	1 90
Flamruss/Vulcan	1 0/4 0	80 5	1 84
Vulcan/Ketjenblack	1 0/0	94 7	1 78
Vulcan/Ketjenblack	1 0/1 0	174 3	1 71
Vulcan/Ketjenblack	0/1 0	397 6	1 64

Fig 4 Electrode performance based on the electrode surface areas, according to Table 3

Surface area measurements of the active layer of the electrode with different catalyst loadings are presented in Table 3 The catalyst loadings are described as the amount of Co and TPP originally added to the carbon before the pyrolysis step and graded in terms of mg/cm^2 by weighing the electrode The surface areas were determined using the same method as for those given in Table 2 As presented in Table 3, unactivated carbons according to the specifications in Table 1 were added with the same proportions among the different carbons as were the catalyst + carbon mixtures in Table 2

Figure 4 shows the electrochemical performance characteristics estimated from polarization measurements at 30 and 100 mA/cm^2, operated with oxygen

and air as a function of the surface areas Although the diffusion layer of these different electrodes prepared using the same methods of fabrication and materials of construction was identical, it was not possible to maintain the same carbon and catalyst loadings on the active layer Poor current–voltage characteristics were exhibited by Flamruss, which had a carbon with catalyst loading almost twice as high as that of the Ketjenblack Increasing the weight ratio of Vulcan XC-72 to Flamruss improved the performance linearly with the electrode surface areas, until it finally reached a maximum at which the electrode material was entirely substituted by Vulcan The electrode activity then rose slightly with increased surface area of the carbon support

From a comparison of the results shown in Fig 4, it may be suggested that high surface area electrodes, due to their larger amount of exposed surface area and a pore structure with many micropores, have a pronounced effect on the overall activity of cathodic applications in fuel cells Therefore, selection of carbon supports with subsequent treatment and effective dispersion of the catalyst particles could yield significant improvements in porous gas diffusion electrodes

In addition, current–voltage characteristics of some porous gas diffusion electrodes promoted with CoTPP, FeTPP and Ag reduced from its oxides are presented in Fig 5 The aim of this comparison is to assess the catalytic activity of these catalysts and to find optimum conditions for further applications in oxygen reduction electrodes As shown in the Figure, the activity decreases in the order CoTPP > Ag > FeTPP Among the catalyst studied, the electrode consisting of CoTPP has a very good performance and can be loaded with high current densities as shown in Fig 6

The cathodic activity improvements encountered in this study for the reduction of oxygen in alkaline fuel cells are due to good utilization of the catalyst particles, augmented especially by high structure carbons with high surface areas on the active layer, and the diffusion processes of oxygen Thus better preparation techniques of both catalyst and double-layered teflon-
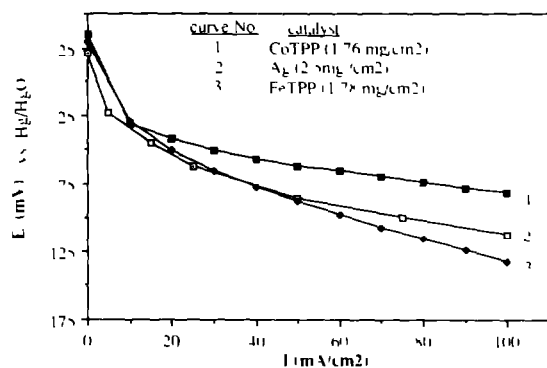

Fig 5 Polarization curves of the double-layer gas diffusion electrodes with different catalysts on Vulcan XC-72, supplied with air
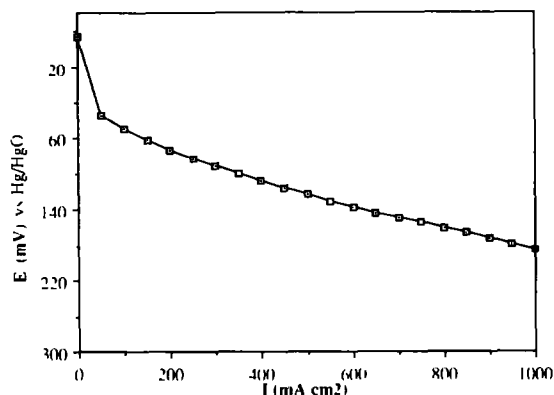
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Fig 6 Current–voltage characteristics of a double-layered CoTPP promoted electrode operating with oxygen

bonded electrodes are of prime concern in increasing the limiting current densities [16]

Conclusions

In this study, electrochemical measurements for oxygen reduction have been performed in 5 M KOH and at 40 °C for Co/FeTPP and Ag promoted double-layered electrodes Surface area analysis, structural and morphological analyses using BET, SEM, TEM, EDS and EELS techniques were used for the characterization of the CoTPP based electrodes

From the cathodic polarization data obtained from the experimental procedures described, it is concluded that high performance oxygen reduction electrodes could be prepared with better utilization of the catalyst particles, especially when supported on high surface area carbons Chemical and heat treatment of the carbon material along with the dispersion and modification of the metalloporphyrins could yield activity enhancement of the electrodes Besides, a number of different surface areas of the active layers, which were composed of mixtures of carbon materials, have revealed that the intrinsic performance of the electrodes increased linearly with increasing surface area of the electrodes The correlation of the surface area to the activity has also shown that raising the surface area beyond 80 m^2/g did not produce a significant gain in the performance of the electrodes

Acknowledgements

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