PREPARATION AND MEASUREMENT OF AIR ELECTRODES FOR ALKALINE FUEL CELLS

JUHANI KIVISAARI*, JAAKKO LAMMINEN, MARKKU J. LAMPINEN** and MINNA VIITANEN

Helsinki University of Technology, Department of Energy Engineering, Laboratory of Thermal Engineering, Otakaari 4, SF-02150 Espoo (Finland)

(Received February 16, 1990)

Summary

The optimum structure and materials for the gas diffusion layer of air electrodes for alkaline fuel cells were studied. These electrodes contain carbon black, pretreated in different ways (*e.g.*, boiling nitric acid, heat treatment in different atmospheres), and polytetrafluorethylene as a hydrophobic binder. The samples prepared were studied by different methods, *e.g.*, air permeability, electrical conductivity and porosity. Heat-treated cobalttetramethoxyphenylporphyrine was used as catalyst in the active layer.

Introduction

To make it possible to use fuel cells for terrestrial applications it is necessary to improve the performance of the air electrode without using precious metal catalysts. One way to achieve this is to use macrocycles such as porphyrins found in nature as catalysts [1, 2].

As important as an active catalyst is a good backing material for the gas diffusion layer so that the polarization due to diffusion resistance and ohmic resistance in the gas diffusion layer of the electrode remain small. In this study several materials for the gas diffusion layer have been investigated.

The aim of the study was to find an optimum material by means of air diffusivity and electrical conductivity.

*Permanent address: The Royal Institute of Technology, Department of Chemical Technology, S-100 44 Stockholm, Sweden. Working in Finland on a scholarship from the Nordic Ministry Council, for the academic year 89/90.

**Author to whom correspondence should be addressed.

0378-7753/90/$3.50

Experimental

Materials

The materials used for the samples in this study were carbon black (Vulcan XC-72 and Black Pearls 2000, Cabot Corp.) and PTFE (Teflon resin 30N, Du Pont and Hostaflon TF2053, TF2071, TF9205, Hoescht AG) as a hydrophobic binder. The characteristic properties of the carbons are listed in Table 1. Heat-treated CoTMPP (CobaltTetraMethoxyPhenylPorphyrine) on carbon black was used as a catalyst.

TABLE 1

Characteristic properties of carbons [3]

Carbon	Surface area ($m^2\ g^{-1}$)	Average particle size (Å)
Vulcan XC-72R	238	300
Black Pearls 2000	1475	150

Preparation of carbons

Many different types of carbon treatment are suggested in the literature *e.g.*, boiling with nitric acid, heat treatment in different atmospheres [4 - 7]. In this study carbon samples were treated in four different ways.

(i) Untreated: carbon directly from the can. The only treatment before use was to grind the carbon in a coffee-mill in order to break down large lumps of carbon.

(ii) Boiling with concentrated nitric acid: the carbon was dispersed in concentrated nitric acid and boiled for 24 h.

(iii) Heat treatment at 850 and 1000 °C in nitrogen atmosphere: the carbon was heat treated in nitrogen atmosphere for 30 min at 850 or 1000 °C.

(iv) Heat treatment at 850 and 900 °C in carbon dioxide atmosphere: the carbon was heat treated in carbon dioxide atmosphere for 30 min at 850 or 900 °C.

Manufacture of electrodes

For the manufacture of electrodes several different methods are proposed, the main methods being: pressing [4 - 6], rolling [8], screen-printing [9] and spraying [10]. In this study the rolling technique was used for electrode manufacture. The preparation of the electrodes was carried out in two different ways depending on the PTFE type used. When using PTFE as a water dispersion, the wet method was used and when using PTFE as a powder, the dry method was used. Flowsheets for the two different methods are shown in Fig. 1.

A total of 30 samples with duplicates was prepared, but only a selection of them is shown in Table 2. Variables which have been changed are: carbon

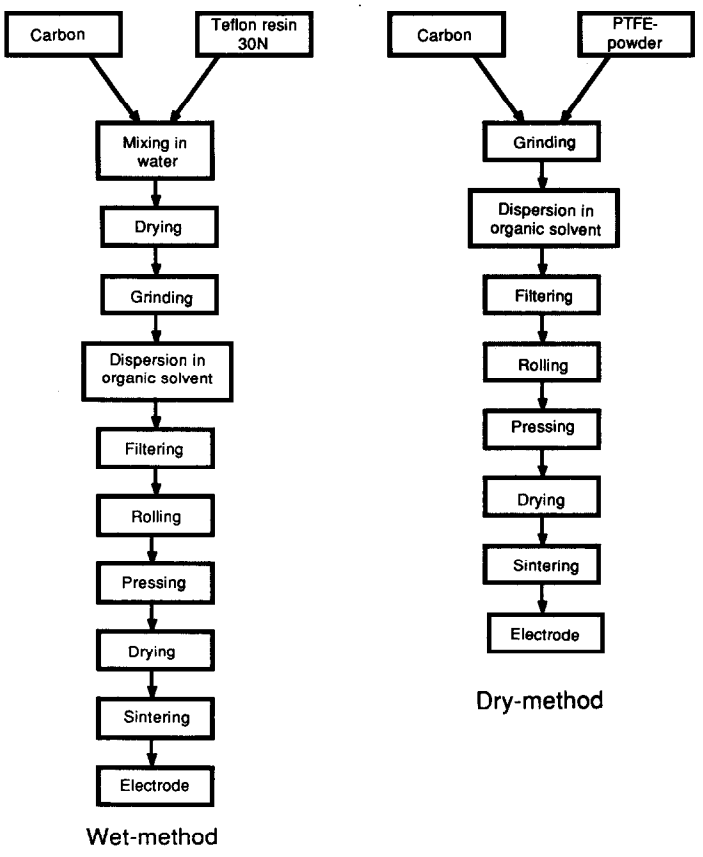


Fig. 1. Flowsheets for electrode preparation.

type, treatment of the carbon, dry or wet method, spacer used or not, solvent used to make the dough.

On top of the diffusion layer was a catalytic layer of the same type in all the samples.

Characterization of electrodes

The following measurements were made to characterize the samples.

(a) Thickness: measured with a micrometer.

(b) Weight: measured with a laboratory balance.

(c) Porosity: calculated by measuring the dimensions of the sample, and knowing the weight of the sample, the porosity could be calculated under the assumption that the density of the compact material in the sample is 1.9 g cm^{-3}.

(d) Air permeability: measured using a sample with a diameter of 20 mm (area of measurement). The thickness of the samples for these measurements can be seen in Table 2.

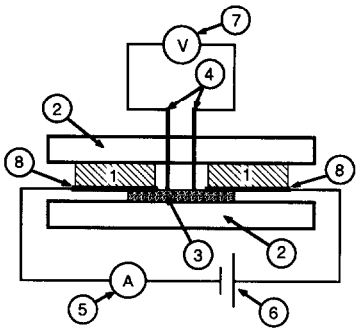
TABLE 2

Manufacture of and characteristic data of samples[a]

Sample	Carbon type, %	Treatment of carbon	PTFE type, %	Spacer (%) NH_4HCO_3	Solvent	Porosity (%)	Air permeability (ml/s) (thickness (mm))	Conductivity (1/Ωm) (thickness (mm))	Comments
1	Vul, 70	no	TF53, 30	no	Sh	70.5	1.3 (0.27)	222 (0.28)	
2b	Vul, 70	HNO_3	TF53, 30	no	Sh	65.2	5.6 (0.33)	120 (0.41)	
3b	Vul, 70	no	TF71, 30	no	Sh	71.0	0.64 (0.43)	228 (0.43)	
4a	Vul, 70	HNO_3	TF71, 30	no	Sh	64.8	0.67 (0.33)	114 (0.37)	
5	Vul, 70	no	TF05, 30	no	Sh			92 (0.84)	brittle
6	Vul, 70	no	PV, 30	no	Sh		3.8	152 (0.18)	brittle
7a	Vul, 70	no	PV, TF71, 15, 15	no	Sh	71.3	3.8 (0.45)	198 (0.71)	
8a	Vul, 70	no	DP 30N, 30	no	Sh	68.4	0.77 (0.39)	254 (0.37)	
9a	Vul, 70	HNO_3	DP 30N, 30	no	Sh	65.6	0.78 (0.33)	123 (0.34)	
10a	BI.P, 70	no	DP 30N, 30	no	Sh	72.7	0.16 (0.50)	363 (0.42)	st d, cr
11a	BI.P, 70	no	TF71, 30	no	Sh	72.9	0.28 (0.41)	347 (0.49)	cracked
12a	Vul, 70	h, N_2, 850	TF71, 30	no	Sh	68.6	1.2 (0.31)	238 (0.51)	
13a	Vul, 70	h, N_2, 850	DP 30N, 30	no	Sh	67.9	1.1 (0.36)	274 (0.35)	
14a	BI.P, 70	h, N_2, 850	TF71, 30	no	Sh	76.0	0.31 (0.48)	331 (0.41)	st d, cr
15a	BI.P, 70	h, N_2, 850	DP 30N, 30	no	Sh	75.2	0.27 (0.42)	291 (0.44)	st d, cr
16a	Vul, 70	h, N_2, 1000	TF71, 30	no	Sh			247 (0.46)	cracked
17a	Vul, 70	no	DP 30N, 30	no	ace	70.1	0.83 (0.57)	187 (0.59)	cracked
18a	Vul, 70	h, CO_2, 900	TF71, 30	no	Sh	69.2	1.6 (0.59)	234 (0.59)	
19a	Vul, 70	h, CO_2, 900	DP 30N, 30	no	Sh	69.2	1.4 (0.46)	227 (0.52)	cracked
20a	Vul, 70	h, N_2, 1000	DP 30N, 30	no	Sh + he	69.5	0.92 (0.49)	243 (0.47)	cracked
21a	Vul, 70	no	TF71, 30	no	n-h	69.7	0.61 (0.66)	232 (0.66)	
22a	Vul, 70	h, N_2, 850	DP 30N, 30	no	n-h	71.6	0.51 (0.88)	194 (0.89)	
23a	Vul, 70	h, CO_2, 850	DP 30N, 30	20	Sh + n-h	70.6	0.93 (0.49)	253 (0.48)	
24a	Vul, 70	h, CO_2, 850	DP 30N, 30	40	Sh + n-h	67.9	0.92 (0.45)	271 (0.48)	
25a	Vul, 70	h, CO_2, 850	DP 30N, 30	60	Sh + n-h	69.8	1.0 (0.47)	234 (0.47)	
26a	Vul, 70	h, CO_2, 850	DP 30N, 30	no	Sh + n-h	69.4	0.76 (0.48)	297 (0.49)	
27	Vul, 70	h, CO_2, 850	TF71, 30	20	Sh + n-h	the electrode fell apart			cracked

28a	Vul, 60	h, CO_2, 850	DP 30N, 40	20	Sh + n-h	67.2	0.69 (0.52)	285 (0.49)
29a	Vul, 65	h, CO_2, 850	DP 30N, 35	20	Sh + n-h	68.4	1.35 (0.47)	226 (0.47)
29b	Vul, 65	h, CO_2, 850	DP 30N, 35	20	Sh + n-h	68.4	1.23 (0.47)	256 (0.46)
30	Vul, 65	h, CO_2, 850	DP 30N, 35	20	Sh + n-h			

[a]Abbreviations: Vul = Vulcan XC72R; Bl.P = Black Pearls 2000; no = no pretreatment of the carbon black; HNO_3 = boiled in conc. nitric acid; h, N_2 = heat-treated in nitrogen atmosphere; h, CO_2 = heat-treated in carbon dioxide atmosphere; TF53 = Hostaflon TF2053; TF71 = Hostaflon TF2071; TF05 = Hostaflon TF9205; PV = doped polyvinylidene fluoride; DP 30N = Du Pont Teflon resin 30N; Sh = Shellsol K; ace = acetone; n-h = n-heptane; he = hexane; solvents mixed 50/50 by vol%; st d, cr = sticky dough, cracked.



1. Compressible cushions
2. End plates
3. Sample
4. Measurement points
5. Ampere meter
6. Current supply
7. Volt meter
8. Copper electrode

Fig. 2. Apparatus for conductivity measurements.

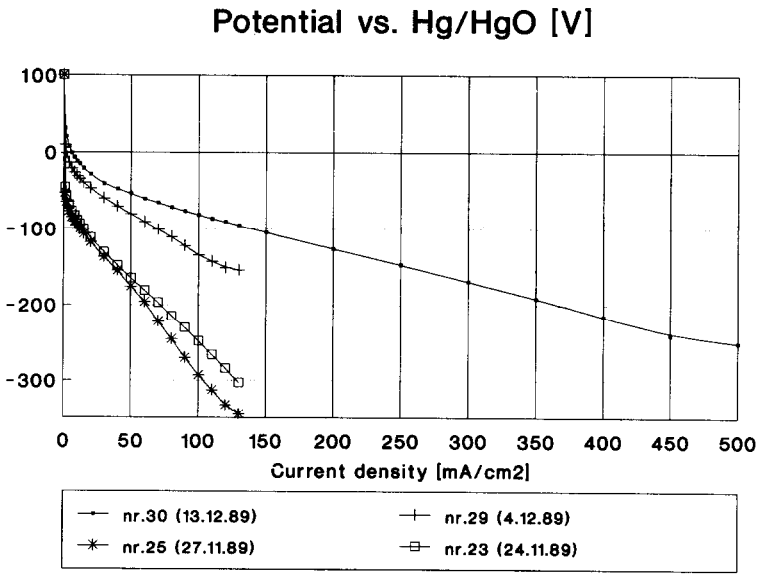


Fig. 3. Polarization curves for some electrodes.

(e) Resistivity: measured by a four-point method; the apparatus is shown in Fig. 2.

(f) Polarization curve: measured using an electrode with an area of 10 cm^2 in an alkaline electrolyte (5 M KOH) and having air on the gas side. As a counter-electrode a stainless steel plate was used. The polarization was measured *versus* a mercury/mercury oxide reference electrode. The results of the measurements can be seen in Fig. 3.

(h) Transfer coefficients (Tafel parameters i_0 and α); measured according to the model in ref. 11 and the results can be seen in Fig. 4.

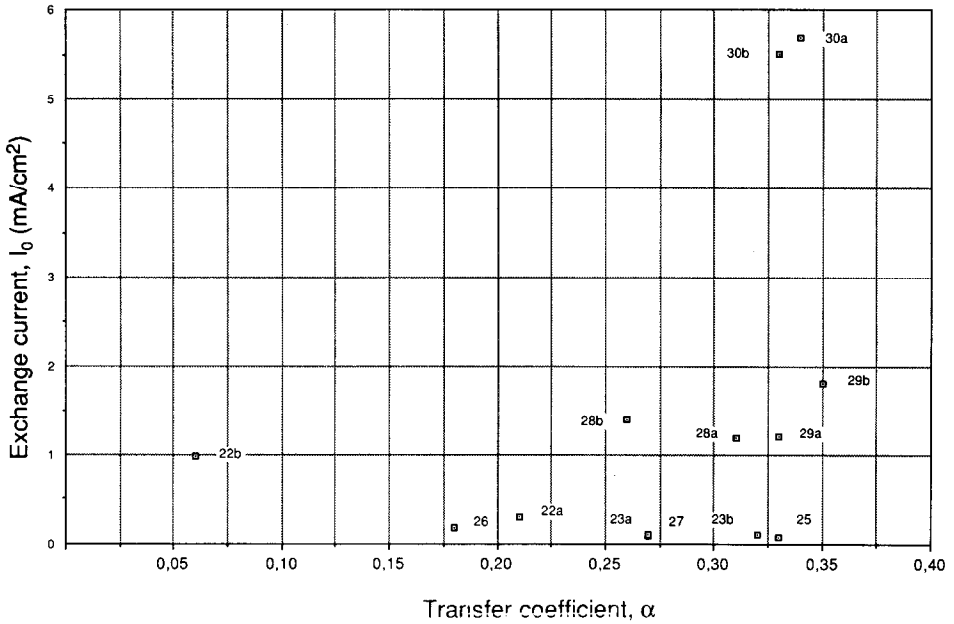


Fig. 4. Correlation between the exchange current, I_0, and the transfer coefficient, α.

Characterization of catalyst

Samples of cobalttetramethoxyphenylporphyrine and hydrogentetramethoxyphenylporphyrine, on carbon black, both untreated and heat-treated at 700 °C were received from I. Iliev. These samples were studied by using ESCA, which is suitable for studying the chemical bonds of the electrode surface. The study was conducted to determine whether the bonding between the nitrogen and the metal atom was still present after the heat treatment.

Results and discussion

In Table 1 it can be seen that the best results in conductivity were obtained with Black Pearls 2000 (samples 10 and 11), but the resulting dough was very sticky and hard to roll to an electrode sheet. The best sample was 6 in terms of air permeability, but the material was very brittle. The best overall result was obtained with samples 29 and 30.

Rough calculations show that a conductivity of 200 $1/\Omega m$ or more gives a polarization of 2 - 3 mV at 100 mA cm^{-2}. A similar calculation for air permeability indicates that a permeability of 0.87 ml s^{-1} is enough to give a polarization of less than 4 mV at 100 mA cm^{-2}.

Figure 3 shows polarization curves for samples 23, 25, 29 and 30. Sample 30 shows a relatively good performance even at 500 mA cm^{-2}, and no tendency to reach its limiting current.

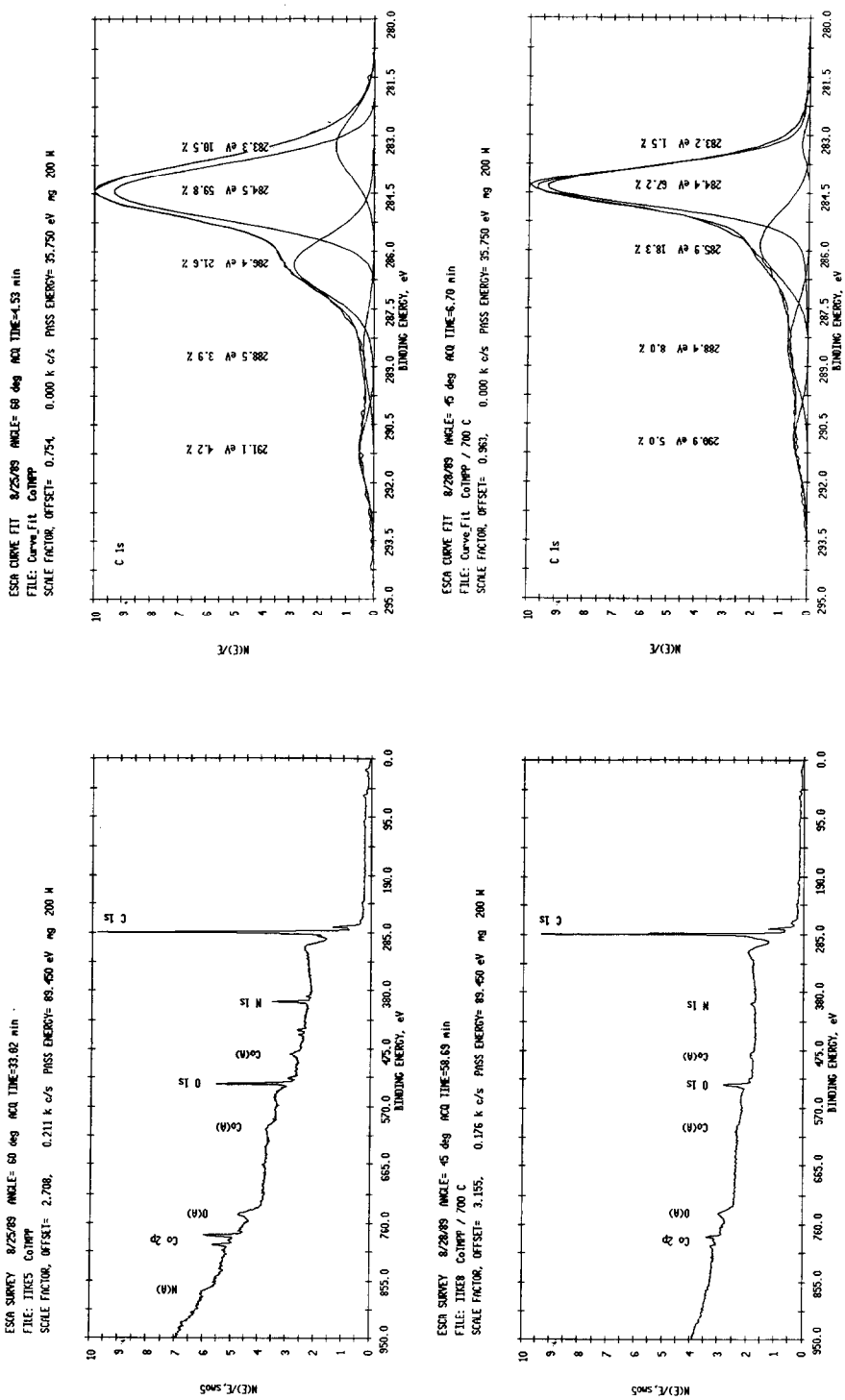


Fig. 5. ESCA curves for untreated and heat-treated CoTMPP on carbon black.

Figure 4 shows the correlation between the exchange current, I_0, and the transfer coefficient, α. The larger these two figures are for a sample, the better the result is.

The ESCA study of the catalyst shows that the peak showing the nitrogen to metal bond has disappeared after the heat treatment of the porphyrine, Fig. 5 on the left hand side. On the right hand side, a small shift in the binding energy of the carbon atoms can be seen. This implies some structural changes in the porphyrine structure during the treatment.

The next step in the investigation reported above is to optimize the materials and structure of the catalytic layer to achieve an electrode with good overall performance. This will be reported later.

Acknowledgements

This work was financially supported by a grant from NEMO and a scholarship from the Nordic Ministry Council.

The authors acknowledge the assistance of and discussions with I. Iliev and A. K. Shukla.

References

1 O. Lindström, E. Björnbom and T. Kaimakis, Low cost macro-cycle black for air cathodes, *American Institute of Chemical Engineers, 1989 Ann. Meet., Symp. Fuel Cells IV, San Francisco, CA, U.S.A., Nov. 5 - 10, 1989.*
2 O. Lindström, *Chemtech., 17* (1988) 495.
3 K. Kinoshita, *Carbon, Electrochemical and Physicochemical Properties*, Wiley, New York, 1988, p. 46.
4 S. Motoo, M. Watanabe and N. Furuya, *J. Electroanal. Chem., 160* (1984) 351 - 357.
5 M. Watanabe, K. Makita, H. Usami and S. Motoo, *J. Electroanal. Chem., 197* (1986) 195 - 208.
6 M. Watanabe, M. Tozawa and S. Motoo, *J. Electroanal. Chem., 183* (1985) 391 - 394.
7 R. Manoharan and A. K. Shukla, *J. Power Sources, 10* (1983) 333 - 341.
8 M. Schautz, Herstellung von Elektroden für alkalische Wasserstoff-Luft-Brennstoffzellen und Bau einer Batterie, *Dissertation*, University of Graz, 1985, pp. 54 - 58.
9 B. J. Krätschmer, Untersuchungen von Kohlenmateriale für Gasdiffusionselektroden, *Dissertation*, University of Graz, 1981, pp. 15 - 22.
10 K. Kordesch, S. Jahangir and M. Schautz, *Electrochim. Acta, 29* (1984) 1589 - 1596.
11 M. Viitanen and M. J. Lampinen, *J. Power Sources, 32* (1990) 207.