STUDY OF CATALYSTS FOR FUEL CELL ELECTRODES. XV.*
STRUCTURAL PROPERTIES
OF CARBON ELECTRODES BONDED
WITH THERMOPLASTIC RESINS

J.Jindra and J.Mrha

*J. Heyrovský Institute of Polarography,
Czechoslovak Academy of Sciences, Prague 1*

Active carbon as a catalyst for electroreduction of oxygen, or as a support for another catalyst, has often been studied[1–6]. Active carbon itself — in special cases an excellent catalytic species-is unfortunately extremely hydrophyllic which hinders its utilization in porous diffusion electrodes, where the establishment of a stable three-phase boundary is mandatory. There is no other way of building up such a boundary in the carbon electrodes, than to combine the strongly wetted carbon material with another material which, contrary to the former, is markedly water repellent. The same procedure has to be applied in the case of carbon supports or oxygen reduction catalysts proper (platinum group metals, silver, *etc*[7–11]). The present paper is devoted to the problem of bonding and impregnating the initial active carbon with different wet-proofing agents, and to the influence of the agents on the structure of the carbon skeletons, prepared to work as porous oxygen electrodes.

EXPERIMENTAL

Test samples of various carbon skeletons were prepared by pressing pre-impregnated active carbon HS-4. In all cases the sieve fraction $<60\,\mu$ was employed; bonding and impregnating was carried out in a way to give 10, 20, 30, and 40% of polystyrene (PST), polyethylene (PET), or polytetrafluorethylene (PTFE) in the mixture. PST and PET were dissolved in xylene which was then removed from the electrode by evaporation at 150°C. Water from the PTEE dispersion (particle size 500—5000 Å) was removed by drying at the same temperature.

The pore size distribution curves of the samples were measured by intrusion of mercury[2]; the specific surface areas were determined by the BET method. Prior to measurement the samples were evacuated at a maximum temperature of 150°C. The imbibition capacity of the samples was determined at 25°C in regular time intervals, from the weight increment of 7M-KOH (the working electrolyte of oxygen electrodes). All data regarding the porosity, specific surface area, and imbibition capacity, were converted to one gram of the initial untreated active carbon.

RESULTS AND DISCUSSION

Fig. 1 depicts the integral porosimetric curves of the carbon structures under study. PST, PET, PTFE were chosen to represent two opposed wet-proofing and bonding agent groups. In the first two cases (PET and PST), the agents were introduced into the finely ground carbon in the form of a solution in xylene. In the case of PTFE, the electrode was prepared by mixing two solid phases, *i.e.* the carbon and the PTFE dispersion in water, stabilized by a non-ionic wetting agent. The different way of impregnation may be seen in Fig. 1 and Table I, depicting the pore volume distributions. When employing PET and especially PST, the total volume of macropores, identical

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TABLE I

Pore Volume Distribution for the Region $r > 100$ Å

The data in the table stand for the % of the porosity measured.

Impregnation Pore radius Å	0% Carbon	10%			20%			30%			40%		
		PET	PST	PTFE	PET	PST	PTFE	PET	PST	PTFE	PET	PST	PTFE
— 35 000	0	0	1·9	0	0	0	1·5	0	2·7	0	0	1·3	0
35 000 — 30 000	0·2	0	0·5	1	0	1·4	0·3	0	0·9	0	0	0·8	0·2
30 000 — 25 000	0·2	0	1·2	1·2	0	1·6	0·8	0	1·4	0·6	0	1·5	0·2
25 000 — 20 000	0·7	0	2·7	1·5	0	4	1·1	0	3·7	0·6	0	3·2	0·2
20 000 — 15 000	1·4	0·5	7·4	2	0·2	9·3	1·4	0	8·2	0·9	0·4	8	0·2
15 000 — 10 000	3·6	5·9	30·5	4·2	6·5	32·7	3·3	2·5	29	2·8	2·6	35	0·6
10 000 — 5 000	34·4	40·2	28·3	32·4	45·1	24·6	33·3	28·7	25·8	11·9	23·3	25	3·6
5 000 — 500	28·1	44·5	20·1	45·5	34·2	22·2	42·2	49·3	22·3	67·5	54·8	22·9	67
500 — 100	31·4	8·9	7·6	12·2	14	4·2	16·1	19·5	6	15·7	18·9	2·3	28

with the voids between the carbon particles, is not greatly influenced. During the formation of the electrode, a film is formed on the carbon surface which is the thinner the better the solubility of the impregnating agent in xylene. In the case of an electrode bonded with PST, the total volume of the big pores thus remains virtually unchanged. In the case of PET, dissolving in xylene to yield a strongly viscous liquid, a slight but regular drop in the macropore volume is observed,
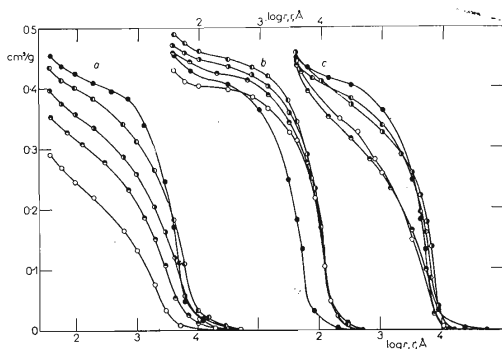

FIG. 1

Integral Porosimetric Curves of Carbon Structures Bonded with PTFE (a), PST (b), and PET (c)
● Initial carbon, ◐ 10, ◑ 20, ◒ 30, ○ 40% of wetproofing agent.

accompanying the increase of the impregnating agent contents. In this way PET may be considered to stand between PST and PTFE. Porous carbon bodies bonded with PTFE exhibit a pronounced decrease of the pore volume in the macropore region. The pore volume distribution shows a marked change (see Table I) in that the PTFE fills the voids between the carbon particles, thus shifting the pore volume distribution to lower values. In its influence upon the macroporous structure of the carbon electrodes, PET stands in the middle between PST and PTFE.

The study of the microporosity of the above electrodes results in a different picture. This concerns those pore regions which are beyond the range of mercury porosimetry, *i.e.* $r < 50$ Å. For this reason the specific surface areas were measured and may be found in Fig. 2. It is evident that an increase in the wetproofing agent contents brings about a decrease in the surface area: in the case of PTFE the decrease is only moderate (from 1 185 to 900 m^2/g). The influence of PST is already more pronounced and the influence of PET is quite apparent. The inner surface increases directly with the radius, the pore volume with its square. The major part of the pore volume is, therefore, given by the macropores (in agreement with the porosimetric measurements), the inner surface is given by the micropores. As is evident from Fig. 2, PTFE left the microporosity almost unchanged. As was already mentioned before, the other two agents probably form on the individual grains consistent films which, however, may form cracks during evaporation of the solvent. This apparently is more frequent in the case of PST; PET films are plastic, and the evaporation of xylene seems to proceed without damage. The micropores of the carbon thus remain inaccessible even for the small molecules of argon.

The porous structure data are in close agreement with the measurements of the alkaline electrolyte imbibition. As will be seen in Fig. 3, PTFE at 20% concentration shows a marked difference in comparison with the other two agents. Its low impregnating ability is evident. A higher content of PTFE probably leads to a more complete coverage of the carbon particles; consequently, the access of the alkaline electrolyte to the inside of the grain is more difficult. The macropores remain unaffected (compare Fig. 2). The dependence in Figs 2 and 3 at higher contents of the impregnating agent may, therefore, in the case of PTFE be interpreted as an example of blocking the microporosity, in the cases of PST and mainly PET of its direct killing. In other words: a carbon
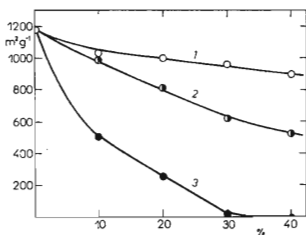
FIG. 2

Specific Surface Area of Carbon Structures *vs* Wetproofing Agent Quantity

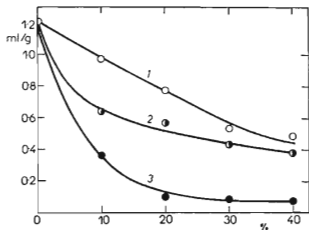Wetproofing agent: *1* PTFE; *2* PST; *3* PET.

FIG. 3

Influence of Impregnation of Carbon Structures on the Imbibition with Alkaline Electrolyte

Wetproofing agent: *1* PTFE; *2* PST; *3* PET.

structure bonded with PTFE consists of agglomerates of carbon and PTFE grains. Bodies wet-proofed with PET and PST are, on the contrary, agglomerates of carbon grains whose micro-porosity was killed to an extent, given by the quantity of the respective agent.

Fig. 4

Dependence Time–Imbibition of Carbon Structures

1 and *3* 10% and 30% PTFE; *2* and *4* 10% and 30% PST; *5* and *6* 10% and 30% PET.
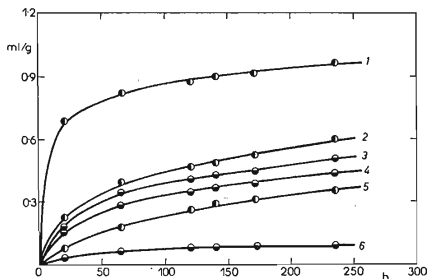
The imbibition curves (Fig. 4) show a steep initial rise which, however, gradually decays; this may be explained by the decrease in the amount of pores, accessible to the alkaline electrolyte. The mutual position of the individual curves corresponds to the aforementioned concept of the function of the individual impregnating agents.

It may be concluded that PTFE as a binding agent leaves the microporosity of the carbon virtually free and that this is, therefore, free for the distribution of the electrolyte throughout the electrode. From the electrochemical standpoint it means that this electrode is capable of forming a rather long three-phase boundary, necessary for the high initial electrochemical activity. On the other hand, however, the unaffected microporosity may cause a rapid shift of the three-phase boundary from the electrolyte to the gas side of the electrode, which may result in drowning of the gas side of the electrode. The time stability of such an electrode has to be ensured by additional constructional arrangements which will be the subject of a forthcoming publication.

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