ELECTROCHEMICAL MEASUREMENTS AND SURFACE STUDIES ON ACID OXYGEN CARBON ELECTRODES BY THE USE OF THE ESCA METHOD

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Summary

Hydrophobic active carbon electrodes for the electrochemical cathodic reduction of oxygen in acid electrolyte were investigated electrochemically with respect to different ways of Teflon precipitation on the active carbon. The ESCA method was used to characterize the catalyst masses. Teflon in two different states on the active carbon was found by this method. These states have been related to Teflon particle size and are believed to influence the hydrophobicity. The hydrophobicity of the different electrodes controls the electrochemical performance and was found to be in agreement with that deduced from the ESCA measurements.

Introduction

The electrochemical performance of semihydrophobic carbon gas-diffusion oxygen and air electrodes in acid solution is controlled mainly by the electrocatalytic activity of the catalyst [1 - 6]. This performance is very complex and the position of the three phase boundary in the porous structure of the electrode is one of the most important controlling factors.

In this paper the results of investigations on the electrochemical behaviour of some carbon gas-diffusion electrodes are reported. The electrodes were prepared from the same active carbon catalyst and the same type of binding and hydrophobic agent which was dispersed onto the carbon in different ways. Current–voltage characteristics with both oxygen and air were studied and the extent of mass transport hindrance in the gas phase was estimated on the basis of $\Delta E(i)$ curves [2, 4, 6] obtained from these measurements.

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The electrochemical activity was correlated with the amount of electrolyte soaked into the electrode. To obtain additional information about the surface character of the solid catalyst–binder system, the ESCA method [7] was used.

This technique is element specific and also very surface sensitive [7]. The binding energies of the electrons in different states in an atom are determined by measuring the kinetic energies of the electrons expelled from the surface by the radiation and using E_{bind} = constant $- E_{kin}$ (where the constant includes the energy of the X-radiation and an apparatus constant). It has been shown [7] that the values of the core electron binding energies correlate rather well with the effective charge on the atoms under study. Furthermore the mean depth from which the electron "escapes" without any loss of energy (*i.e.* giving a sharp signal) is of the order of 10 - 50 Å.

Experimental

In all cases circular single-layer Teflon bonded carbon electrodes with 70 mg/cm^2 of a mixture consisting of 90% active carbon Norit NK + 10% Teflon were used. The projected area of the electrodes was 5 cm^2 and the thickness was about 1 mm.

Three different modes of Teflon treatment of the active carbon were used:

(1) 5 g active carbon Norit NK were stirred in 40 cm^3 water and the corresponding amount of 60% Teflon dispersion (Dupont 30-N) was added dropwise to this suspension. After filtering and rinsing the resulting mass was dried and milled.

(2) 5 g active carbon Norit NK were stirred in 10 cm^3 water and then the same procedure as in (1) was used.

(3) 5 g active carbon Norit NK were stirred in 40 cm^3 ethanol and then the same procedure as in (1) was used.

The electrodes were cold pressed with a gold grid as a current collector, using a pressing pressure of 400 kg/cm^2. The electrochemical measurements were performed in a half cell arrangement with 2.3 M H$_2$SO$_4$ as electrolyte. The potentials were measured against a Hg/Hg$_2$SO$_4$ reference electrode in the same solution and a Pt-wire served as a counter electrode. A slight gas overpressure of 15 cm H$_2$O was used. The electrodes were loaded with a constant current of 10 mA/cm^2 for about 16 h using pure oxygen and steady state current–voltage characteristics were then measured with oxygen and, after having obtained stable potentials, also with air. The amount of electrolyte soaked into the electrode was estimated by the difference in weight of the electrode before and after the electrochemical measurements.

The ESCA investigations were carried out on unused active mass which was pressed onto a copper net with a spatula in a layer of such thickness that the copper threads were not visible. The instrument used was an AEI ES 200 spectrometer using Al K$_\alpha$ radiation and a vacuum level of 10^{-8} Torr.

Results and Discussion

Electrochemical measurements

Figure 1 presents the current–voltage characteristics of oxygen electrodes using the three different modes of preparation of the active mass described above. In Fig. 2 the current densities corresponding to the potentials $E = -100$ mV and $E = -200$ mV are plotted against the amount of electrolyte soaked into the electrodes. A distinct difference between the behaviour of the three types of electrodes is visible in Figs. 1 and 2. The higher the amount of electrolyte soaked into the electrode the higher is the electrochemical performance of the oxygen electrode. Figure 3 shows the $\Delta E(i)$ curves calculated from Fig. 1 and from the corresponding current–voltage characteristics obtained using air instead of oxygen. Electrodes in which the catalyst–binder mixture was prepared according to method (3) (ethanol treatment) show a distinct difference compared to the electrodes of types (1) and (2) for current loads greater than 5 mA/cm^2. This indicates a high gas transport hindrance for electrodes of type (3) which is probably caused by the relatively high amount of electrolyte soaked into the electrode, thus decreasing the gas-supplying porous part of the electrode [8]. On the other hand, the Teflon treatments (1) and (2) have no noticeable effect on the rate of gas transport.
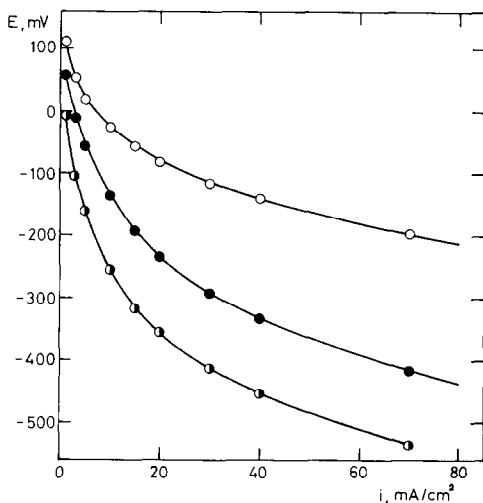

Fig. 1. Current–voltage characteristics of oxygen electrodes using three different modes of Teflon treatment of the active carbon. ◑, Mode 1; ●, mode 2; ○, mode 3.

ESCA investigations

The results are shown in Table 1 where the electrochemical results and the corresponding amount of electrolyte soaked into the electrodes are also included. Typical ESCA spectra are presented in Figs. 4 and 5. In the latter figure the expanded spectra of the fluorine 1s signals are shown.
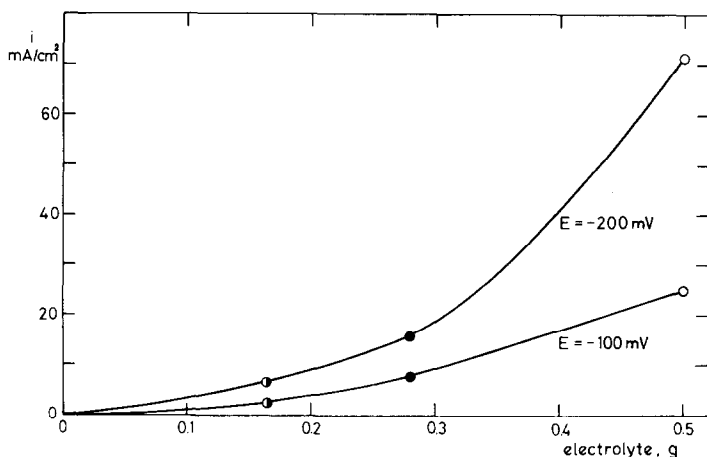
Fig. 2. Current densities at potentials $E = -100$ mV and $E = -200$ mV as a function of the amount of electrolyte (g) soaked into the electrode. ◑, Mode 1; ●, mode 2; ○, mode 3.
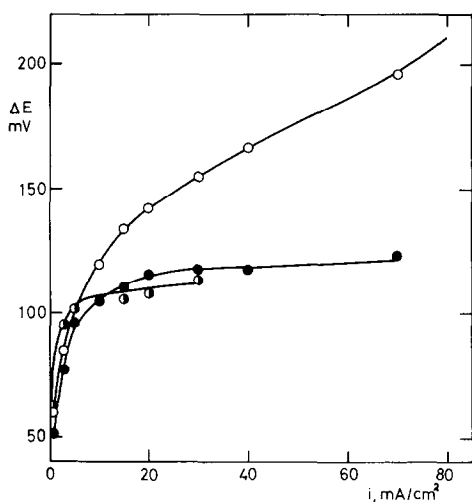

Fig. 3. $\Delta E(i)$ curves calculated from oxygen (Fig. 1) and air curves. ◑, Mode 1; ●, mode 2; ○, mode 3.

One notices at once that two fluorine 1s signals are found corresponding to two types of Teflon in the electrodes. Also the carbon signal of high binding energy corresponding to the highly positive carbon in Teflon is found doubled in the spectra.

The reason for the existence of the two signals is not quite clear. Although other explanations might be offered, e.g. some kind of specific interaction between the Teflon and the graphite structure of the active carbon, we presently favour an interpretation based on the proposed existence of two types of Teflon particles in contact with the active carbon particles.

It is well known that the charging of an insulating sample by X-ray bombardment causes the recorded energies to shift. Therefore all spectra

TABLE 1

Comparison of the ESCA data and the electrochemical activities

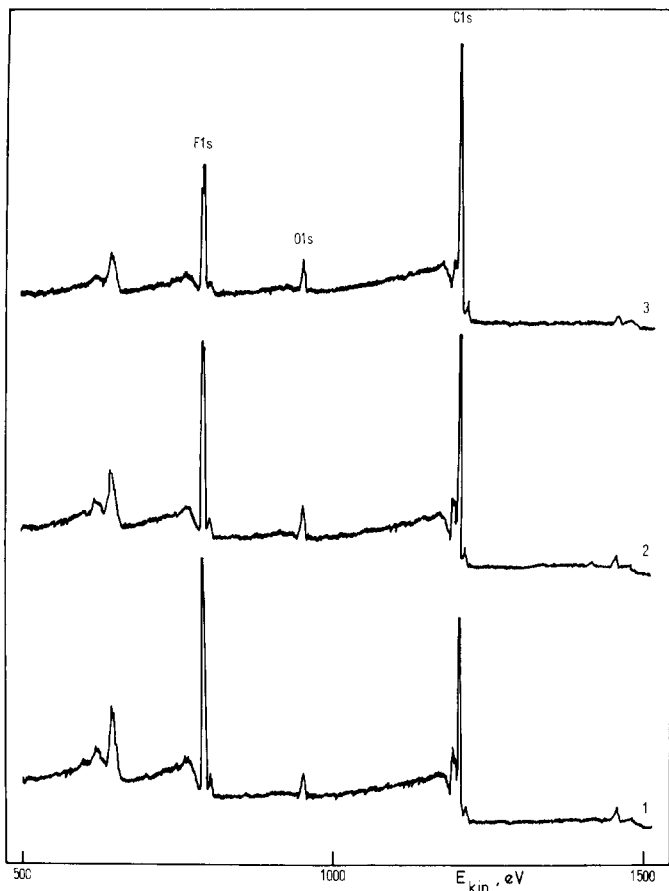| Mode of treatment with Teflon	Binding energies (eV)			Ratio of peak intensities		Current density of oxygen electrodes (mA/cm^2) at $E = -200$ mV after 16 hours operation at 10 mA/cm^2	Amount of electrolyte (g) soaked into the electrode
	F_{1s}^1	F_{1s}^2	C_{1s}	$\dfrac{F_{1s}^1}{F_{1s}^2}$	$\dfrac{F_{1s}^1 + F_{1s}^2}{C_{1s}}$		
1	691.7	689.0	284.5	1.38	1.95	6.7	0.165
2	691.7	689.0	284.5	1.24	1.52	15.7	0.280
3	692.2	688.8	284.5	0.91	0.85	71.7	0.501

Fig. 4. ESCA spectra of the different samples. The binding energies $E_{bind} = 1484.1 - E_{kin}$ (the numbering of the samples refers to Table 1).

except those for perfectly conducting samples have to be calibrated against some suitable standard. In our case this standard is the carbon signal of the highest intensity (binding energy 284.5 eV, Table 1). Because of its intensity it must correspond to the active carbon of the carbon electrode.

We can suggest then that one of the F_{1s} signals is due to small Teflon particles, thus in close contact with the active carbon (F_{1s}^2) and not very "charged". The other signal (F_{1s}^1) should then correspond to larger Teflon beads. The surface visible for the X-radiation of these beads is thus far away from the active carbon particles and consequently this Teflon is liable to become charged by the radiation.

This interpretation is in accordance with the finding that Teflon precipitated as a "thin layer" on blank platinum exhibits a binding energy, 689.0 eV, close to the lowest one under discussion here (F_{1s}^2). In this case the calibration signal is that of C_{1s} due to "pump oil" adsorbates on the sample (binding energy 285.0 eV). This C_{1s} binding energy differs by 0.5 eV from the value of
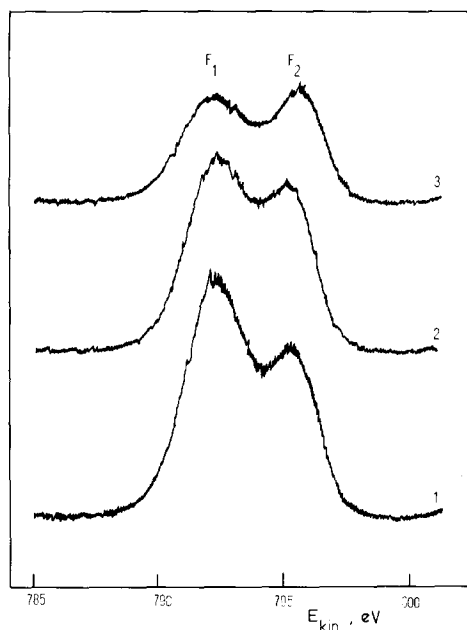
Fig. 5. Expanded ESCA spectra of the fluorine 1s signals (the numbering of the samples refers to Table 1).

the active carbon used as a calibration signal above (284.5 eV, Table 1), which can be explained by structural differences between these two kinds of reference substances. It is also rather probable that the Teflon bead signal F_{1s}^1 should have a positive shift of the binding energy as the isolated beads are most reasonably positively charged by loss of electrons.

Using different modes of Teflon deposition different sizes of Teflon particles and contacts to active carbon particles are to be expected. When using water treatment a large amount of small Teflon particles is probably spread over the outer surface of the active carbon particles. This should result in a high value of the $(F_{1s}^1 + F_{1s}^2)/C_{1s}$ ratio, especially when excess of water is used as is actually found (Table 1). The use of ethanol, on the other hand, suppresses the influence of the stabilizer in the Teflon dispersion and increases the tendency of the Teflon particles to coagulate, thus forming big isolated beads (F_{1s}^1). The bigger these beads the smaller is their surface giving the ESCA signals. If the only effect of the change in preparation is the coagulation into bigger beads one would expect an increase in free carbon surface and a smaller F_{1s}^1 signal compared to that from Teflon in close contact with carbon (F_{1s}^2) resulting in an increase of the carbon signal intensity relative to the fluorine signals intensities and a decrease of the ratio F_{1s}^1/F_{1s}^2. This is actually observed (Table 1).

Conclusions

The results presented in Figs. 1 and 2 and Table 1 show that the improvement of the electrochemical activity is accompanied by a rise in the amount of electrolyte soaked into the electrode and by a decrease in the F_{1s}^1/F_{1s}^2 and $(F_{1s}^1 + F_{1s}^2)/C_{1s}$ ratios. This means that an increase of free carbon surface leads to more hydrophilic properties of the electrode surface. Figure 3 shows moreover a corresponding negative effect on the rate of mass transport from the gas side. This also is in agreement with our interpretation that the ethanol treatment leads to bigger Teflon beads. Thus the ethanol treatment has a beneficial effect on the position of the three phase boundary in the oxygen electrode, but a negative effect on the transport rate when air instead of oxygen is used.

We find it interesting and stimulating that the ESCA method can be used to supply information for the description of surfaces of electrochemically important solids. Work is in progress to study electrodes of other types of active carbon materials.

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