INFLUENCE OF COMPOSITION ON THE ACTIVITY OF TUNGSTEN CARBIDE GAS DIFFUSION HYDROGEN ELECTRODES

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Summary

Efforts were aimed at full utilization of tungsten carbide in double-layer electrodes operating on hydrogen in sulphuric acid. By varying the proportions of WC:PTFE:active carbon:NH_4Cl, a current density of 580 mA/g of the catalyst was obtained with an electrode consisting of 180 mg/cm^2 WC, 14 mg/cm^2 PTFE, 10 mg/cm^2 carbon and 10 mg/cm^2 NH_4Cl at 350 mV (R.H.E. in the same solution) and 60 °C. The addition of NH_4Cl as a pore forming agent had a beneficial effect on the activity of the electrodes. The electrodes had a service of 2000 hours.

Introduction

In a previous paper [1], efforts were made to prepare a gas diffusion anode with a tungsten carbide catalyst operating without hydrogen over-pressure in sulphuric acid. The result of the study were electrodes yielding 400 mA/g of tungsten carbide at 350 mV (S.H.E.) and 60 °C. However, it was found that only a part of the catalyst took part in the reaction. Consequently, the work reported here was devoted to finding conditions for complete utilization of the catalyst.

Experimental

Tungsten carbide preparation

Tungsten carbide was prepared by reducing and carburating blue oxides of tungsten (W_4O_{11}). The first step involved treatment at 600 °C with hydrogen for 2 hours (flow rate 30 l/h) and the second treatment at 750 °C with carbon monoxide for 2.5 hours (flow rate 50 l/h). The composition of the

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product was monitored by X-ray diffraction and chemical analysis. X-ray analyses showed that complete carburization had taken place and no traces of tungsten or its oxides remained. Chemical analyses showed slight variations in the composition: there was a deficiency in carbon (4.2 - 5.2% against 6.1% for stoichiometry) although free carbon was always present in minor quantities (<0.3%). Oxygen was sometimes present in quantities below 0.1% (probably in the form of a surface oxide and/or as oxygen filling up carbon vacancies in the tungsten carbide lattice [2]). The particle size distribution was determined by a Sartorius sedimentation balance [3] (aqueous medium with 0.05% detergent added for complete dispersion) and showed that more than 50% of the particles were <1 μm equivalent Stokes diameter. Surface area was determined using a BET method employing adsorption of nitrogen and was found to have a value between 12 and 16 m^2/g.

Electrode preparation and characterization

Double layer electrodes were prepared to ensure a stable position of the three phase boundary. The gas supplying layer consisted of Teflonized carbon black (60 mg/cm^2 acetylene black P 1042, GDR) containing 35 wt.% of PTFE (Hostaflon TF 31). This layer had been used before [4] for oxygen electrodes as it is highly permeable to gases but practically impermeable to electrolytes. The active layer consisted of the catalyst, PTFE and active carbon (Norit NK) with or without NH_4Cl (AR grade, fractionated to 20 - 40 μm) added as pore-forming agent. In order to obtain a homogeneous mixture, the carbon was first treated with PTFE dispersion, dried and finally mixed with tungsten carbide (and NH_4Cl). The electrodes were cold-pressed under a pressure of 250 kg/cm^2. Electrodes containing NH_4Cl were heated to 300 °C for 1 hour to decompose the chloride. The composition of the active layer was varied by keeping the quantities of any two/three of the components constant and gradually increasing that of the third/fourth. Detailed data are given in the Tables and Figures. The exposed geometrical area of an electrode was 2 cm^2. Pore size distribution was measured on a mercury high pressure porosimeter (Carlo Erba) over the range 7500 - 7.5 nm; total porosity was calculated from the true and apparent densities which were determined pycnometrically in toluene and mercury. The volume of electrolyte containing pores was calculated from the increase in weight after the electrode had been operating at a current density of 30 mA/cm^2 for 8 hours.

Activity measurements

The activity of the electrodes was estimated by comparing potentiostatic polarization curves obtained in 4.5 N H_2SO_4 at 60 °C. Potentials are reported against a Giner hydrogen reference electrode [5] in the same electrolyte; current densities, if not stated otherwise, at 350 mV. A lead counter electrode was used. Experiments were performed in an electrolytic cell made of acrylic glass with a tantalum ring pressed to the electrode to collect the current. The cell was water-jacketed for temperature control.

Results and Discussion

Preliminary investigations showed that electrodes containing 30, 45 and 60 mg/cm^2 of tungsten carbide with only PTFE and catalyst in the active layer display poor characteristics. A substantial improvement was observed when active carbon was added to the active layer. In this case it was established that the activity of the electrodes increases with the amount of the catalyst up to a composition of 60 mg/cm^2. This observation leads to this amount of catalyst being taken as a standard in studies into the optimization of electrode structure. The amounts of active carbon and PTFE were separately changed in two experimental runs.

For given amounts of other components, an increase in the amount of active carbon results in an increase in the current density (Fig. 1). The latter passes through a broad maximum within the active carbon concentration range 14 - 21 mg/cm^2, which is very well defined at higher polarizations. This effect is probably due to increase in the extent of the three-phase boundary when the catalyst is mixed with Teflonized carbon aggregates two orders of magnitude larger in size than the individual catalyst particles. If tungsten carbide is distributed during mixing on the surface of these aggregates, a structure will develop which will ensure the contact of the catalyst with (i) the electrolyte (through part of the carbon micropores which are hydrophilic), and (ii) the gas phase (via the pores formed by PTFE and the gas
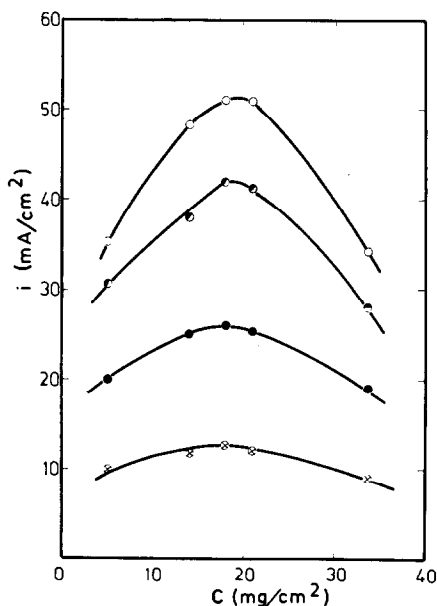

Fig. 1. Dependence of current density on the quantity of carbon in the active layer at constant quantities of tungsten carbide (60 mg/cm^2) and PTFE (14 mg/cm^2).Polarization: ⊗, 100; ●, 200; ◑, 300; ○, 350 mV (R.H.E.).

TABLE 1

Influence of carbon content on the nature and activity of double layer electrodes

Composition of active layer WC/PTFE/C (mg/cm^2)	Thickness (mm)	Pore volume (%)			Activity (mA/cm^2) at 350 mV (R.H.E.)
		Gas (A)	Electrolyte (B)	Ratio (B/A)	
60/14/ 0	1.15	0.39	0.08	0.20	22
60/14/ 5	1.2	0.27	0.10	0.37	34.6
60/14/14	1.4	0.16	0.19	1.19	47.5
60/14/18	1.5	0.10	0.17	1.7	52
60/14/21	1.55	0.10	0.26	2.6	51
60/14/33	1.7		0.61		34

pores in the active carbon which are very active although restricted in number). A better distribution of the gas in the active layer when the carbon content is increased is suggested also by the fact that the maximum in current density is distinct at high gas consumption, *i.e.* high polarization (Fig. 1). A further increase in the content of active carbon induces, however, a decrease in the current density. This is evidently due to the fact that the number of electrolytic pores increases at the expense of gas pores until, eventually, all pores contain electrolyte and there are no channels free to distribute gas (see Table 1). In addition, an increase in active carbon content also leads to a deterioration in the mechanical strength of the electrodes.

A current density maximum is also observed when the PTFE content is varied (Fig. 2). The maximum is very sharp at all polarizations (cf. Figs. 1 and 2). The same dependencies can be obtained when the active layer does not contain active carbon. In this case, however, the maximum in the dependence i (mA/cm^2)/PTFE (mg/cm^2) is considerably lower (31 mA/cm^2 at 350 mV polarization for the active layer-composition 60 mg WC and 6 mg/cm^2 PTFE). Because of this the influence of PTFE content on their nature and activity has not been investigated for this series of electrodes. Table 2 shows that at small PTFE contents, the electrode pores are flooded (the ratio of electrolyte to gas pores is 5.29) whilst at PTFE concentrations above the optimum value, contact between electrolyte and catalyst is hindered (the ratio of electrolyte to gas pores falls to 0.41). It appears that to obtain a satisfactory performance, the volume of electrolyte pores should be approximately equal to that of gas pores, which is in fair agreement with theory [6].

An effort to correlate the efficiency of the electrodes with their pore size distribution met with failure. Porosimetric curves were poorly reproducible and enabled only qualitative information to be obtained for the structural changes in the active layer when the relative ratios of the components were altered. The difficulties encountered in porosity measurements probably reflect the fact that the active layer comprises materials with quite different wetting angles. Owing to this, the penetration of mercury into the pores is non-uniform, and it is very difficult to decide whether the changes
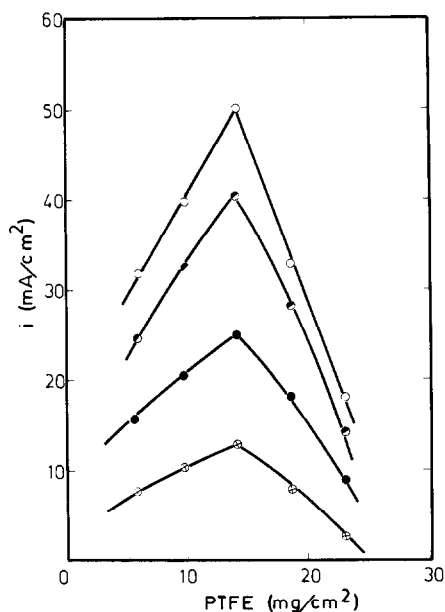
Fig. 2. Dependence of current density on the quantity of PTFE in the active layer at constant quantities of tungsten carbide (60 mg/cm^2) and carbon (18 mg/cm^2). Polarization: ⊗, 100; ●, 200; ◐, 300; ○, 350 mV (R.H.E.).

TABLE 2

Influence of PTFE content on the nature and activity of double layer electrodes with carbon in active layer

Composition of active layer WC/PTFE/C (mg/cm^2)	Thickness (mm)	Pore volume (%)			Activity, (mA/cm^2) at 350 mV (R.H.E.)
		Gas (A)	Electrolyte (B)	Ratio (B/A)	
60/ 6/18	1.45	0.07	0.37	5.29	32
60/10/18	1.5	0.230	0.17	0.74	38.6
60/14/18	1.5	0.10	0.17	1.7	52
60/18/18	1.55	0.26	0.15	0.58	32.4
60/22/18	1.6	0.32	0.13	0.41	18.4

in the slopes of porosimetric curves reflect wetting difficulties or increase in the volume of pores of a given size. Some general conclusions, however, are possible. When tungsten carbide and PTFE are the only components of the active layer, pore dimensions are distributed within the narrow range 0.08 - 0.4 μm, but when active carbon is added, smaller pores (0.03 - 0.04 μm) are formed. It can be seen in Table 1, that this leads to an increase of the number of electrolyte containing pores; hence the development of a three phase interface is enhanced.

The increase of PTFE content while the catalyst and active carbon concentration remains constant causes a corresponding increase in the number of the larger pores (0.1 - 0.6 μm). Since these hydrophobic pores have a relatively large volume, a slight change in their number causes a significant change in the ratio of the gas to electrolyte pore volumes, *i.e.* changes in the gas delivery rate and the distribution of the electrolyte in the active layer. This may explain the fact that small changes in the amount of PTFE cause substantial differences in current density values (Fig. 2).

Increase in tungsten carbide content up to 120 mg/cm^2 for a fixed tungsten carbide/PTFE/active carbon ratio within the optimum figures (optimum structure) did not result in any increase in activity (55 mA/cm^2 as compared to 52 mA/cm^2 for an electrode with 60 mg/cm^2 tungsten carbide). The reason lies probably in transport difficulties induced by the increase in the thickness of the active layer. Efforts were, therefore, made to reduce the thickness by decreasing the amount of PTFE and active carbon. This, however, had an unfavourable effect on the optimum structure, and as shown in Table 3, did not solve the problem. To improve gas distribution and to reduce ohmic losses in the electrolyte pores, NH$_4$Cl was added to the active layer and, as was shown by porosimetric measurements, pores within the range 1 - 10 μm were thus formed. The effect on the electrochemical behaviour was substantial, as can be seen in Fig. 3. The performance of the electrodes increased with the content of NH$_4$Cl. Unfortunately, concentrations >6 mg/cm^2 had to be avoided because of subsequent deleterious effects upon the mechanical properties of the electrode.

Similar difficulties were encountered when the catalyst content was increased to 180 mg/cm^2. In order to obtain the best voltage–current characteristics, it was necessary to decrease the amount of active carbon from 18 to 6% and that of PTFE from 20 to 8%, but to raise the content of NH$_4$Cl from

TABLE 3

Influence of PTFE and carbon content on the activity of double layer electrodes

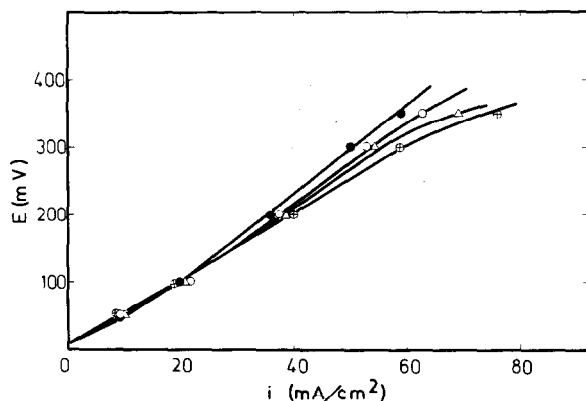| Composition of active layer, WC/PTFE/C (mg/cm^2)	Activity, (mA/cm^2) at 350 mV (R.H.E.)
120/28/9	33
120/28/18	36
120/28/22	40.5
120/28/28	41
120/28/32	36
120/28/36	34
120/18/22	50.5
120/22/22	52.5
120/24/22	60
120/28/22	40.5

Fig. 3. Influence of pore forming agent on current–potential curves. Electrode composition: 120 mg/cm^2 tungsten carbide, 24 mg/cm^2 PTFE, 22 mg/cm^2 carbon; ●, 0; ○, 2; △, 4; ⊗, 6 mg/cm^2 NH$_4$Cl in the active layer.
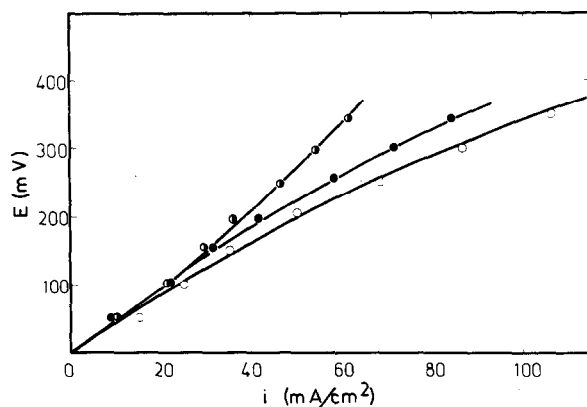

Fig. 4. Influence of pore forming agent on current–potential curves. Electrode composition: 180 mg/cm^2 tungsten carbide, 14 mg/cm^2 PTFE, 10 mg/cm^2 carbon; ◑, 0; ●, 5; ○, 10 mg/cm^2 NH$_4$Cl in the active layer.

5 to 6% (10 mg/cm^2). With this amount of catalyst in the active layer addition of NH$_4$Cl results in a considerable improvement of the voltage–current characteristics (cf. Figs. 3 and 4). These electrodes yielded 580 mA/g of tungsten carbide at 350 mV polarization (Fig. 4); the value for 200 mV polarization (306 mA/g) compares well with the values reported by Böhm [7, 8] (320 mA/g) and is higher than those of Mund [9] (200 mA/g) and Palanker [10] (150 mA/g). During long-term investigations the electrodes operated on hydrogen without overpressure up to 2000 hours without a noticeable decrease of activity.

Conclusions

To prepare an efficient tungsten carbide electrode, the addition of active carbon as an electrolyte carrier proved to be of advantage. In electrodes containing >60 mg/cm^2 of the catalyst, a gas pore forming agent had to be employed to form a network of large pores for effective gas distribution in the electrode active layer.

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