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MICROGRAVIMETRIC PREPARATION AND CHARACTERISATION OF CATALYST CANDIDATES FOR FUEL CELL ELECTRODES*

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ABSTRACT

In the search for noble-metal-free cathode materials resistant to acid electrolytes and capable of catalysing the conversion of oxygen, thermogravimetric methods have been used to determine the conditions of preparation, to analyse the chemical properties, and to characterise the pore structure of the potential catalysts. The paper comprises results of investigations on inorganic compounds, such as ammonium tungstates, chromates, vanadates, molybdate and permanganate, and on organic polymers, such as polyamide nitriles, other CN polymers and polyacenoquinone pyrolysates.

1. INTRODUCTION

Catalytically active materials for fuel cell electrodes have to be electrically conductive and corrosion-resistant. So far these requirements are fulfilled satisfactorily only by noble metals which, however, are unsuitable for extensive use for reasons of price and availability. In view of this situation, a research project conducted at Battelle-Frankfurt[1] covered different materials free from noble metals which were hoped to be suitable as cathode catalysts for oxygen reduction. The investigations were based on thermogravimetric methods on a microscale and were aimed at determining the conditions of preparation, analysing the chemical properties, and characterising the pore structure of the catalyst candidates.

2. MEASURING METHODS AND APPARATUS

2.1 *Thermogravimetry*

Thermogravimetry was applied for the

(i) chemical characterisation of the substance partly in comparison with literature data by the TG-method under vacuum or under inert gas with the temperature rising linearly.

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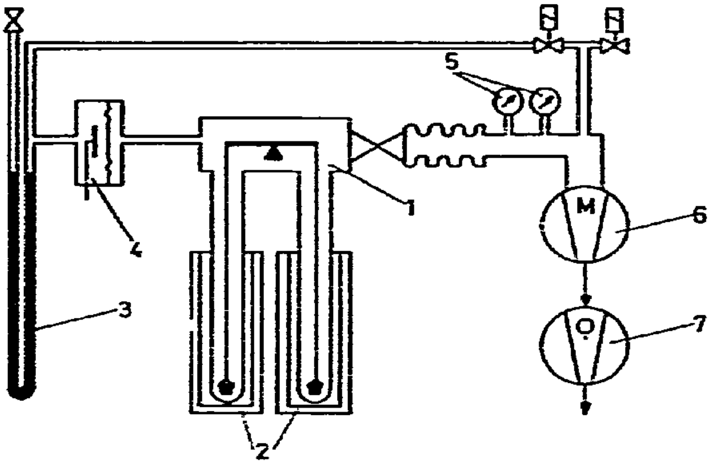

Fig. 1. Schematic drawing of thermogravimetric apparatus. 1 = Gast microbalance; 2 = heaters; 3 = mercury U tube manometer; 4 = diaphragm manometer; 5 = vacuum gauges; 6 = turbo-molecular pump; 7 = backing pump.

(ii) the evaluation of preparation conditions of such substances. For this purpose, the weight loss of the sample was observed with the temperature rising linearly and then at constant temperature. A temperature value within a defined range was chosen as the preparation temperature at which the weight of the sample did not change over an extended period of time after completed conversion of the substance. In a few cases, the substance prepared in the pan of the scales could be worked up directly to an electrode; more frequently, however, the catalysts were prepared separately in an oven on the basis of the temperature values chosen as described above.

The experiments were carried out in two different units; the apparatus shown schematically in Fig. 1 was equipped with a Sartorius microbalance after Gast with a sensitivity of 1 μg. A turbomolecular pump produced a vacuum of 10^{-5} Pa. Pressure measurements were performed with ionisation Pirani- and diaphragmmanometers. Using a control device with cam plate, the different ovens were controlled[14] so that a linear temperature rise of 9.4 K h^{-1} was obtained. The actual temperature of the sample was calculated by calibration from the temperature measured in the oven. In most experiments, the sample mass was 50 mg.

For routine measurements we used the DuPont instrument 950 TG. The sensitivity of the instrument is 50 μg. The temperature was increased at different rates, the lowest being 120 K h^{-1}. In all experiments, the sample was kept in an inert gas atmosphere.

2.2 *Sorption measurements*

In addition to the area of the surface in contact with the electrolyte the pore radius is one of the main electrode parameters. The pores have to be large enough to enable the transport of both the reacting species and the reaction products. The

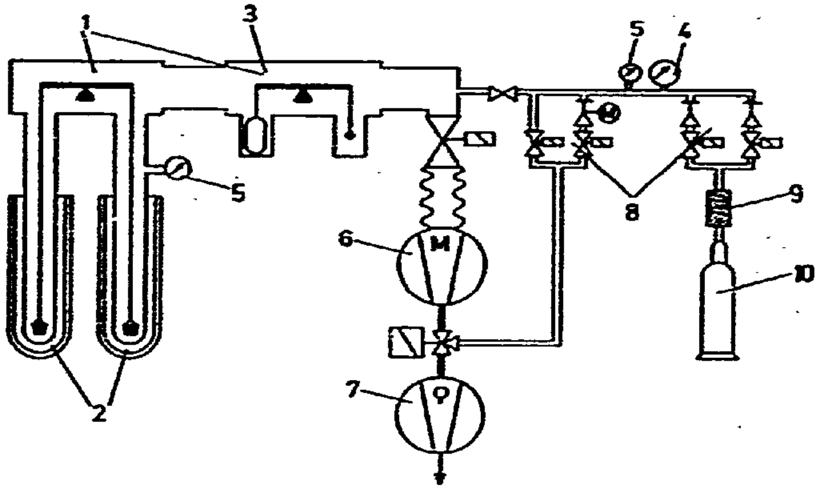

Fig. 2. Schematic drawing of gravimetric sorption apparatus. 1 = Gast microbalance; 2 = Dewar vessels; 3 = buoyancy manometer; 4 = diaphragm manometer; 5 = vacuum gauges; 6 = turbomolecular pump; 7 = backing pump; 8 = pressure control; 9 = gas scrubber; 10 = nitrogen vessel.

kinetics of the electrode reaction and thus its efficiency under load as well as the limits of performance can be influenced drastically by transport processes in the pores[12]. An external electric field is distorted when penetrating into the interior of the electrode as a function of pore size. For this reason, we carried out measurements of specific surface area and pore size.

In previous investigations of platinum electrodes[3], we found good correlation between the specific surface area according to the BET method and the electrocatalytic activity of the electrode. From this finding, we derived an electrochemical method for surface area measurement[3]. In addition, we observed that a change in electrode activity is accompanied by a change in the specific surface area and also by a change in the pore system.

For surface area and pore size analysis, an instrument* as shown in Fig. 2 was used. The instrument comprises two Sartorius microbalances, one for weighing, the second as buoyancy gauge for pressure measurement and control. Sample and counterweight are cooled by liquid nitrogen whose temperature is measured using thermistor and vapour pressure gauges. The apparatus described elsewhere[5] performs automatically the stepwise isobaric measurement of complete adsorption and desorption nitrogen isotherms.

For these investigations, the gravimetric method of sorption measurement has the advantage that degassing of the sample can be controlled by observing the weight loss. Degassing of microporous materials is a slow process and as it is confirmed by gravimetry that degassing is complete, vaporisation and decomposition by thermal treatment of the sample can be avoided.

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* The instrument developed at Battelle-Frankfurt[4] is manufactured under the trade name "Gravimat" by Netzsch Gerätebau, Selb, F.R.G.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 *Thermogravimetric decomposition*

The methods described in the foregoing were used to investigate ammonium tungstates, chromates, vanadates, molybdate and permanganate. Typical degradation curves with the plateaus are shown in Fig. 3. A very slight weight loss observed below 150°C in case of the chromates was neglected because it was due to evaporated water traces. For comparison, the chromate curve referring to the literature values known[11] is reproduced in Fig. 3. A plateau was measured for the acid tungstate at a temperature range of 130 to 240°C, for the neutral tungstate at 150 to about 210°C. All the tungstate decomposition products were soluble in dilute sufuric acid and are not suitable for the intended purpose.

Ammonium permanganate gave an insoluble oxidic substance which decomposes by explosion at temperatures ≥ 80°C if the temperature was raised at a rate higher than 10 K h^{-1}.

Since ammonia containing inorganic species is entirely unsuitable as a catalyst

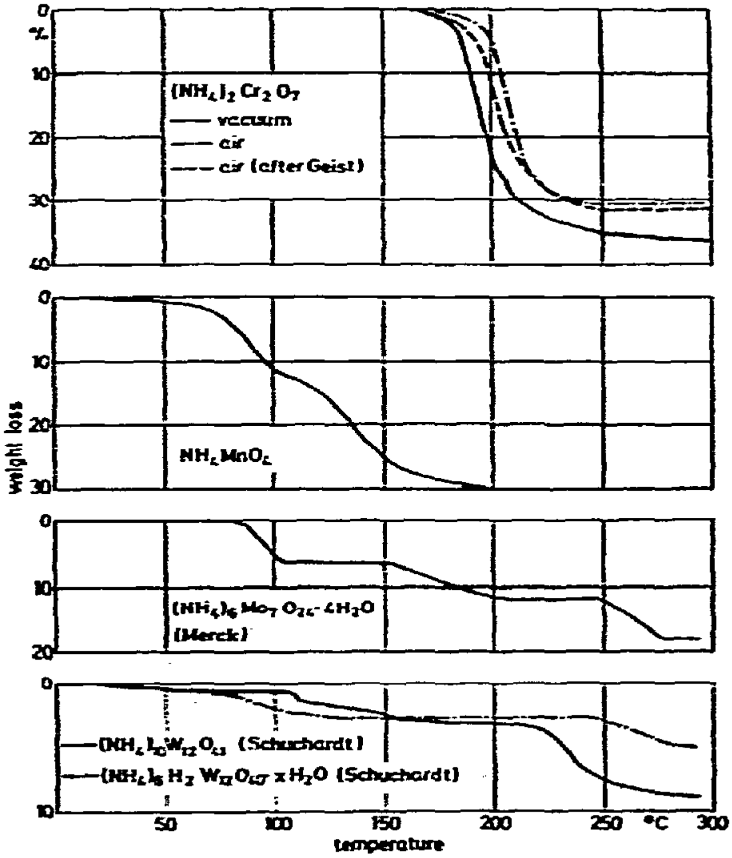

Fig. 3. Thermograms. Temperature increase 9.4 K h^{-1}. (Curve for comparison in Fig. 3a after Geist[11].)

TABLE 1

SURFACE AREA AND PORE SIZE CALCULATED FROM SORPTION MEASUREMENTS OF POLYACENOQUINONE PYROLYSATES

Subst. No.	*Grain size (µm)*	*Specific surface area ($m^2\,g^{-1}$)*			*Specific pore (mm^3g^{-1})*	*Porosity*	*Mean pore (nm) width*	*Most frequent pore width (nm)*	
		BET	*Cumulat*					*Cyl. model*	*Slit model*
			Cyl model	*Slit model*					
5034	<85	460	61	46	353	0.41	1.5	1.2/2.0	1.5/2.0
5041	<32	899	392	263	590	0.54	1.3	1.3	1.2/2.0
	32–85	520	120	78	306	0.38	1.2	1.0	1.2
5042	<32	424	83	55	265	0.35	1.3	1.0	1.2
	32–85	370	71	46	233	0.32	1.3	1.0/2.0	1.2/2.0
5045	32–85	857	118	96	532	0.52	1.2	1.2/2.0	1.5/2.0
5167	32–43	494	60	42	285	0.36	1.2	1.2	1.2/1.5
5203	<85	774	401	189	497	0.50	1.3	1.2/2.0	1.5/1.7
	<85	812	137	86	477	0.49	1.2	1.2/2.0	1.2

after thermal treatment, we tried the thermal degradation of organic polyamide nitrile. Nearly no weight loss was encountered at temperatures up to 400°C; even at 1000°C more than 30 percent of the starting weight was retained. The pyrolysate showed some catalytic activity which, however, was not high enough for practical application.

3.2 *Discussion of surface area and pore structure*

By means of gravimetric sorption measurements, specific surface area and pore structure of the thiospinel $FeCo_2S_4$[6] and a number of polyacenoquinone pyrolysates (PAC) were determined. The PAC samples used in the investigation were all sieved to obtain particle diameters below 85 µm. Some of the substances were examined using a narrow grain size fraction, see Table 1.

The calculations were made by a computer routine[7]; the surface area calculations were based on three different methods:

(i) The BET method (calculation of multilayer adsorption).

(ii) The *t*-method: this is based on the BET formalism comparing the slope of a transformed isotherm (the thickness of the adsorbed nitrogen layer is used as abscissa) with a standardized isotherm of non-porous material (Fig. 5). The lack of universal standard isotherms for the different substances is a difficulty of this method.

(ii) The cumulative method after Cranston and Inkley[13] using both a cylindrical and a slit-shaped pore model as well the modelless method.

The values resulting from the cumulative calculation in almost all cases are remarkably smaller than the BET values. This is due to the fact that in the cumulative method only the surface area within mesopores is added up, whereas the BET values are influenced by the adsorption in micropores as well. We may thus conclude that

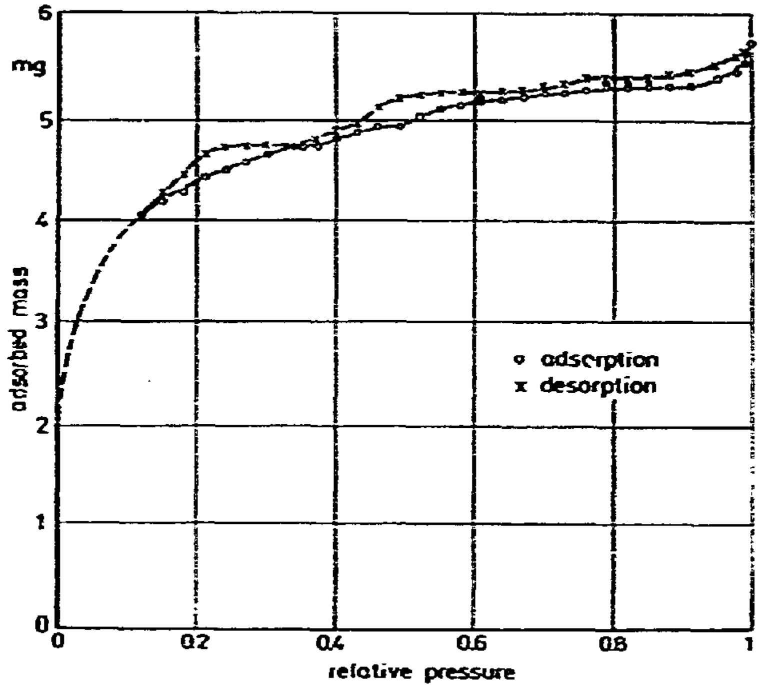

Fig. 4. Nitrogen adsorption isotherm of polyacenoquinone pyrolysate at 77.5 K.

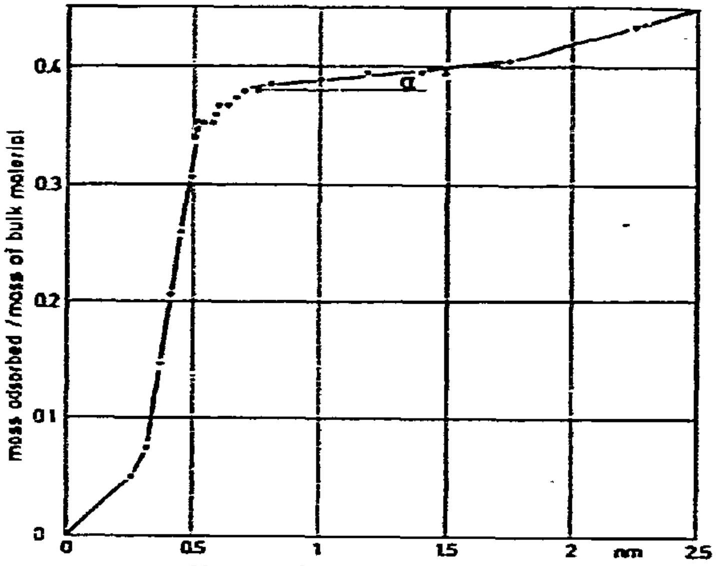

Fig. 5. *t*-plot corresponding to the isotherm in Fig. 4.

the substances have many micropores with pore width below 2 nm. The same result is found by the *t*-plot (Fig. 5) which shows a steep slope in the monolayer region. It should be noted that the BET calculation for microporous materials is somewhat doubtful[15].

TABLE 2

COMPARISON OF ELECTROLYTIC ACTIVITY FOR OXYGEN REDUCTION AND SPECIFIC SURFACE AREA OF POLYACENOQUINONE PYROLYSATES

No.	*Substance*			*Electrode*	
	Preparation NH_3 activation	*Resist. (Ω)*	*Specific BET surface area ($m\ g^{-1}$)*	*Rest potential (mV)*	*Potential at 20 ($mA\ cm^{-2}$)*
5034	900°C/30′	0.1	460	700/720	0
5042	1000°C/30′	0.05	424	880/910	0
5167	1000°C/30′		494	880	240
5041	1000°C/30′	0.05	899	880/920	590[a]
5045	1000°C/30′	0.17	857	870/960	660
5203	1000°C/30′		793 ± 20	960	720

[a] 545 mV after 600 h at 20 ($mA\ cm^{-2}$) operation.

Some of the isotherms (see Fig. 4) show distinct steps representing groups of energetically very different sites on a chemically or geometrically heterogeneous surface. The hysteresis of the isotherm shown extends to a relative pressure down to 0.2. In the case of rigid structures, no hysteresis is found at such a low value. Therefore, the pore structure may be expanded owing to adsorption between thin layers of the bulk material. The *t*-plot of that material (Fig. 5) indicates a substantial proportion of micropores (pore width below 2 nm) in the pore structure which is a common characteristic of all pyrolysate samples. The mean width is found to range between 1.2 and 1.5 nm for all polyacenoquinone pyrolysate (PAC) samples, the porosity being 0.32 to 0.54. The most frequent pore widths calculated according to the different theories are in the range of 1.0 to 2.0 nm for all samples; some of the samples show two maxima of the most frequent pore widths within this range.

The results at the surface area measurements are compared with the measurements of electrocatalytic activity of oxygen reduction in Table 2. Arranging the substances in the order of increasing electrocatalytic activity, measured by the electrode potential at a constant current density of 20 mA cm^{-2}, the PAC species of lower activity seem to possess the lower BET surface area, i.e., in the range between 400 and 500 $m^2\ g^{-1}$. The PAC samples of relatively high electrocatalytic activity (potential values exceeding 500 mV at 20 mA cm^{-2}) show the higher BET surface area of 800 to 900 $m^2\ g^{-1}$. Nevertheless, a factor of two between these surface area values (400/500 and 800/900 $m^2\ g^{-1}$) does not sufficiently explain the increase in current densities by more than a factor of 100 at constant potential. A high specific surface area seems to be a necessary but not a sufficient condition to reach high electrocatalytic activity of the porous three-phase oxygen electrode. Although the most active pyrolysates show the highest specific surface area, no clear physicochemical correlation between these two quantities has been derived.

Since the microporosity is nearly the same in different samples (Table 1), the transport processes might also be similar in both active and inactive PAC samples. The reaction rate of the molecular electrocatalytic reduction process and the existence of "active sites" should be the reason for the different activities. Some speculative models of the electrocatalytic oxygen reduction are described in the literature (e.g., refs. 8 and 9). It is suggested that adjacent carbon atoms with special substituents (e.g., quinone structure) may be suitable to bind oxygen. After the chemisorption and the consecutive electron transfer, the reduced (and negatively charged or protonated) oxygen molecule should be able to leave the chemisorption site. Different reaction pathways including hydrogen peroxide and water as reduction products will be considered separately[10].

Summarising the PAC results, it is pointed out that

(i) active PAC catalysts were obtained;

(ii) the high surface area and the pore sizes reported in the foregoing are necessary for a catalytic structure;

(iii) special active sites are assumed.

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