JOURNAL OF APPLIED ELECTROCHEMISTRY 2 (1972) 211–215.

The preparation and characterization of high performance Ag/C oxygen electrocatalysts

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Received 27 January 1972

The factors influencing the spatial distribution of metal catalyst on catalyst substrates have been investigated by studying the wettability, drying process and chemical interaction between the catalytic metallic salt solution and substrate, using $AgNO_3$/graphite as a model system. $AgNO_3$ reacts with graphite at temperatures above 100°C and hence very uniform dispersion of Ag on graphite is achieved by simple thermal treatment. On the other hand, for other systems which do not involve chemical reaction, such as H_2PtCl_6/graphite, freeze-drying gives better results. Teflon bonded electrodes prepared from impregnated catalysts containing 10% Ag on C gave 800mA/cm^2 at 0·84 V for the reduction of oxygen in 5 N KOH at room temperature.

1. Introduction

The increased use of precious and semi-precious metals in heterogeneous catalysis and electrocatalysis has necessitated the production of a great variety of supported catalysts. The main function of the catalyst substrate or support is to provide a structural framework for the catalytic component and to increase the surface area per weight of metal compared to the unsupported. metal. Other desirable effects may include (i) increased stability due to the small crystallites being sufficiently separated to prevent sintering; (ii) a greater resistance to poisoning; (iii) alteration of the catalyst structure to allow better mass transfer.

Supported catalysts are normally prepared by:

(a) Impregnation
(b) Co-precipitation
(c) Chemical reduction.

Most of the published literature and patent disclosures on the preparation of supported catalysts are specific to a particular combination of materials and are often empirical in nature.

In this paper, the fundamental factors governing the spatial distribution of catalyst on catalysts supports, prepared by the impregnation method, are studied in some detail. Ag/C catalysts were chosen as the 'model' system. These catalysts are widely used as cathode catalysts in metal/air batteries and alkaline fuel cells. In addition, a limited amount of work was done on a Pt/C catalyst.

2. Experimental

2.1. *Materials*

Graphite powder (~500 m^2/g) was obtained from a commercial source. Pyrolytic graphite was purchased from Le Carbone Ltd. Unless otherwise stated, all the other chemicals used in this investigation were of Analar Grade.

2.2. *Measurement of contact angle*

Since the first stage in the preparation of any supported catalyst usually involves the impregnation of the catalyst substrate by the metallic salt solution, followed by thermal treatment, it is important to ascertain whether the liquid phase (metallic salt solution or molten salt) wets the

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solid substrate. In the absence of wetting, the liquid phase cannot penetrate the pores of the catalyst substrate. The contact angle of the metallic salt solution and molten $AgNO_3$ on pyrolytic graphite was measured by the sessile drop method [1].

2.3. *Thermal treatment*

After impregnating the catalyst substrates with the metallic salt solution, they were either dried in an oven or by freeze-drying [2]. They were then thermally decomposed in a furnace. A Stanton thermogravimetric balance was used to investigate the kinetics of the decomposition process.

2.4. *Physical examination of the supported catalysts*

Since the Ag concentration is normally restricted to about 10%, B.E.T. nitrogen adsorption methods are not accurate enough to evaluate the surface area of the Ag crystallites with sufficient accuracy. It is difficult to use selective gas adsorption methods to get an accurate measurement of the Ag surface area, since the adsorption properties of silver and graphite are very similar. In the study of other supported catalysts, such as Pt/C, the selective adsorption of CO on Pt is used to evaluate the Pt black area [3].

On the other hand, electron microscopic examination is useful in evaluating the spatial distribution and size of the Ag crystallites in the supported catalyst, since the densities of Ag and graphite are significantly different from each other.

2.5. *Evaluation of catalyst performance*

The reduction of oxygen on graphite and carbon surfaces [4] has been shown to undergo the following steps, via the perhydroxyl route:

$$O_2\,(\text{ads}) + H_2O + 2e \rightarrow HO_2^- + OH^-$$

Carbon and graphite are inactive towards the decomposition of H_2O_2 and hence lead to inefficiencies. On the other hand, if H_2O_2 decomposition catalysts such as Ag or Pt are added to the graphite, the reaction will be:

$$HO_2^- + H_2O \rightarrow OH^- + H_2O_2$$

$$H_2O_2 \xrightarrow[\text{decomposition}]{\text{catalytic}} \tfrac{1}{2}O_2 + H_2O$$

Overall reaction $HO_2^- \rightarrow OH^- + \tfrac{1}{2}O_2$

The regenerated O_2 could then be re-used, resulting in improved efficiency.

A manometric technique based on the design of Cota *et al* [5] was used to study the kinetics of H_2O_2 decomposition. The tests were conducted at 25°C and atmospheric pressure. The H_2O_2 concentration was 0·25 M, prepared by diluting 5 ml of 2·5 M H_2O_2 into 45 ml of 5 M KOH. A small quantity of catalyst, typically 15 mg, was used in each run to prevent excessive heat generation during the H_2O_2 decomposition reaction. The rate of O_2 evolution was measured extrapolation of the results to zero time.

For the evaluation of their electrochemical performances the catalysts were mixed with Teflon (p.t.f.e.) dispersion and painted onto 100 mesh nickel screens to form Teflon bonded electrodes [6]. These electrodes were then cured at 300°C for 1 h and tested in a 'floating' half cell [7] in 5 N KOH, 25°C, 1 atmosphere O_2. The potential of the working electrode (versus a Dynamic H_2 electrode—DHE [8]) was regulated by a Chemical Electronics potentiostat and the I.R. drop between the working electrode and the tip of the Luggin capillary was measured by the interrupter technique [9].

3. Results and Discussion

3.1. *Contact angle measurements*

Contact angle measurements at room temperature confirmed that distilled water, 10% $AgNO_3$ and 10% H_2PtCl_6 wet pyrolytic graphite, giving contact angles (θ) of 70°, 72°, 73° respectively. Similar measurements for molten $AgNO_3$ on pyrolytic graphite gave the following results: in air, 210°C (melting point of $AgNO_3$)—70°, 250°C—45°, 300°C—15°; in N_2, 210°C—95°, 250°C—90°, 300°C—30°. Fig. 1 shows the final distribution of Ag salt on a pyrolytic graphite plate after heating a 1% $AgNO_3$ droplet at 300°C in air for ½ h, revealing that Ag is very uniformly dispersed on the pyrolytic graphite surface.

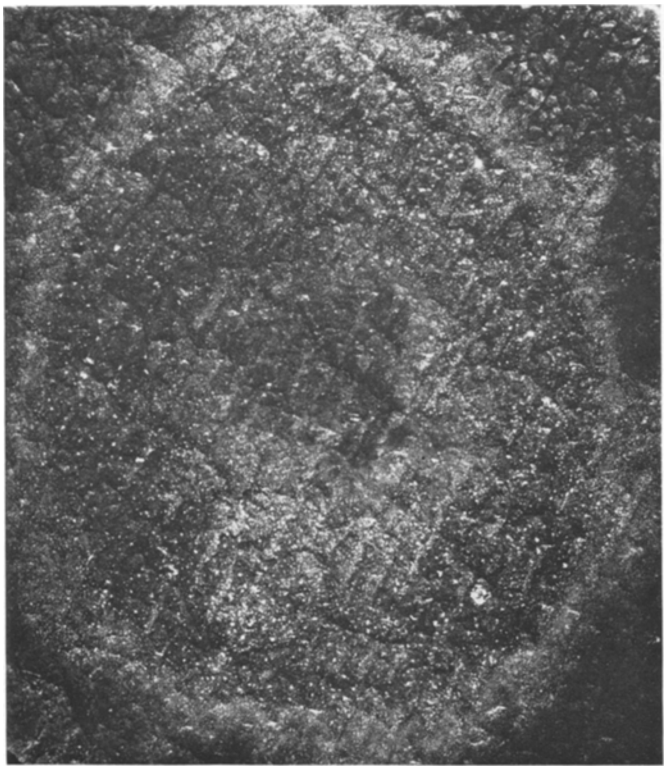
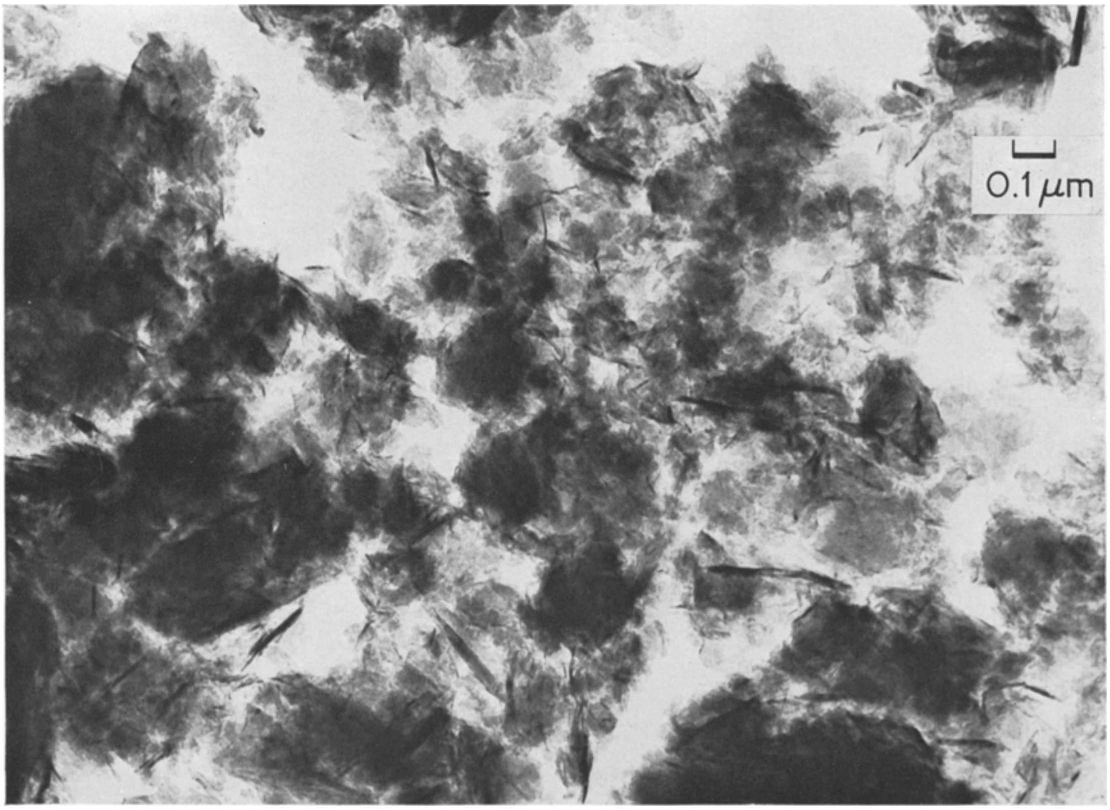


Fig. 1. Distribution of Ag salt on a pyrolytic graphite plate after heating a 1% $AgNO_3$ droplet at 300°C in air for ½ h (×10).



Figs 1 *and* 3 *between pp.* 212 *and* 213

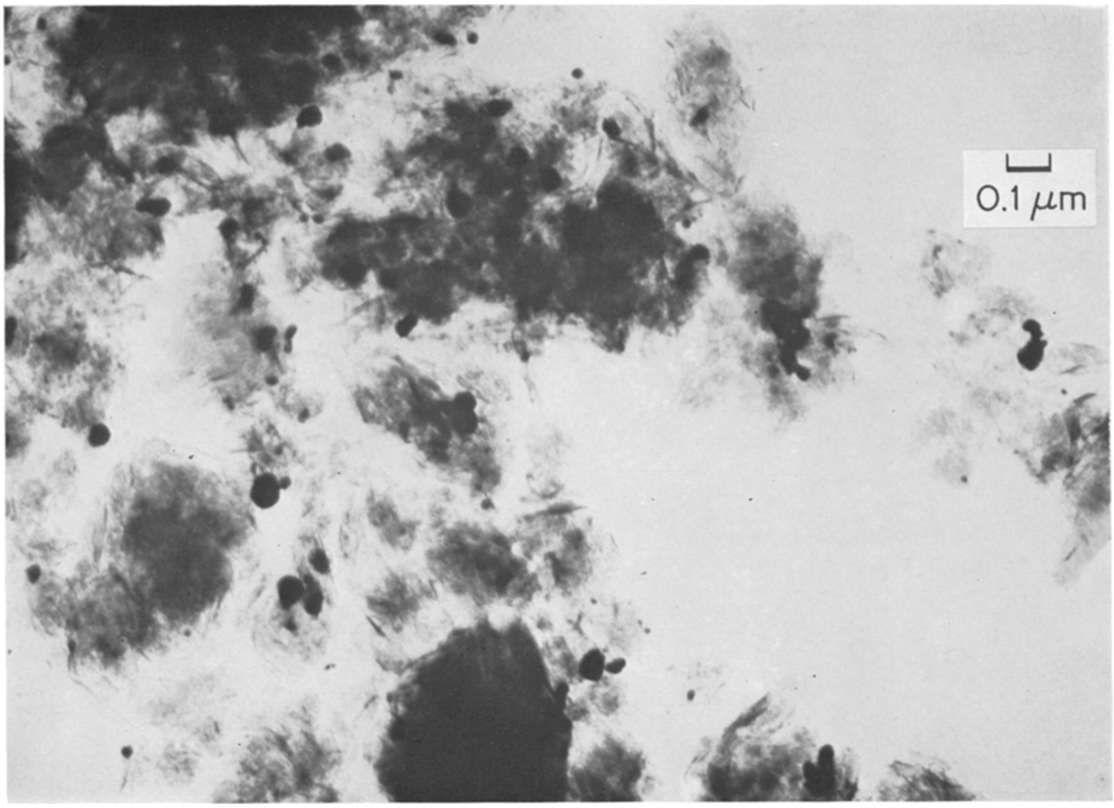


Fig. 4. Oven-dried, 10% Ag/C, without further heating. (×60 000).

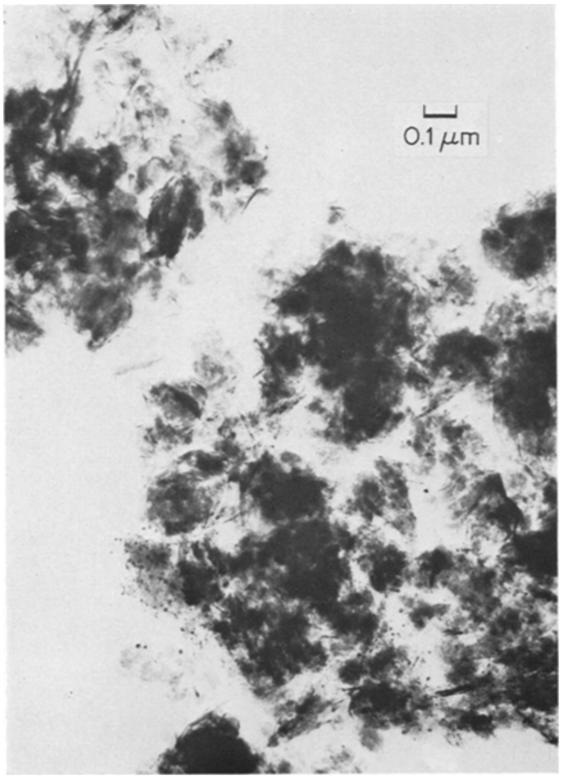


Fig. 5. Freeze-dried, 10% Ag/C, without further heating. (×60 000).

Figs 4 *and* 5 *between pp.* 212 *and* 213

Whether a liquid spreads on a solid depends on their interfacial surface energy relationships as given by [10]:

$$S = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \qquad (1)$$

Where S = the spreading coefficient, if S is positive, spreading occurs; i.e. $\theta < 90°$;

γ_{sv} = interfacial surface energy between solid and vapour;

γ_{sl} = interfacial surface energy between solid and liquid;

γ_{lv} = interfacial surface energy between liquid and vapour.

In our case, γ_{sv} for graphite = 118 erg/cm^2 [11]

γ_{lv} for molten $AgNO_3$ = 148 erg/cm^2 [12]

Since $\gamma_{lv} > \gamma_{sv}$, S is negative. This indicates that molten $AgNO_3$ should not wet pyrolytic graphite, unless some surface reactions occur at the interface, altering the interfacial surface energy relationships.

The possible reactions are:

$$AgNO_3 + C + \tfrac{1}{2}O_2 \rightarrow Ag + NO_2 + CO_2 \qquad (2)$$

when heated in air, and

$$AgNO_3 + C \rightarrow Ag + CO + NO_2 \qquad (3)$$

when heated in N_2.

Since the surface energy, γ_{sv} of Ag is 909 erg/cm^2 [13], which is very much greater than the surface energy of molten $AgNO_3$ (148 erg/cm^2), it is possible for the unreacted $AgNO_3$ to spread on the surface of the Ag produced during the chemical reaction. The spreading will continue until the reaction between $AgNO_3$ and graphite has reached an equilibrium.

If the above mechanism is correct, it should be of interest in practice, since the decomposition temperature of $AgNO_3$ is reduced from 440°C to 210°C (melting point of $AgNO_3$). This leads to the formation of finer Ag particles, evenly distributed on the surface of the graphite substrates.

3.2. *Thermogravimetric studies*

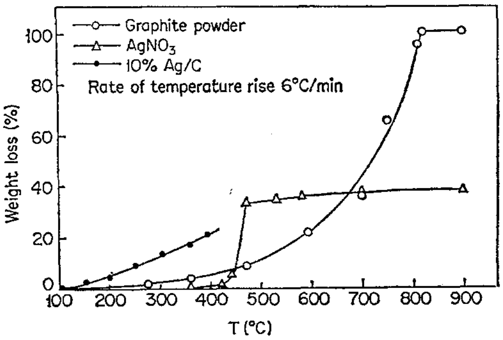


Fig. 2. Thermal gravimetric studies of graphite powder, silver nitrate and a 10% Ag/C catalyst, prepared by impregnation, followed by oven-drying at 110°C for 24 h

Fig. 2 shows the weight loss of graphite powder $AgNO_3$ and a 10% Ag/C catalyst. The catalyst was prepared by impregnation, followed by drying in an oven at 110°C for 24 h. The rate of oxidation of graphite increased gradually with temperature and by 300°C lost 3% by weight. $AgNO_3$ starts to decompose at about 440°C. However, the 10% Ag/C catalyst started to lose weight at about 100°C and by 300°C showed a 15% weight loss. The reaction between $AgNO_3$ and C, for a catalyst containing 10% Ag, can only account for a weight loss of 7% according to Equation (2). The oxidation of graphite by air accounts for another 3%. The additional 5% weight loss is most probably due to the enhanced oxidation of graphite due to the presence of finely dispersed Ag [14].

3.3. *Electron microscopic examination*

Samples prepared by oven-drying and freeze-drying were examined in a Siemens Elmiskop 1A electron microscope. Since earlier results indicated that there was reaction between $AgNO_3$ and graphite, some Pt/C catalysts were prepared by oven-drying and freeze-drying for comparison since tests have shown that there was no chemical reaction between H_2PtCl_6 and graphite under our experimental conditions.

The shape of the graphite powder is nonregular and flake-like (Fig. 3). There was a marked difference in particle size and distribution of $AgNO_3$ particles in samples prepared by oven-drying and freeze-drying before they were subjected to heat treatment, at 300°C for 1 h (Figs. 4 and 5). However, after heat treatment no significant differences were detected (Figs. 6 and

Table 1

Catalyst	*Preparation method*	*Rate of H_2O_2 decomposition* $\frac{ml \times 100}{s \times g\ catalyst}$
10% Ag/graphite	Freeze-dried, 300°C, 1 h	$5{\cdot}82 \times 10^3$
10% Ag/graphite	Oven-dried, 300°C, 1 h	$5{\cdot}51 \times 10^3$
10% Pt/graphite	Freeze-dried, 300°C, 1 h	$1{\cdot}51 \times 10^3$
10% Pt/graphite	Oven-dried, 300°C, 1 h	$2{\cdot}13 \times 10^3$
10% Ag/graphite	Commercial supplier	$2{\cdot}00 \times 10^3$
graphite	Commercial supplier	$0{\cdot}071 \times 10^3$

7). On the other hand, there were marked differences in Pt particle size and distrbution in samples prepared by oven-drying and freeze-drying (Figs. 8 and 9).

When impregnated graphite powders are subjected to oven-drying, the water vapour escapes at the mouth of the pores. As further evaporation proceeds the metallic salt solution is drawn up to the surface by capillary suction and eventually all the metallic salt is concentrated at the mouth of the pores. This results in a larger particle size and uneven distribution. On the other hand, in the freeze-dried samples, the application of vacuum to remove H_2O ensures that the process is carried out below the triple point for H_2O and H_2O goes straight from the solid state (ice) to vapour without going through the liquid state. This enables the metallic salt to remain inside the pores of the catalyst substrate. However, for $AgNO_3/C$ samples, subsequent heat treatment effectively ensures that the final distribution of Ag particles will be uniform, since the reaction between $AgNO_3$ and C at temperature enables the molten $AgNO_3$ to wet the graphite surfaces completely.

3.4. H_2O_2 *decomposition study*

Table 1 shows the rate of H_2O_2 decomposition on different samples at 25°C, 5 N KOH. The initial peroxide concentration was 0·25 M.

Since there are hardly any differences in the Ag particle size or distribution in the freeze-dried or oven-dried samples, it is not surprising to see that their H_2O_2 decomposition rates are similar. On the other hand, despite the finer particle size and better distribution of Pt in freeze-dried samples, the H_2O_2 decomposition rate is lower than on oven-dried samples. The H_2O_2 decomposition reaction yields O_2 and as soon as O_2 is produced inside the pores, the electrolyte will be pushed out, rendering the Pt inside the pores ineffective. Thus, most of the reaction would only occur at the mouth of the pores, i.e. at the places where the Pt is concentrated in the oven dried samples.

3.5. *Electrochemical evaluation*

Fig. 10 shows the current-voltage curves of Teflon bonded electrodes (10 mg catalyst/cm², catalyst/Teflon ratio = 10/3) for the reduction O_2 in 5 N KOH. There is hardly any difference in the performance between the 10% Ag/C catalysts prepared by oven-drying or freeze-drying and their performance is better than that

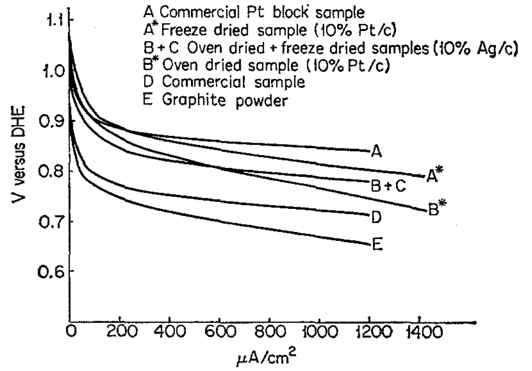


Fig. 10. Performance of Ag/C and Pt/C electrodes.

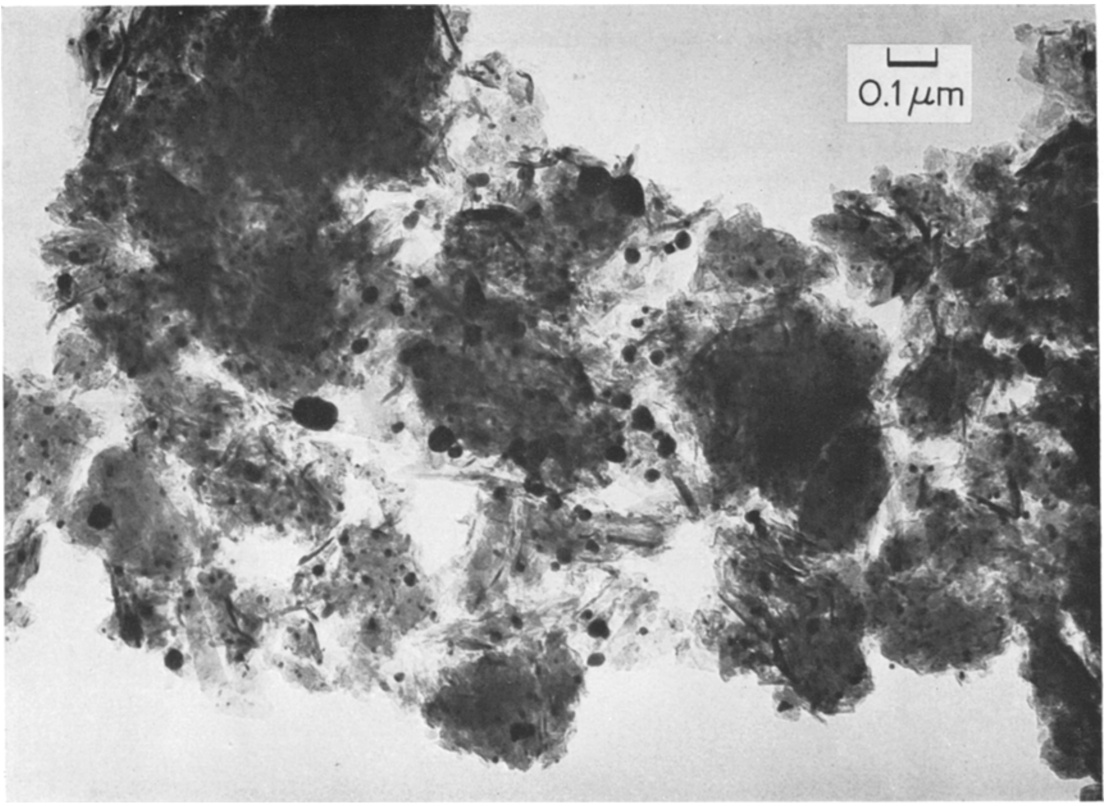


Fig. 6. Oven-dried, 10% Ag/C, 300°C for 1 h (× 60 000).

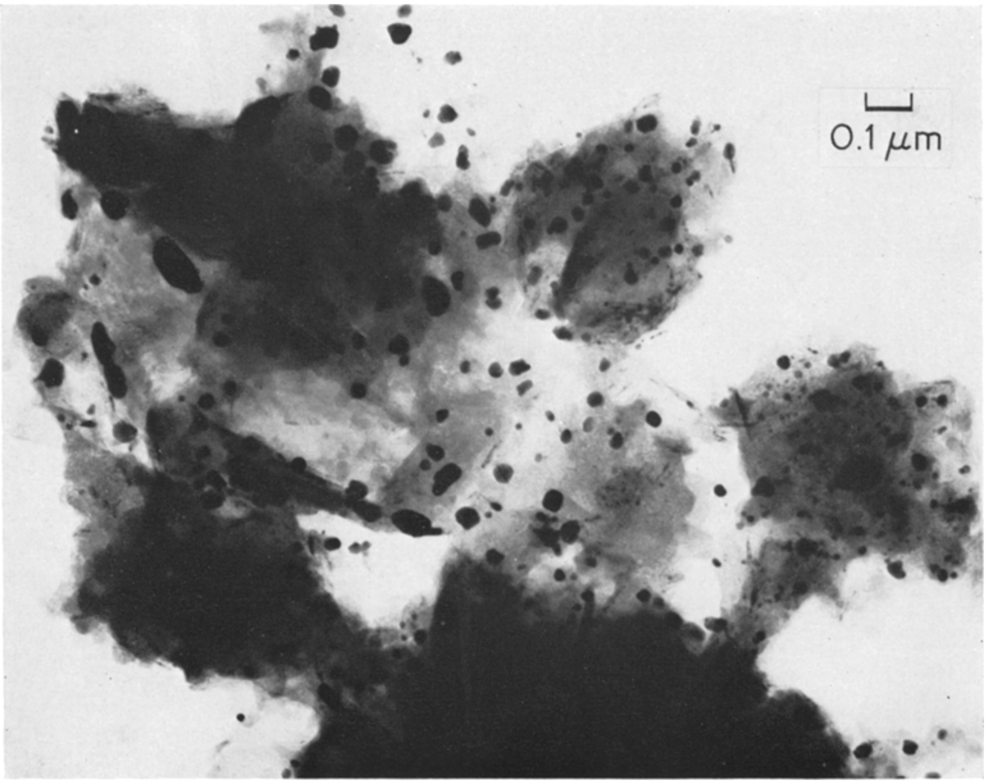


Fig. 7. Freeze-dried, 10% Ag/C, 300°C for 1 h (× 60 000).

Figs 6 *and* 7 *between pp.* 214 *and* 215

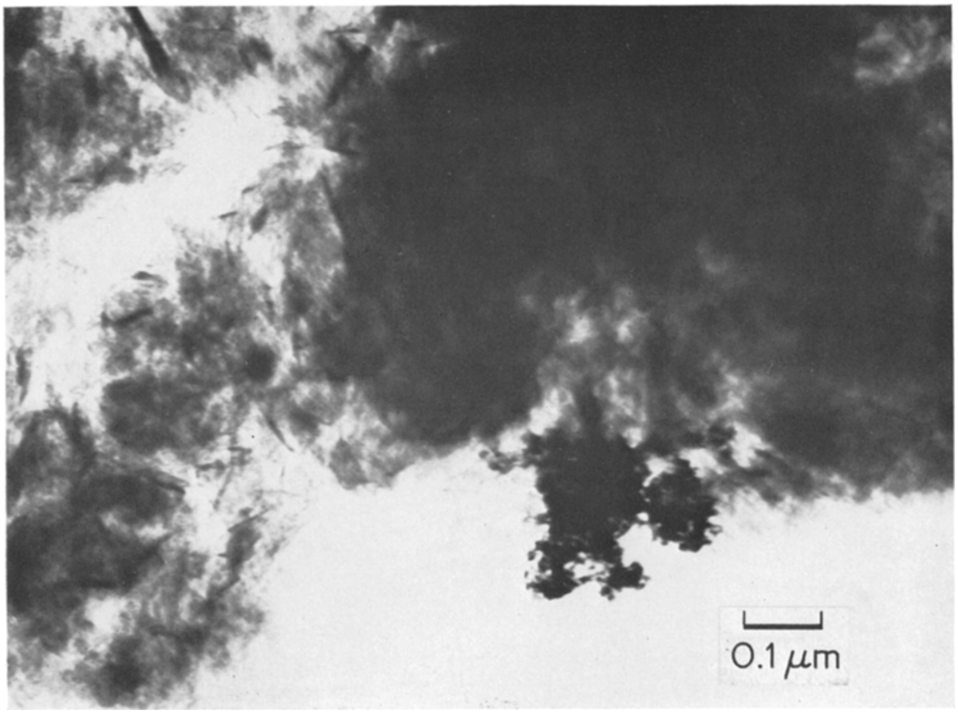


Fig. 8. Oven-dried, 10% Pt/C, 300°C for 1 h (× 100 000).

Fig. 9. Freeze-dried, 10% Pt/C 300° C for 1 h (× 100 000).

Figs 8 *and* 9 *between pp.* 214 *and* 215 *facing p.* 215

for electrodes prepared from oven-dried 10% Pt/graphite catalyst as well as that for a commercial 10% Ag/C catalyst. It is not possible to correlate the H_2O_2 decomposition activity with their electrochemical activity since both Ag and Pt [15] reduce oxygen via a metal oxide route as well as acting as H_2O_2 decomposition catalysts.

Acknowledgement

This investigation was supported by Energy Conversion Ltd.

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