

Short Communication

# Pretreatment of acetylene black: influence on electrochemical behaviour

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## Abstract

Electrochemical methods and two other non-electrochemical methods, viz., transmission electron microscopy (TEM) and Fourier-transform infrared spectroscopy (FT-IR) have been used to study changes in the characteristics of acetylene black in the cathode of fuel cells when acetylene black is treated under three different conditions: (i) no further treatment; (ii) in air at 450 °C, and (iii) in a CO<sub>2</sub> stream at 900 °C. The latter two methods increase the surface area of acetylene black at a given condition from 70 to 116 and 104 m<sup>2</sup> g<sup>-1</sup>, respectively. By contrast, there is a large difference in the electrochemical behaviour. This phenomenon is considered to be due to the partial graphitization of acetylene black at high temperature.

*Keywords:* Fuel cells; Porous electrode; Acetylene black

## 1. Introduction

There have been considerable efforts to develop an effective fuel-cell system. The first goal is conversion of chemical energy to electric power with high efficiency at practical current densities. Second, the cell must have long operational life, or a low cost for replacement of ageing parts. Finally, it should compete with existing forms of power generation.

Without question, a porous electrode substrate with high surface area on which a suitable catalyst is effectively dispersed is one of the key factors for high-performance electrodes. Selection of a suitable substrate material is dictated by the following factors: cost, inertness in the operating medium, high electrical conductivity, effectiveness as a substrate for a highly dispersed catalyst. Various types of active carbon have been used as the carrier for the platinum catalyst in the electrodes [1–4]. Both the activity and the corrosion resistance of such electrodes have been found to depend markedly on the nature of the carbon substrate.

Acetylene black has long been a favoured material for various cells and batteries on account of its low cost and special properties. Nevertheless, its relatively

low surface area (about 70 m<sup>2</sup> g<sup>-1</sup>) impedes its use in fuel cells, in which the surface area of the carbon substrate is required to be over 110 m<sup>2</sup> g<sup>-1</sup>. Suitable materials include Vulcan XC 72R (254 m<sup>2</sup> g<sup>-1</sup>, cabot), Mogul (138 m<sup>2</sup> g<sup>-1</sup> cabot) Monarch (1300 m<sup>2</sup> g<sup>-1</sup> cabot). Obviously, it is necessary to increase the surface area of acetylene black for its effective use in fuel cells.

Carbon materials are usually heated in three kinds of atmosphere, namely, ammonia, water vapour and carbon dioxide [5]. These treatments can all change the original BET areas of the materials to a certain extent. For a material with a high surface area, these treatments would reduce the surface area under the conventional condition, and for a material with a low surface area, the inverse occurs provided the time of heating is not excessive.

A very common view about the role of gas activation is that CO<sub>2</sub> or H<sub>2</sub>O can oxidize off unstable sites attached to the treated materials. Therefore, the stability of carbon materials would be strengthened. As far as the air activation of carbon materials is concerned, it can also oxidize away unstable sites. Why is this pretreatment only seldom adopted in operation? Do the CO<sub>2</sub>-treated carbon materials show even more advantages than what are known to date? The present study compares air activation with CO<sub>2</sub> activation.

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## 2. Experimental

### 2.1. Pretreatment of acetylene black

Acetylene black was obtained from Tianjin Institute of Power Sources, China. Its main physical and chemical parameters are as follows:

- surface area  $68 \text{ m}^2 \text{ g}^{-1}$
- particle sizes 50 to 2000 Å
- apparent density  $25 \text{ g l}^{-1}$
- specific density  $1.95 \text{ g cm}^{-3}$

This carbon material was subjected to air treatment at 450 °C for 1 h or to a CO<sub>2</sub> stream at 900 °C for different times. A quartz pipe furnace was employed to allow activation gas flow from one end to the other. The surface area was determined using a model ST-03 BET surface area chromatometry.

### 2.2. Electrode fabrication

The electrode manufacturing technique has been described previously [4]. The main difference with the present study is that no catalyst is used. The main aim of this work is to assess the characteristics and corresponding changes of carbon materials. Thus, the catalyst layer stated in the present study is a 'quasi-catalyst' layer. The polytetrafluoroethylene (PTFE)/carbon layer was prepared by mixing an appropriate amount of suspension agents, e.g., isopropanol. Ground filler particles (ammonium bicarbonate) were added to adjust the porosity of the carbon materials. The mixture was homogenized with strong stirring to yield a workable dough. Thin foils were prepared using cross-rolling techniques. The thickness of the foils is adjusted to 0.4 mm. The foils were heated according to the following programme. The temperature was increased slowly to 100 °C, held at 120 °C until no white gases were evolved, and then to 320 °C for 20 min. Individual layers were cut to the appropriate size. A platinum screen, set between the 'quasi-catalyst layer' and the diffusion layer, served as a current collector. Finally, the layers were pressed to one unit under a pressure of  $80 \text{ kg cm}^{-2}$ . The composition of the different layers is given in Table 1.

### 2.3. Characterization techniques

Fourier-transform infrared spectroscopy (FT-IR) was employed to detect the functional groups on the acetylene-black powders using 170 sx FT-IR NICOLET (USA) equipment. As is well known, such analysis is difficult because of the highly absorbing nature of carbon [6]. In the present study, improved resolution and sensitivity was obtained by a computer-assisted analysis of the infrared spectra.

Table 1

Composition of electrode layers

Element	Quasi-catalyst layer (g)	Diffusion layer (g)
Acetylene black <sup>1</sup>	20	20
60% Teflon emulsion	5.2	20
Filler	4.0	20

<sup>1</sup>Three kinds of acetylene black were used separately, namely: untreated, air-treated and CO<sub>2</sub>-treated samples. Electrodes made from these three materials were named E-1, E-2 and E-3, respectively.

Transmission electronic microscopy (TEM) was used to observe the profiles of carbon powders. A TEM-100CX microscope made by the Japanese Electronic Company, Japan, was employed. A small amount of acetylene black was dispersed in acetone with strong ultrasonic blending. A copper foil dipped into this suspension served as an analytical sample.

#### 2.3.1. Measurements of electrochemical behaviour

The cell used to measure electrochemical performance parameters was composed of three electrodes: (i) the working electrode (E-1, E-2 and E-3) with a size 2.0 cm<sup>2</sup>; (ii) a Hg/Hg<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> reference electrode equipped with a Luggin capillary, and (iii) a high surface-area, flat-bed platinized platinum counter electrode. A 2.5 M H<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte and was agitated with a magnetic stirrer. A gas-supply tube was mounted on the back side of the working electrode. Further details of the cell design have been described elsewhere [7,8].

Galvanostatic polarization studies were carried out using a regulated d.c. power supply and a high-power-rated rheostat in series with the electrochemical cell. Current-potential curves at room temperature (about 30 °C) for cathodic reduction of oxygen were obtained for all the electrodes described above.

## 3. Results and discussion

The heating condition and the corresponding specific surface area of acetylene black are summarized in Table 2. Samples 1, 2 and 4 were selected as substrate materials for the porous electrodes E-1, E-2 and E-3, respectively. Both air and a CO<sub>2</sub> atmosphere increase the BET area of acetylene black. It is suggested that this is because both oxygen (in air) and CO<sub>2</sub> can oxidize off various residues on acetylene black. These residues are formed during the manufacture of acetylene black. This effect will reduce the size of acetylene black and accordingly will produce a higher BET area.

On the other hand, both oxygen in the air and CO<sub>2</sub> can oxidize off those active sites of acetylene black

Table 2  
Heating conditions and corresponding BET area

Sample no.	Atmosphere	Temperature (°C)	Heating time (h)	Weight loss (wt.%)	BET area ( $\text{m}^2 \text{g}^{-1}$ )
1	oxygen-lean	600			68
2	air	450	1	2.1	116
3	CO <sub>2</sub>	900	2	44.6	83
4	CO <sub>2</sub>	900	1	1.7	104

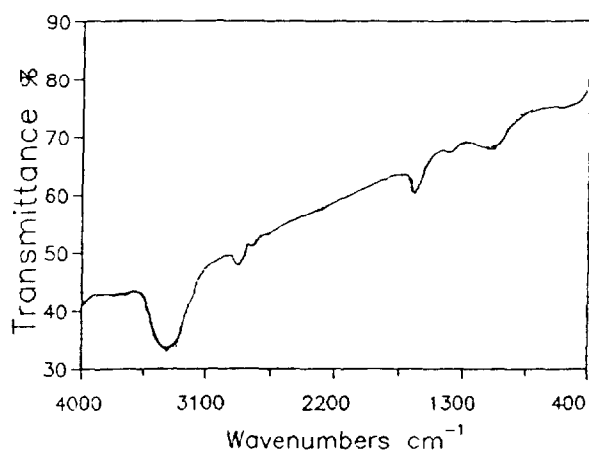


Fig. 1. FT-IR spectrum of untreated acetylene black (sample 1).

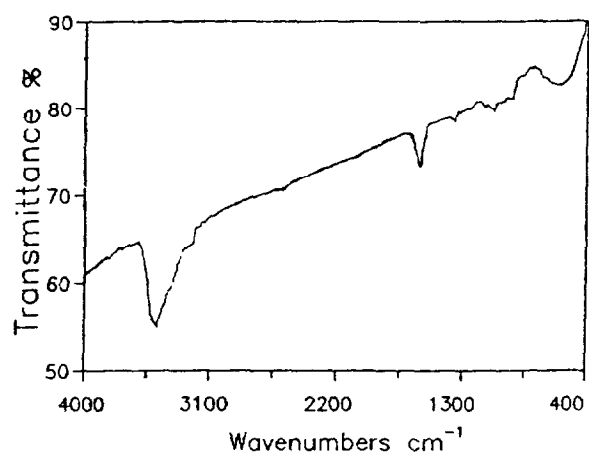


Fig. 2. FT-IR spectrum of air-treated acetylene black (sample 2)

that are usually those particles with acute angles or with the smallest size. This effect will reduce the BET area. At over 500 °C, carbon will be burned off in air. Excessive heating in CO<sub>2</sub> at 900 °C will decrease the BET. This accounts for the smaller BET area of sample 3 compared with sample 4. Therefore, the activation condition should be selected carefully. The foregoing speculation can be drawn from FT-IR spectra and TEM micrographs.

Figs. 1 to 3 are the FT-IR spectra for samples 1, 2 and 4, respectively. These data show that the  $\nu_{\text{asy}}\text{CH}$  or  $\nu_{\text{sy}}\text{CH}$  vibration (between 3000 and 2700  $\text{cm}^{-1}$ ) that

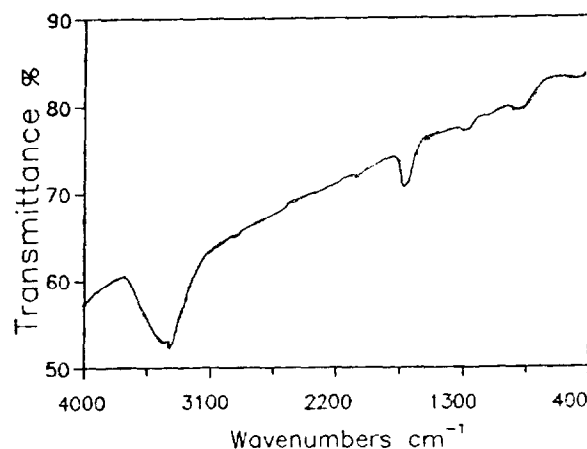


Fig. 3. FT-IR spectrum of CO<sub>2</sub>-treated acetylene black (sample 4).

occurs in untreated acetylene black has disappeared completely in air-treated and CO<sub>2</sub>-treated acetylene black. The strengthened absorbance peak of the C=O stretching vibration (around 1633  $\text{cm}^{-1}$ ) suggests that the oxygen or CO<sub>2</sub> can oxidize carbon itself and form C=O group on the surface of the acetylene black. The strong absorbance peak around 3400  $\text{cm}^{-1}$  is the  $\nu\text{OH}$  stretching vibration absorbance from H<sub>2</sub>O, which comes from hydrated potassium bromide, a dispersing agent commonly used in infrared analysis. The oxidation of acetylene black does not take place uniformly on its whole surface, active sites take priority over others. The following processes probably occur in heat treatment given in Fig. 4.

Fig. 5 shows TEM images taken from different parts of copper foils that carry sample 3. Fig. 4(c) and (d) display a tendency for partial graphitization of the acetylene black. This phenomenon was not observed in the TEM images of samples 1 and 2. Clearly, high temperature plays an important role in the graphitization of carbon materials. The graphitization gives rise to two effects: (i) reduction in BET area, and (ii) a more uniform and stable state of acetylene black. The first effect is confirmed by the data given in Table 2. The second effect will be confirmed by subsequent experiments.

Current-potential curves for the cathodic reduction of oxygen in 2.5 M H<sub>2</sub>SO<sub>4</sub> are shown in Fig. 6. The IR drop has been corrected. As mentioned before, all the electrodes, E-1, E-2 and E-3, are free of any catalyst if carbon is not considered to be a 'catalyst'.

The slightly small cathodic polarization of electrode E-3 at high current is attributed to the partial graphitization of acetylene black. As is known, graphite has the lowest ohmic resistance of all carbon materials. Thus, electrode E-3 has smaller ohmic polarization.

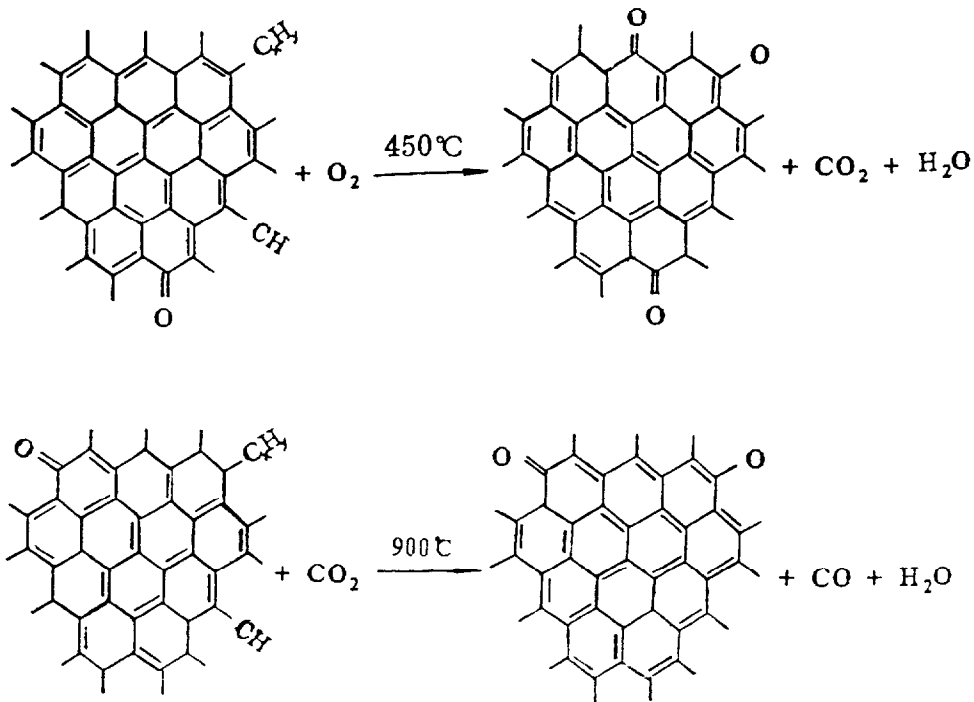


Fig. 4 Oxidation of acetylene black.

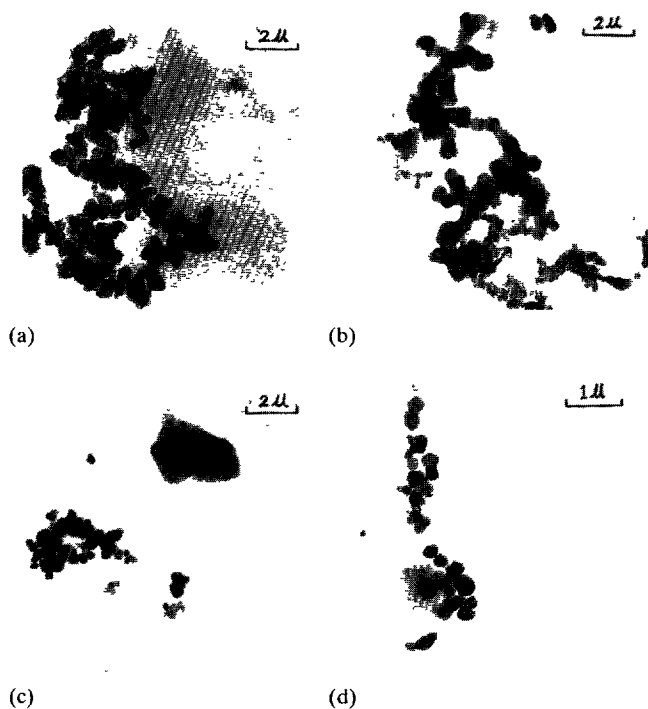
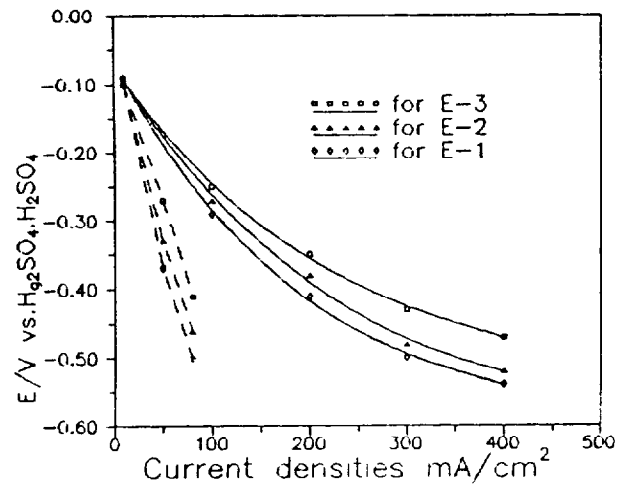


Fig 5 TEM analysis of sample 3 Images (a) to (d) were taken from different sites of a copper foil dipping into sample 3

#### 4. Conclusions

The present study has clearly shown that the  $\text{CO}_2$  activation of acetylene black produces some positive

Fig. 6. Current-potential curves for oxygen reduction in 2.5 M  $\text{H}_2\text{SO}_4$  at 30 °C (---) in air and (—) with an oxygen supply of 200 ml per min on electrodes as indicated

effects i.e., lower, cathodic polarization for oxygen reduction, enhancement of electrode surface area. Heat treatment in a mild oxidation atmosphere, such as  $\text{CO}_2$  on water vapour, can be conducted at a higher temperature. This results in partial graphitization and lowering of the ohmic resistance of acetylene black. By contrast, air activation cannot produce this effect because acetylene black will be burned completely at high temperature.

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