

CARBON MATERIALS AS ELECTROCATALYSTS FOR OXYGEN REDUCTION IN PHOSPHORIC ACID MEDIUM

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The behaviour of acetylene black (Indian grade) as catalyst support material is reported. The acetylene black is heat treated (activated) at various temperatures in nitrogen atmosphere. The surface area of the various heat treated samples is obtained. Platinum is deposited into the carbon by a reported technique. The type of platinum agglomeration on the carbon is identified through scanning electron microscope.

The above catalyst is applied to glassy carbon disc. The electrochemical surface area of the catalyst is determined by the hydrogen absorption and oxidation in alkaline medium. Similar electrodes (disc, dia 6 mm) are used in H_3PO_4 medium. Cyclic voltammograms are obtained in the oxygen evolution region and oxygen reduction region. The exchange current density of the catalyst for oxygen evolution and reduction is reported for different catalyst loadings.

Key words: Electrocatalyst, oxygen reduction-phosphoric acid fuel cell

INTRODUCTION

The fuel cells, which are currently in an advanced stage, employ phosphoric acid as the electrolyte. Different types of carbon materials viz thermal black, acetylene black, bone-black, furnace black, channel black and activated coconut shell charcoal, are characterized [1] as catalyst supports in the fabrication of electrodes. The reduction of oxygen on platinum supported on carbon has been the subject of extensive research investigations in recent years [2-8].

In this paper, the results of a few preliminary investigations on the behaviour of Indian grade acetylene black powder with and without the impregnation of platinum have been reported.

EXPERIMENTAL

Catalyst supports

Acetylene black powders (Indian grade) were heat treated in order to activate the surface of the carbon particles at different temperatures for different durations in a controlled atmosphere of carbon dioxide under steady rotation conditions. While carrying out the heat treatment, the temperature was increased in a programmed manner from 301K to the temperature required in each case. After maintaining at the required temperatures for the specified durations, the samples were allowed to cool down to room temperature in nitrogen atmosphere. The surface area of these powders as a function of heat treatment temperature and time were evaluated with surface area analyser (Quantasorb). The particle size of the catalyst was determined using Malvern Particle Size Analyser.

Electrode fabrication, electrochemical cell and electrolyte pretreatment

The Pt catalyst was deposited by dithionite reduction method [9]. The activated acetylene black powder was mixed with teflon T-30

emulsion to yield a 10% PTFE content by weight. This was then made into a slurry form with required quantity of 2-propanol. The resulting slurry was applied on to already polished and clean surfaces of glassy carbon (0.33 cm^2 geometric area) embedded in teflon rods. The surface of the coat was smoothened with an agate plate. Then the electrodes were baked at 590K for 1/2 an hour.

The electrochemical cell used in the present investigation was a three-limbed standard double walled cell. A large surface area Pt foil and $\text{Hg}/\text{Hg}_2\text{SO}_4$ $\text{SO}_4^{2-}(2\text{M})$ were used as counter and reference electrodes respectively. The reference electrode was connected to the main cell via salt bridge and luggin capillary. The electrolyte was 85% H_3PO_4 . The oxygen gas was 99.9% pure and further purified prior to its entry into the investigation cell. The electrodes were pretreated anodically at 1.0 V over a period of 30 minutes to get steady oxygen evolution currents.

The voltammograms were recorded under identical conditions on all the electrodes at a scan rate of 0.1 V sec^{-1} up to the oxygen reduction potential. The waves corresponding to the oxygen reduction at a constant potential were analysed to identify the best heat treatment procedure of the carbon powder [10].

RESULTS AND DISCUSSION

The physical and bulk characteristics of the Indian grade acetylene black carbon powder employed in the present investigations are listed in Tables I and II. The distribution of deposited platinum

TABLE-I: Physical and bulk characteristics of the acetylene black powder

Apparent density (gm.ml^{-1}) :	0.05
Electrical resistivity (ohm cm^{-1}) :	0.025
Heat loss (%) :	0.6
Ash content by mass (%) :	0.2
Average particle diameter (μm) :	29.8
Specific surface area ($\text{m}^2 \text{ ml}^{-1}$) :	0.08
pH =	6

TABLE-II: Physical characteristics of the carbon samples

Sample	Activation temperature (K)	Activation duration (hrs)	BET surface area ($\text{m}^2, \text{gm}^{-1}$)
1	773	3	127.7
2	873	3	153.4
3	1073	3	192.2
4	1073	6	201.3
5	1073	20	251.2
6	nil	nil	71.5

particles on carbon support has been uniform (Fig. 1). The platinum particle diameter is estimated to be 0.05 to 0.2 μm .

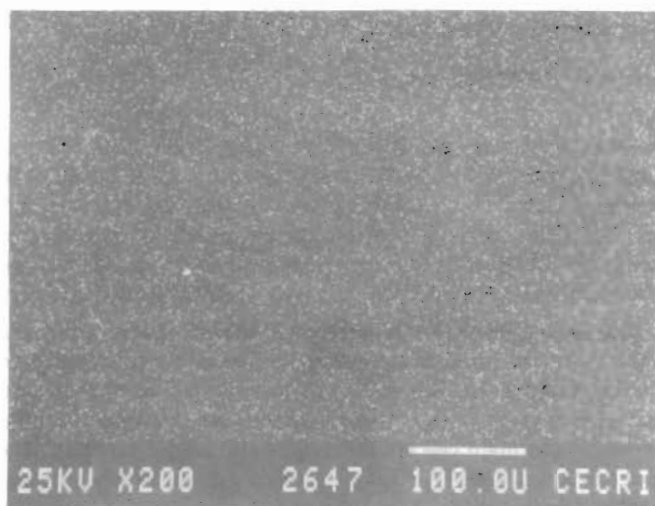


Fig. 1: Scanning electron micrograph of Pt – deposited on carbon

The potentiostatic steady state polarisation behaviour of the platinised carbon electrodes for the electrochemical reduction of dissolved molecular oxygen in 85% H_3PO_4 at room temperature is shown in Fig. 2 as a function of the thermal activation variables

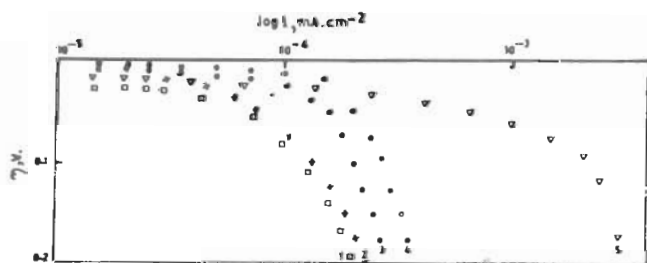


Fig. 2: Tafel plot for the reduction of oxygen on carbon electrodes in 85% H_3PO_4 at room temperature – Curve numbers correspond to sample numbers (Table II)

of the carbon powders employed in the fabrication of the disc test electrodes. The electrode that was fabricated from the carbon activated at 1073K had shown minimum polarization. The tafel parameters are shown in Table III. The magnitude of the tafel slope

TABLE-III: Tafel parameters obtained on carbon electrodes

Sample No.	Test temperature	Tafel slope (mV decade^{-1})	Apparent i_0 values (A. cm^{-2})
1	303	40	8.0×10^{-8}
2	303	35	7.0×10^{-7}
3	303	30	1.0×10^{-6}
4	303	30	1.0×10^{-5}
5	303	25	1.3×10^{-5}
6	303	45	1.5×10^{-10}

was 0.04V, whereas the exchange current density values varied regularly as a function of activation temperature. The tafel slope values agreed with the values reported [6,7,11]. The currents observed due to the reduction of dissolved oxygen at a constant potential of 0.9V vs RHE in 85% H_3PO_4 are shown in Table IV as a function of test temperature and activation variable.

TABLE-IV: Oxygen reduction current densities at 0.9 V vs RHE in 85% H_3PO_4 on carbon electrodes

Sample No.	Test temperature (K)	Current density (mA. cm^{-2})
1	303	0.020
	373	0.140
2	303	0.040
	373	0.140
3	303	0.045
	373	0.150
4	303	0.175
	373	0.475
5	303	0.300
	373	0.675
6	303	0.010
	373	0.060

In Fig. 3, the effect of pre-anodisation at different anodic starting potentials on the oxygen reduction behaviour is shown for the electrode fabricated from carbon activated at 1073K. It is observed that as the pre-anodisation potential increases, the oxygen reduction current also increases. This is because the oxygen absorbed on the surface of the electrode tends to be maximum at the highest anodic potential. The anodic branch of the voltammogram contains an extended peak at 0.7 V and this seems to be due to the redox processes associated with the platinum particles

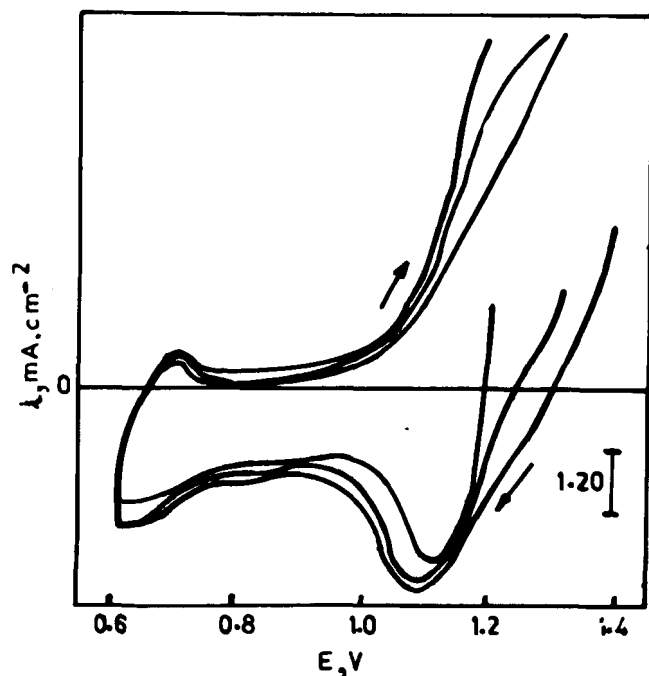


Fig. 3: Cyclic voltammograms for the reduction of oxygen on carbon electrodes from different anodic starting potentials

dispersed on the carbon, which might be in the oxide state due to the anodic pretreatment. In Fig. 4, the effect of scan rate on the general voltammetric behaviour of the carbon electrode fabricated from carbon activated at 1073K is shown, covering the hydrogen evolution potentials also. It is observed that a reversible redox process occurs at 0.1 V. Since this occurs at the hydrogen evolution potential region, the reverse process could be assigned to the oxidation of hydrogen available at the electrode surface. The peaks associated with redox behaviour of the quinonoid structure on the surface of the carbon [5] is not observed in the samples heat treated for longer durations.

CONCLUSIONS

The general and the electrochemical characteristics of the Indian grade acetylene black have been investigated with a view to use these carbon supports to fabricate cost-effective electrodes for fuel cell application. The preliminary results are encouraging when compared with literature [12] available on the subject.

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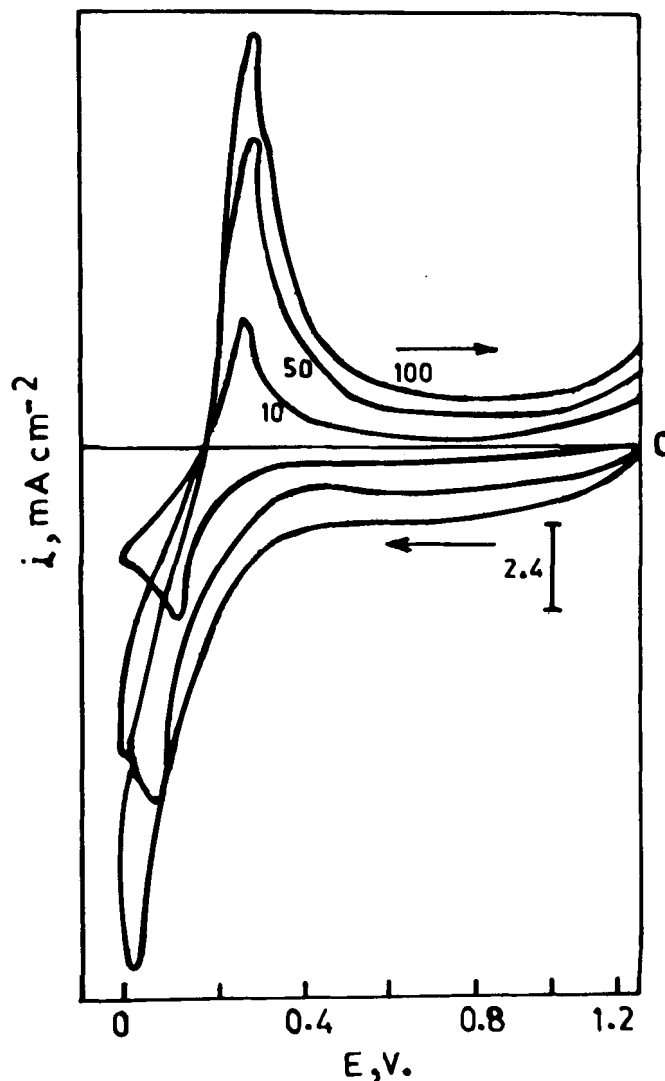


Fig. 4: Cyclic voltammograms for the redox process on carbon electrodes at different scan rates - 10, 50 and 100 mV. sec⁻¹

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