Functionalized Acetylene Black as an Effective Additive for ORR Electrocatalysts

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Abstract

Platinum-based electrocatalysts are the most effective materials for Oxygen Reduction Reaction (ORR) in Polymer Electrolyte Membrane (PEM) fuel cells. However, limitations in adapting platinum-based electrocatalyst have greatly hampered fuel cell commercialization. Therefore, studies on functionally active materials and additives have gained significant interest recently, as their addition can partially replace platinum content in the electrocatalysts. Herein, for the first time, we demonstrate the use of Functionalized Acetylene Black (FAB) as an additive to reduce the platinum content in a commercial catalyst 20% Pt/C (Vulcan XC-72). An optimized electrocatalyst recipe was determined by carrying out cyclic voltammetry studies, linear sweep voltammetry, and accelerated degradation test. The optimized electrocatalyst containing 15 wt% of FAB added to the commercial catalyst exhibited better performance than the commercial catalyst, with the platinum content reduced to 17% from 20%. This research concludes that functionalized acetylene black is an effective additive for ORR electrocatalyst.

Keywords: *ORR electrocatalyst; additive; functionalized acetylene black; Platinum reduction*

1. Introduction

Electrochemical methods of energy handling are major contributors for energy sources that can circumvent the environmental problems. Fuel cells, a type of electrochemical device, are potential alternative to existing fuel – consuming systems. The high expense involved has led to efforts to reduce costs and increase efficiency. In the case of PEM fuel cells, improving the kinetics of the reduction reaction at the cathode, which is slower compared to the oxidation at the anode, is crucial to increase the efficiency. Platinum (Pt) or platinum alloy with carbon support are the most common ORR electrocatalysts. However, platinum being an indispensable but expensive and rare element, it is important to reduce it while maintaining efficiency. Further, the formulation of such a catalyst should be facile for large-scale production to reduce costs effectively [1–6].

Several investigations on catalyst supports have proven that Pt-Pt-catalysts with acetylene black (AB) exhibit better performance [5,7]. Pretreatment of carbon enhances the catalytic activity towards ORR by increasing surface functional groups and porosity, thereby contributing to higher surface area and increasing the adsorption sites [8]. Acetylene Black, owing to its high ORR activity on its own due to excellent absorption properties, negligible charge transfer resistance has been considered a primary candidate [9]. Studies on 30 wt% Pt decorated on functionalized acetylene black, 30% Pt/FAB report improved performance in terms of mass activity (MA) and electrochemically active surface area (ECSA), where the acetylene black was chemically pretreated [10,11].

This study explores the use of functionalized acetylene black as an additive to a commercial catalyst. In contrast to the substitution of platinum using other metals via reduction reaction processes to reduce the Pt content [12,13], the functionalized material is added by mechanical mixing. The

functionalization increases the binding between the catalyst particles, enhancing the diffusion of oxygen onto the catalyst owing to the oxygen moieties present, thereby improving the kinetics of ORR without loss in mass activity [8]. The functionalized AB was added in different weight ratios to the commercial catalyst 20 % Pt/C (Vulcan XC-72) and the ORR activity of the Pt/C – FAB mixtures was examined using cyclic voltammetry, linear sweep voltammetry and accelerated degradation test.

2. Materials and methods

Commercially procured acetylene black (AB) from Alfa Aesar, and 20% Pt/C (Vulcan XC-72) from Sigma Aldrich were used.

2.1. Pretreatment of acetylene black

Pretreatment of acetylene black was done by mineral acid functionalization. The commercially procured acetylene black was dispersed in a concentrated acid mixture of sulphuric acid and nitric acid (3: 1 ratio of H_2SO_4 and HNO_3), and ultrasonicated for 3 hours. The resulting functionalized and exfoliated AB was then diluted with deionized water and recovered by vacuum filtration. The filtrate was subsequently washed thoroughly with deionized water until the pH was neutralized to remove any acid contaminants. This was then dried at 80 °C overnight in a vacuum oven to obtain functionalized acetylene black [10].

2.2. Characterization

The surface morphology of the AB and FAB was characterized using field – emission scanning electron microscopy (FESEM, Carl ZEISS in SE – Inlens Duo mode) and transmission electron microscopy (JEOL). The thermal stability of the commercial catalyst due to the addition of FAB was studied in air atmosphere at a heating rate of 10 °C per minute using thermogravimetric analysis (Netzsch STA 449 F1). X-ray diffractograms were recorded in the 2θ range of 10°–90° with a step size of 0.01 at 0.3 sec per step speed in Rigaku SmartLab X-ray powder diffractometer with copper radiation (Cu Kα: λ = 1.542 Å).

To evaluate the electrochemical performance, cyclic voltammetry (CV), linear sweep voltammetry (LSV) and accelerated degradation test (ADT) were conducted. The FAB added catalyst ink was prepared by mixing DI water, isopropyl alcohol and 5 Wt% Nafion (in the ratio – 3:2:0.44) to 1 mg of the catalyst and ultrasonicated for 15 minutes to prevent agglomeration. This catalyst was coated onto a glassy carbon electrode (GCE) of area 0.0707 cm^2 and dried at room temperature.

For electrochemical measurements, 0.1 M of perchloric acid was used as the electrolyte solution. CV and ADT were performed at room temperature using Solartron 1470 Cell system. The working electrode was GCE coated with the catalyst ink, with platinum and silver-silver chloride (Ag/AgCl) as counter and reference electrodes, respectively. CV measurements were scanned in the potential range of -0.2 V and 1 V (vs. Ag/AgCl) at 50 mV s^{-1}. The linear sweep voltammetry was conducted using CH instrument (PINE Research Instrumentation) between 0.2 V and 1 V (vs. Ag/AgCl). The working electrode, GCE coated with the catalyst ink, was rotated at different rpm (rotations per minute) ranging from 200 rpm to 1600 rpm to study mass transport effects. The ADT was performed by pulsing square wave potential between 0.6 V and 1.2 V vs. Ag/AgCl with a hold time of 10s and 50s at a scan rate of 10 mV s^{-1} for 18 cycles [14,15]. CV was performed before and after ADT at a slower scan rate of 10 mV s^{-1} to quantify the degradation of the catalytic support against corrosion.

3. Results

3.1. Morphological, structural and thermal characterization

The FESEM micrographs of acetylene black (AB), functionalized acetylene black (FAB), and the TEM micrograph of FAB are presented for comparison in figure 1 (a), (b) and (c). Figure 1(b) clearly exhibited a deep functionalization, as evinced by the formation of a disintegrated and spongy surface against the once rigid grain structure, as seen in acetylene black in 1(a). This can be attributed to the oxidation and functionalities introduced through the mineral acid functionalization. Though the intensity of functionalization could not be determined, the

acid treatment had resulted in a well networked matrix. The TEM micrograph in figure 1(c) further confirmed the disintegrated and well-dispersed nature due to functionalization [10].

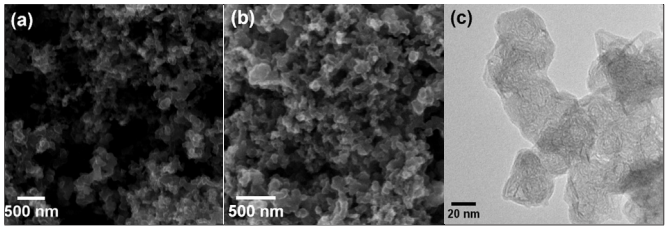


Figure 1. FESEM images of (a) acetylene black (AB), (b) functionalized acetylene black (FAB), and (c) TEM micrograph of FAB

Thermogravimetric analysis was conducted for the catalysts containing FAB in 20% Pt/C - 1wt%, 10wt%, 15wt% respectively. The actual weight content of platinum decreased to 19.8 %, 18 %, and 17 % as the weight percentage of FAB increased. Figure 2(a) revealed that carbon started decomposing above 400 °C and was oxidised completely by 650 °C leaving behind only platinum metal. The calculated weights closely matched the actual values, with an error of 10% from the instrument. The X-Ray diffractogram in figure 2(b) confirmed the presence of graphitic (002) planes at 25.46°of AB and FAB [16]. A slight increase in full width half maximum (FWHM) was observed for the (002) peak of FAB indicating functionalization.

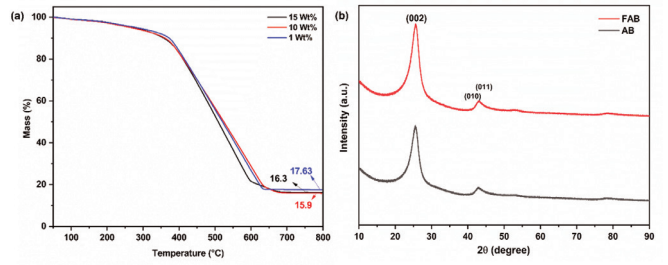


Figure 2. (a) Thermograms for 1, 10, and 15 Wt% of FAB in Pt/C in air atmosphere; (b) - X Ray diffractograms of AB and FAB

3.2. Electrochemical characterization

3.2.1. Cyclic voltammetry studies

Cyclic voltammetry studies for an ORR electrocatalyst has key features like a hydrogen desorption peak in the anodic sweep, from -0.2 V to 0 V vs Ag/AgCl, and a hydrogen evolution region around 1 V. In the reverse sweep, a peak around 0.9 to 0.5 V indicate the ORR region, while the peak region near 0 V to -0.196 V correspond to the hydrogen adsorption region. Several parameters, including onset potential, peak potential for ORR, current density at the ORR peak potential, mass activity at the ORR peak, electrochemically active surface area (ECSA) could be estimated from the CV plot from the figure 3 are tabulated below in Table 1 [14].

The onset potential, signifying the ease of oxygen reduction, initially decreased with FAB addition, reaching a minimum at 5 Wt%. However, further FAB loading resulted in a progressive increase in onset potential, exceeding the commercial catalyst. The ORR peak potential dipped with addition of FAB, but with increase in the addition, a gradual increase was observed reaching a maximum at 15 Wt% with a value of 0.472 V compared to 0.464 V of Pt/C, but only to decrease drastically at 20 Wt% inclusion of FAB.

In case of peak current density, that reflects the maximum achievable ORR activity, highest value was recorded with 15 Wt% FAB addition, exceeding the commercial catalyst by nearly 3%. But further FAB addition resulted in a decrease in current density.

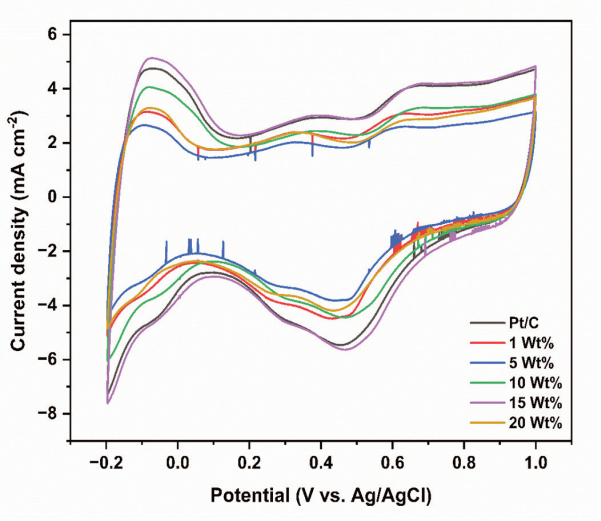


Figure 3. Cyclic Voltammogram for 20% Pt/C and 1, 5, 10, 15, 20 wt % FAB in Pt/C in 0.1 M Perchloric acid, Scan Rate = 50 mV/s

Mass activity, relating current density to catalyst mass, and ECSA, representing the electrochemically active surface area, followed a trend like the ORR peak potential and the peak current density. The mass activity and ECSA for the 1 wt % addition of FAB were less than that of the commercial catalyst and decreased further for 5 wt %. But, as the percentage of FAB addition increased, the mass activity increased, indicating FAB's addition acted as a matrix for dispersion. This was due to the electrochemically active surface area being greater, contributing to enhanced activity. The 15 wt % had the maximum value of MA with a large ECSA value of 32 m^2 g^{-1}, exceeding the commercial catalyst's value of 25.3 m^2 g^{-1}, while further increase in FAB to the catalyst caused a fall in ECSA and the mass activity.

Table 1- Electrochemical parameters of the electrocatalysts calculated from CV in figure 3.

Catalyst (FAB in wt%)	Onset Potential for ORR (V) vs. Ag/AgCl	ORR Peak Potential (V) vs. Ag/AgCl	Current Density at ORR Peak (mA cm^{-2})	Mass Activity (mA mg^{-1})	ECSA (m^2 g^{-1})
Pt/C	0.737	0.464	5.45	18.18	25.242
1 wt%	0.702	0.433	4.48	15.68	17.327
5 wt%	0.696	0.444	3.82	13.92	15.622
10 wt%	0.763	0.466	4.45	17.92	25.141
15 wt%	0.785	0.472	5.63	22.82	32.066
20 wt%	0.741	0.439	4.18	17.92	19.808

3.2.2. Linear sweep voltammetry studies

Linear sweep voltammetry was performed for the best performing catalyst, 15 wt% FAB and Pt/C, in rotating disk electrode setup. It was observed that with an increase in rotation speed of the electrode, the current increased as expected for the electrodes in diffusion-controlled environment; however, the onset was maintained at the same potential. Comparing the limiting current densities obtained through LS voltammograms in figure 4 of the two catalysts, 15 wt% FAB in Pt/C had better current density as compared to the 20% Pt/C. Interestingly, both catalysts exhibited a similar onset potential of 0.6 V vs Ag/AgCl, but the peak potentials for the ORR were shifted for 15 Wt% FAB added Pt/C.

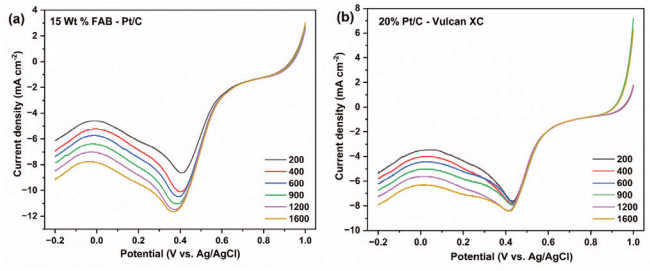


Figure 4. LSV for (a) 15 wt% FAB-Pt/C and (b) 20% Pt/C – Vulcan XC in 0.1 M Perchloric acid, Scan Rate = 50 mV/s for different rpm

3.2.3. Accelerated degradation test

The Accelerated degradation test was conducted to confirm the stability of FAB as catalytic support against corrosion. Cyclic voltametric studies before and after the pulsing of potential were performed to quantify the degradation by calculating the ECSA under the hydrogen desorption peak. It was found that even after the ADT, there was not a major difference in the CV, indicating a stable catalytic support. While 1 wt%, 5 wt%, and 15 wt% - FAB in Pt/C show an increased marginal difference in the active area under the hydrogen desorption peak after the pulsing of potential, 10 wt% and 20 wt % FAB-Pt/C exhibited more degradation.

4. Discussion

4.1. Thermogravimetric analysis

The TGA analysis was conducted to investigate the weight percentage of Platinum in FAB – Vulcan XC-72 and to confirm that there was no detrimental effect in the thermal stability of the catalyst due to the addition of functionalized acetylene black. In figure 2 (a), the carbon forms decompose at a temperature above 400 °C and oxidize completely by 650°C owing to the evaporation of the adsorbed water, the decomposition of oxygen-containing functional groups, and the combustion of carbon skeleton. Thus, at higher temperatures, only platinum was found to be the residual content.

4.2. Electrochemical Analysis - Rationale for efficiency from CV studies

Cyclic voltammetry studies have revealed the following as the order of efficiency for the catalysts

15 wt % > 10 wt % > 20 wt % > 1 wt % > 5 wt %

The rationale behind the above order is hypothesized as; the 1 wt% to 5 Wt% addition of FAB to 20% Pt/C disrupts the existing pristine network of Pt/C, leading to an obstruction in the conductivity and hence decreased current density. Additionally, FAB not being completely dispersed in the matrix does not allow proper transfer of charges, leading to a disturbance in the distribution of charges. With further increase in FAB, a small increase in the electrochemical properties of the catalysts is observed, which could be due to the uniform dispersion of FAB and its inherent properties like absorptivity and conductivity contributing to the matrix in unison. The 15 wt% FAB-Pt/C exhibits the best performance due to optimal FAB dispersion leading to higher ECSA that indicates available sites for catalysis, MA and higher current density. However, when the amount of FAB is increases from 15 wt% to 20 wt%, a detrimental effect is observed, which might be due to the crowding of the functionalized acetylene black around the active sites, potentially blocking the access. These results suggest that an optimal amount of FAB addition can maximise the ORR activity. Figure 5 represents a schematic representation of this hypothesis.

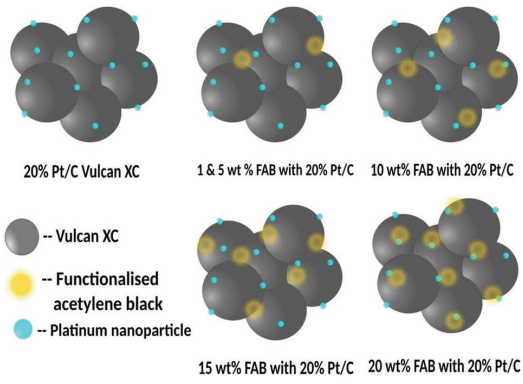


Figure 5. Schematic representing dispersion of FAB in 20% Pt/C Vulcan XC

4.3. Confirmation through Linear Sweep Voltammetry

Linear sweep voltammetry studies confirm the observations from CV studies. 15 wt% FAB-Pt/C exhibits higher limiting current density, indicating an improved ORR activity compared to the commercial 20% Pt/C. Despite the shift in their ORR peak potentials, possibly due to a larger reduction of oxygen species at the electrode, the onset potentials remain similar at 0.6 V vs. Ag/AgCl for both the catalysts. The peak potential shift observed only in the 15 wt% FAB-Pt/C might be due to a stronger interaction between FAB and oxygenated species, leading to more efficient reduction, enhancing the current density and hence mass activity. The mass activity calculated for the 15 wt% FAB in Pt/C (22.82 mA g^{-1}) demonstrates an 18 % increase compared to the unmodified commercial catalyst (18.18 mA g^{-1}), deeming the 15 wt% FAB added commercial catalyst to be a better one. This result aligns with the findings from the cyclic voltammetry test.

4.4. Stability assessment through accelerated degradation test

Corrosion testing, performed using the accelerated degradation test, reveals good stability for most samples. Electrocatalysts with 1 wt %, 5 wt %, and 15 wt % - FAB additions exhibit a slight increase in the ECSA after the ADT, which can be attributed to the activation of (111) plane of Pt within the catalyst. The ECSA difference is negligible in 10 wt% FAB-Pt/C, while 20 Wt% FAB-Pt/C shows a larger reduction in ECSA following the ADT, suggesting degradation due to the amorphous nature in FAB. These observations suggest that there might be an optimal FAB loading that balances improved activity with acceptable durability.

5. Conclusion

The optimized electrocatalyst containing 15 wt% addition of FAB in the commercial 20% Pt/C catalyst exhibits superior performance in terms of mass activity and higher onset potential. This composite not only demonstrates higher catalytic activity, but also maintains stability under pulsating potentials. Long duration stability studies constitute the future scope of this work. In conclusion, these experimental findings confirm that incorporating an optimal amount of functionalized acetylene black does not hinder the ORR activity but rather enhances the ORR kinetics even at lower platinum content, offering a promising strategy for developing Pt-based electrocatalysts.

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