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Surface modification of carbon black by nitrogen and allylamine plasma treatment for fuel cell electrocatalyst

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ABSTRACT

Carbon black used for fuel cell catalyst support system is modified using nitrogen and allylamine plasma and its effect on the carbon surface and fuel cell performance are reported. Custom designed radio frequency tumbling plasma reactor is used to surface modify the carbon black. Boehms Titration method, XRD and TEM are performed to confirm and analyze the effects of plasma treatment on the carbon surface. In the fuel cell electrochemical study both the nitrogen and allylamine modified catalyst support system exhibited better discharge performance than the control system. Nitrogen moieties on the carbon surface helped to decrease the particle size of catalytically active sites and provided good anchoring of Pt to the surface thereby resulted in increased electrochemical performance in the fuel cell evaluation.

Introduction

Polymer Electrolyte Membrane fuel cell (PEMFC) is an excellent source for portable and transport applications because they can provide high energy efficiency. High cost of the noble metal catalyst used in the fuel cells prevents the commercialization of the fuel cells. But there is an extensive research on non noble metal catalyst, alternate ways to improve the performance and reduce the material costs [1–4,29]. The current state of art uses carbon as a support for metal particles (i.e. Pt) as a catalyst to increase the efficiency of the electrochemical reaction on the cathode and the anode. The electrocatalyst is supported onto a porous carbon support in order to increase its contact area with the reactants [1] and also it acts as a pathway for electron diffusion. The performance of the catalyst not only depends on the metal particle, but also influenced by the morphology and functional groups on the carbon support.

In recent years, the carbon support material has been pretreated in order to improve the electrocatalytic activity. Suitable chemical modification i.e. Functionalization is required to modify the carbon support in order to facilitate the interaction with the catalyst particles [5,6]. Functionalization of carbon surface can be done through gas phase (ozone, plasma) and the liquid phase (concentrated and aqueous solutions) acids. Earlier the carbon support material was pretreated with different acids such as HNO_3 [7,10], H_2O_2, $(NH_4)_2S_2O_8$ [8,10] and NaOH [9]. These wet treatments require cleaning of residuals on the carbon. The disadvantage with

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these processes is that it cannot be controlled easily. O_3 treated carbon as a catalyst support was also studied [11]. Modification of carbon surface is attracting attention in other energy storage applications as well [30,31].

Plasma treatment is one of the popular surface treatments for carbon materials because of its unique advantage of modifying the carbon surfaces without affecting its bulk properties. Additionally, the plasma treatments are possible under oxidative, reductive or inactive atmospheres [12]. Researchers has reported the plasma treatment of carbon with C_2F_6, O_2, Ar, H_2 and studied their electro catalytic activity [13–16]. Park et al. reported that the nitrogen plasma treatment is significantly essential to the improvements in the surface properties, microstructures and peeled off the outer layers of carbon surfaces [12]. Researchers have reported the usage of the plasma treatment for modifying the catalyst support materials in the steam reforming applications [32,33]. Fuel cell catalyst was surface modified through plasma polymerization of vinyl phosphonic acid and its effect in the fuel cell performance was reported [34].

Park et al. [17] studied the catalytic activity of nitrogen treated carbon black with different treatment time. It is reported N_2 plasma creates different functional group such as $-NH$,$C-N$,$=NH$,$-NH_3^+$,$C=N$, and $-NH_2$. But the best catalytic activity was shown by the carbon with amine functional group such as $=NH$,$-NH_3^+$ along with all other reported functional groups. Though nitrogen plasma treated carbon support was reported, its effect on fuel cell performance was not studied to best of our knowledge. Researchers have studied the plasma polymerization of allylamine in the past [18]. It was never used to modify the carbon surface and its effect on the fuel cell as a catalyst was not reported to best of our knowledge.

In this paper, nitrogen and allylamine treated carbon black are used as a support material for the fuel catalyst and its effect on fuel cell performance is evaluated and compared with the untreated Pt/C system.

Experimental

Plasma treatment of carbon material

A custom designed RF tumbling plasma reactor (Fig. 1) was used for plasma treatment of carbon black (Vulcan XC-72).

The apparatus mainly consists of a radio frequency (RF) source, a glass vacuum reactor and a pressure transducer. The plasma reactor is inductively coupled to a 13.56 MHz RF generator and the 250 cm^3 reactor vessel which can allow the random tumbling of the loaded particles through the reactive plasma zone at the desired rotation speed. In the typical coating procedure, carbon black of about 200 mg is loaded in the reactor vessel and the system is evacuated below 100 mTorr and the plasma is ignited. Then the feed inlet tube is opened slowly and the plasma deposition is done for 60 min. The reactor vessel is rotated approximately at 100 rpm. During the experiment, 5 mL allylamine (Sigma Aldrich) is feed in the monomer tube and N_2 gas from the cylinder is passed into the reactor for allylamine and nitrogen plasma deposition respectively.

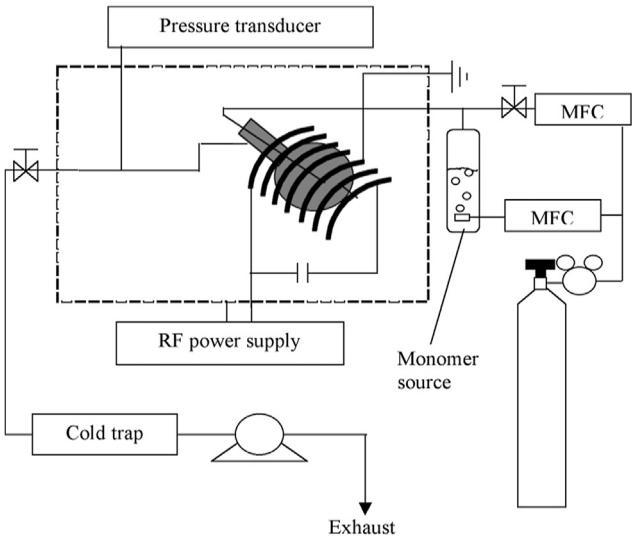

Fig. 1 – Custom designed RF tumbling plasma reactor.

Preparation of catalyst

10 wt% Platinum carbon catalyst preparation procedure is adopted from reported literature [15] with slight modification as mentioned below. Plasma treated carbon black is mixed with ethanol and distilled water in 1:1 ratio and ultrasonicated for 30 min. Chloroplatinic acid, H_2PtCl_6 (sigma) is used as the precursor for platinum and it is added to the mixture above and then ultrasonicated again for 30 min 1.0 M sodium hydroxide is added to adjust the pH of the mixture to 8–9. The mixture is heated up to 80 °C and the formaldehyde is added slowly followed by stirring for 2 h.

After cooling the mixture, HCl is added to adjust the pH to 1–2. The mixture is then purged with argon for an hour, filtered washed with copious amount of hot distilled water. The prepared powder is then dried at 80–100 °C for 12 h. The catalyst prepared with the nitrogen and allylamine treated system is denoted as Pt/C(N) and Pt/C(AA),whereas the untreated system is denoted as Pt/C.

Preparation and test of the MEAs

Nafion membrane (Ion-power Corp, DE) is used in this study. Nafion membrane is pretreated by boiling in 5% H_2O_2 for 30 min and then in 0.5 M H_2SO_4 for 30 min and washing in distilled water for several times. The catalyst ink is made from 5% Nafion solution (Ion-Power Corp, DE), ethanol and the prepared catalyst. MEAs are made by spraying the catalyst ink directly on both sides of the membrane with 0.2 mg/cm^2 loading. Gas Diffusion Layer (GDL), and the gasket purchased from Ion-power Corporation are used in the cell assembly. MEAs are tested using 5 cm^2 single cell purchased from Fuel Cell Technologies. The cell is tested at 80 °C and the hydrogen and air humidification are also maintained at 80 °C. The polarization curve is recorded at the conditions mentioned above.