

Using Cobalt-Doped Carbon Nanofibers as Catalyst of Cathode in Fuel Cell

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Abstract

Conventional fuels have severely impacted the environment; therefore, renewable sources are considered a very good alternative to conventional ones. Fuel cells could be regarded to be an excellent alternative source of energy. Platinum and their alloys have long been considered as the perfect catalyst for oxygen reduction reaction in fuel cells at the current stage of this technology. Platinum is highly expensive for cathode catalyst, the objective of this work is to prepare and characterize catalyst as non-precious metallic nanostructures as novel, cheap and effective cathode catalysts for fuel cells. Cobalt- doped carbon nanofibers (Co-doped CNFs) as catalyst for cathode in fuel cell, has been prepared and characterized by using TEM and XRD measurements the oxygen electroreduction activity was studied by technique of cyclic voltammetry (CV), thus results indicated that (Co-doped CNFs) has high current density for the reduction in fuel cell where it is cobalt only not iron-cobalt or Platinum cobalt alloy so (Co-doped CNFs) has high oxygen reduction reaction (ORR) activity.

Keywords: Fuel cell, Carbon nanofiber, cobalt, oxygen reduction reaction, electrospinning

1. Introduction

Over the past several years, a growing interest has increased in developing alternative power sources, and these by replacing the fossil fuel with hydrogen fuel (fuel cell), which can substantially decrease greenhouse gas emissions and pollution of smog [1-3].

Because of many features of fuel cell as cleanliness, high efficiency, usability of exhaust heat, and flexibility for mobile, transportation and stationary applications [4-6]. Fuel cells (FCs) have been regarded to be a promising power source of alternative energy.

Attention has recently been paid to proton exchange membrane fuel cell (PEMFCs) type, under consideration of transportation and also emergency electric power sources

due to its by-products to be friendly to the environment, high power density, low operating temperature and low noise. Nevertheless, fuel cell couldn't be in large

scale commercialization because of the expensive cost of their constituents and specially the cost of Pt. To enhance the reactions in the fuel cell using catalysts at the anode for hydrogen oxidation reaction (HOR) and at the cathode for oxygen reduction reaction (ORR), The ORR generally faces slow kinetics so it requires efficient catalyst with high amount [7], the amount of catalyst to activate ORR at cathode is ten times more than that amount at anode [8].

Platinum and their alloys have long been considered as the perfect catalyst for ORR in fuel cells at the current technology stage [9-12]. Nevertheless, it's expensive

price, limited reserves, and low tolerance to the crossover effect of platinum-based catalyst, especially in acid media [13, 14], in addition to that Pt-catalyst also during the long term operation, it suffers stability problems, due to the agglomeration and dissolution of its partials.

Therefore, some research has been conducted to try to reduce the cost and performance improvement has been researched for many years. Two major paths are to reduce catalyst cost are being actively studied; one path is to minimize Pt loading and the other path is to explore Pt free catalysts. At the short term, the practicality of the catalysts containing a low amount of Pt makes them the priority, but over the long term, the use of Pt-free catalyst would be the better solution.

The Pt -free cathode catalyst has taken the most attention over several years Pt-free cathode catalysts such as; palladium alloys [15, 16], metalloporphyrins [17], nitrogen doped carbon [18], Ir- based chalcogenides [19], carbides and nitrides [20], transition metal oxides [21] and transition metal macrocyclic compound-based catalysts [22, 23] have been suggested as probable alternatively catalysts for ORR because of the relatively high activity of electrocatalytic and low cost of catalyst.

In the past, a lot of research has been done about the activity and stability of transition metal macrocyclic compound based catalyst and by using the heat treatment in an inert atmosphere at high temperature, this could improve the sopped onto carbon support [24], then after that it's found this catalysts with similar activities could be prepared via using metal and nitrogen precursors cheap than the $M-N_4$ macrocyclics ($M=Fe, Co$) [25], In the end, the matter sums up in that three compounds I- nitrogen II- Fe or Co III- carbon are needed to form catalytic

sites at high temperature [26, 27] although the transition metal was not an active site for the ORR, but it's presences enhanced the formation of the active site for the ORR and the using techniques of nanotechnology thus will increase the number of active sites so increasing in electrocatalytic activity, the most nano shape effective is nanofibers because of its high surface area to volume ratio and therefore important for any catalyst in all reactions, the best technique to form nanofibers is electrospinning technique [28].

For this work in, transition metal doped carbon nanofibers (Co-CNFs) have been synthesis by using technique of electrospinning, using source of carbon and nitrogen polyacrylonitrile (PAN), because of its high nitrogen and carbon content after calcination, and cobalt acetate tetrahydrate as a source for cobalt (Co). Then make the physical characterization by using, analysis of XRD, TEM and SEM. Finally make the electrochemical measurements of the catalyst by cyclic voltammetry.

2. Experimental Work

Materials

Polymer of polyacrylonitrile (PAN, Sigma-Aldrich, Co. Ltd.), solvent of dimethylformamide (DMF, Oxford chemical, Ltd.), metal of cobalt acetate tetrahydrate (Co/Ac, Alfa Aesar, Co. Ltd.), sulfuric acid (H_2SO_4), 5 wt % Nafion (Sigma-Aldrich, Co. Ltd.), and distilled water have been used in this work.

Preparation

The preparation of cobalt doped carbon nanofibers are carried out according to the following proceedings: The first step is preparing PAN solution with (12 wt. %) by dissolving 1.437 g of PAN into 11 mL of DMF, a homogenous solution of PAN

in DMF was obtained by stirring under heating at 60°C for 1 h then was stirring at room temperature for one night [28]. The second step is preparing cobalt solution with (1 wt. % of PAN) after calculation dissolved 0.06 g of Co/Ac in solvent 1 mL DMF by stirring at room temperature for 1 h, then mixed to 11 mL of 12% PAN solution and stirred at room temperature for 3 h, to be a homogenous solution.

With the same steps prepared different Co wt. % concentration (0%, 2%, 3%, 4%, 4.6%, 6% and 9.2%).

Electrospinning steps

Using electrospinning device to get the solution in nanofibers form, making electrospinning for a sample of 12 mL at applied voltage 12kv at the working distance among the needle contain solution and the metallic collector 30 cm, at zero amperes at low rpm and room temperature 25°C

Drying and stabilization steps

The nanofibers mats results from electrospinning were initially dried in air at room temperature 25°C for 3h, and then at 80°C. The dried nanofibers mats are stabilized by heating it at 250° C for 4h in air.

Carbonization steps

The stabilized nanofibers mats were carbonized at 900°C for 1h in an inert atmosphere; the heating process was constant all time at heating rate 5°C/min.

Characterization

Analysis of X-ray diffraction was carried out on dry catalyst as powder using a Philips X'pert MRD with Cu K α radiation. The distribution of cobalt in carbon was also characterized by a JEOL JEM-2100 transmission electron microscope (TEM).

The electrocatalytic activity for ORR of the catalyst has been investigated by cyclic voltammetry with A GAMRY (reference 3000) potentiostat, a three electrode cell, and glass carbon electrode (GCE) (0.3 mm in diameter); the working electrode was a thin layer of Nafion bonded catalyst 0.15 mg cat./cm² on (GCE), a Pt wire as counter electrode and Ag/AgCl as a reference electrode. The electrolyte is 0.5 M H₂SO₄ solution and before working purged ultra-pure nitrogen and oxygen for 20 min to maintain inert and oxygen atmosphere near the working electrode, with scan rate 5 mv/s.

3. Results and discussion

Morphology of catalyst prepared

To present the morphology and structure of prepared catalyst Co-CNFs as fuel cell's catalyst of cathode, several analyses as TEM analysis transmission electron microscopy, EDX analysis energy dispersive X-ray spectroscopies, and finally XRD analysis X- diffraction, were performed.

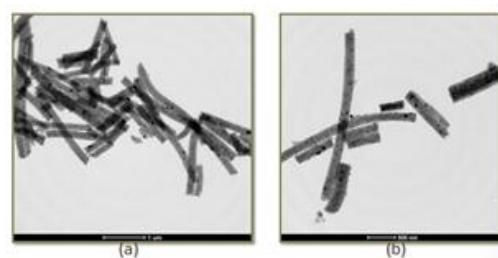


Fig.1 .TEM images of cobalt-doped carbon nanofibers

Figure 1 indicates TEM images of prepared catalyst Co-CNFs, where these images showed that the catalyst had been succeeded in the preparation to be in form of nanofibers, where the fiber shown in fig. 1(a), also from TEM images, it has been shown that cobalt has successfully uniform doping on carbon nanofibers, which show in fig. 1(b).

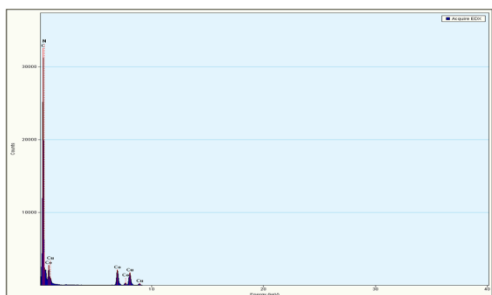


Fig.2 EDX analysis of cobalt – doped carbon nanofibers

The EDX analysis is usually used to confirm the composition, percent and atomic ratio of catalyst components. **Figure 2** show the EDX elemental composition (weight %) of the Co-CNFs catalyst from this fig it can be seen that the carbon component is the dominant component in catalyst, and the cobalt is less weight % and atomic, thus shown in **Table.1** from the table, the obtained weight ratio of cobalt atoms to carbon atoms were around 5% while the expected ratio should be 4.6% so thus is prepared successfully.

Table 1 atomic % and weight % from EDX analysis for prepared catalyst

Element	Wt. %	A %
C	90.01	94.22
N	5.33	4.78
Co	4.65	0.99
	100.00	100.00

Figure 3 displayed the XRD pattern of prepared catalyst (Co-CNFs). From that, it can be seen that this catalyst content on cobalt, where it is shown in the weaker diffraction peaks, the peaks located at

44.37, 51.52, and 75.88 are corresponding to Co (111), Co (200), and Co (220) respectively which indicates the metallic form of cobalt in doping with carbon , thus our target.

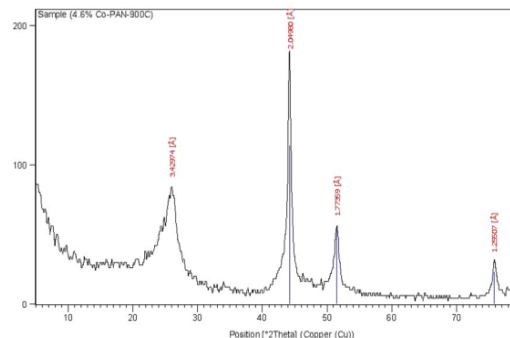


Fig.3. XRD pattern of prepared cobalt-doped carbon nanofibers as catalyst

Activity of catalyst prepared

The oxygen reduction reaction activity of prepared catalyst could be estimated by cyclic voltammetry technique. **Figure 4** presents cyclic voltammogram of Co-CNFs catalyst with different concentration of cobalt (0, 2, 4.6 and 6) coated glassy carbon electrode in O₂-saturation 0.5 M H₂SO₄ solution at room temperature, scan rate is 5 mv/s, thus could be seen cobalt alone doped carbon have a reduction peak of oxygen at about 0.6 about 0.6 V vs. Ag/AgCl, which indicated (Co-CNFs) catalyst have activity for ORR, and this onset potential 0.6 V is good as iron-cobalt doped carbon [29], also have a good current density for the different ratio of cobalt wt.% and the optimum ratio of cobalt is 4.6 wt.% where it has a high current density around 3mA/cm² compare with pt. around 3.5 mA/cm² as shown in Fig. 3. From these results, the catalyst Co-CNFs might be used as a catalyst of the cathode for the fuel cell.

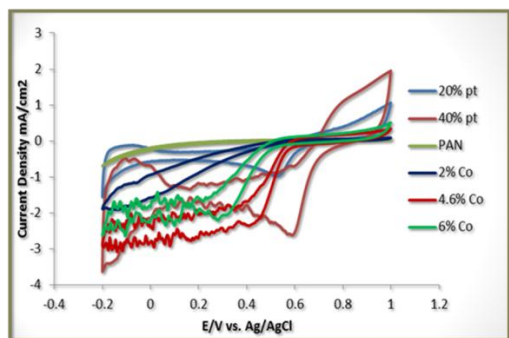


Fig.4. CVs of (Co-CNFs) in O₂ saturated 0.5M aqueous H₂SO₄ electrolyte solution at a scan rate 5mV/s

4. Conclusions

In this work, the cobalt-doped carbon nanofibers prepared to be cathode catalyst in fuel cell were synthesized by sol-gel, electrospinning – calcination at 900°C successfully from different analyses of TEM, EDX, XRD, and CV these results show that;

- The Co-CNFs catalyst has a nanofiber form with uniform distribution of cobalt.
- The cobalt in the catalyst is in a metallic form, not oxide form.
- The Co-CNFs catalyst has ORR activity for fuel cells, and the best ratio of cobalt is 4.6 wt. % which has current density 3mA/cm², with onset potential 0.6V vs Ag/AgCl.

From these results, it's suggested that Co - CNFs catalyst in this work could be used as a cathode catalyst for the fuel cell. Nevertheless, the current density is still lower than pt.-catalyst, but because of the high cost of pt.-catalyst, it might be used as a cathode catalyst for the fuel cell.

5. References

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