

Synthesis and Characterization of Pt/NTC Electrocatalysts for Oxygen Reduction Reaction

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ABSTRACT

Recent research has found that the decomposition of the support and particularly in the cathode side is compromising the useful life of the fuel cells, since the carbon vulcan is oxidized to CO₂ in the operating conditions of the cell. In order to improve operation, carbon support has been modified with an exfoliation treatment to increase capacitance of carbon nanotubes (CNTs). The enhanced capacitance can be attributed to improved effective surface area and increased defect density of the tubular structure. The results declared that the exfoliated CNTs are promising electrode materials for high capacitance supercapacitors.

Results on cathode electrocatalyst synthesized by the polyol method are shown. This method was chosen in order to obtain nanometric particle sizes, because according to the literature, smaller particle size produce enhanced catalytic activity by increasing contact area. A solution of diethylene glycol (DEG) with platinum chloride and multiwalled carbon nanotubes was refluxed for 4 hours at 214 ° C. Resulting solution after reflux process was filtered and washed with ethanol to remove DEG excess. Nanotubes underwent an exfoliation treatment to increase the surface area and get a higher dispersion of the active phase, which allow oxygen diffusion and improvement of reaction kinetics.

The results are shown by means of linear sweep voltammetry (LSV), scanning electronic microscopy (SEM), transmission electronic microscopy (TEM) and X-ray diffraction (XRD) and compared with the performance of catalyst 10% Pt/90% NTC.

Keywords: Electrocatalyst, PEM fuel cell, polyol mediated synthesis.



1. Introduction

For a long time it was believed that oil supplies would be safe and almost unlimited, but the oil shocks transformed the secure supply of cheap oil in an unsafe and expensive delivery. In view of the available reserves and so pessimistic projections, it is clear that in the near future will require alternative energy sources, taking into account the huge energy needs of the industrialized world. Clean, available and efficient: a new energy regime, which must comply with the following characteristics is required. Has recently been paid much attention to fuel cells, electrochemical devices that are intended or being one of the preferred sources of energy in the future medium.

Interest in fuel cell proton exchange membrane (PEMFC) is its cleanliness, versatility and high efficiencies obtained from the conversion of chemical energy to electrical energy, especially for portable applications such as cell phones, laptops and cars, because its low operating temperature.

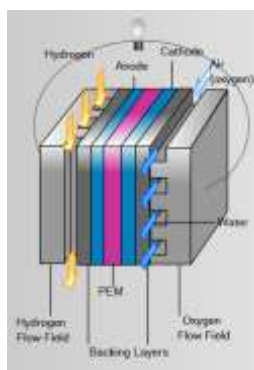
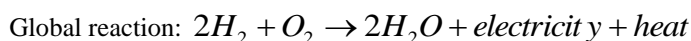
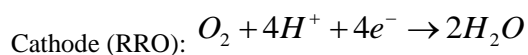
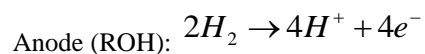


Figure 1. Inputs and outputs of a fuel cell

The chemical reactions taking place in a fuel cell are the follows:



Of the two half-reactions that occur in the cell, the RRO is the limiting reaction in a fuel cell, for presenting a slow kinetics that is crucial to the overall performance of the fuel cell (CC) that is why it is considered very important to study and develop catalysts that offer good performance at the lowest possible cost RRO. When RRO occurs in the fuel cell a high overpotential is needed, associated with the fact that the O-O bond requires high energy to be dissociated which causes reduction occurs three orders of magnitude slower than the reaction requires hydrogen oxidation (ROH). Although studies have been performed for the reaction mechanism of the RRO is not fully understood, however the most acceptable model is the simple and Damjanovic numbered individually and consecutively in square brackets (figure 2) [1-4].



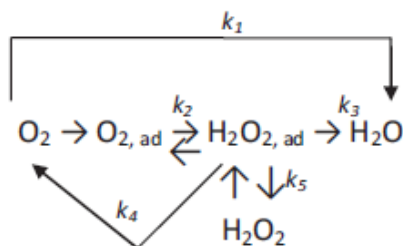


Figure 2. Pathways proposed by Damjanovic reaction [4].

- k1. Route without intermediaries known as "direct" or 4 e-.
- k2. Adsorbed hydrogen peroxide is formed.
- k3. The adsorbed peroxide formed with K2 can be reduced to water.
- k4. Adsorbed hydrogen peroxide can be chemically broken by the electrode surface.
- k5. Desorbing and can be diluted in the solution.

Catalysts based platinum, carbon supported high surface are widely used in fuel cells to low temperature (CC), however, the corrosion of the materials of carbon support for the catalyst as the vulcan carbon, has been recognized as a causes of performance degradation of the CC, particularly under repeated start-stop cycles or conditions of high potential. To improve the stability of the carbon support, materials with higher graphitic character as nanotubes or carbon nanofibers have been tested in terms of the CC. These nanostructured carbons show lower corrosion rate, however, does not prevent oxidation of the carbon, simply reduce its velocity. With lower Pt loadings, the average distance between the metal particles is larger, therefore, the conduction of electrons involving filtration or electron hopping mechanism is unlikely [5].

Carbon nanotubes (CNTs) are emerging as new electrode materials for oxygen reduction reaction (ORR), due to their high conductivity, high surface area and good corrosion resistance. The effective surface of a supercapacitor material is referred to the active layer that is accessible by electrolyte ions; however it is energetically unfavorable for solvated ions to diffuse into the inner tube of CNT, in particularly for multi-walled carbon nanotubes (MWCNTs). In this regard, the specific capacitance of MWCNTs, especially at high current operation, can be limited by the slow diffusion of ions. Considerable efforts have been placed to improve the specific capacitance of MWCNTs. For example, the CNTs treated with sulfuric acid or nitric acid showed several times enhanced capacitance due to the increased surface detected density, which facilitated the diffusion of ions into the inner tube. In this work was used a simple way to enhance the capacitance of MWCNTs by increasing the active surface area and defect density trough exfoliation.

2. Experimental

2.1 Synthesis of catalysts

For the synthesis and characterization of catalysts Pt/C multi walled carbon nanotubes (MWCNTs) were used as support. As platinum precursor salt, platinum dichloride was used (PtCl₂ Sigma Aldrich®) and diethylene glycol (DEG) as solvent (Alfa Aesar®). First and to obtain a homogeneous distribution of nanotubes were dispersed in DEG for 30 minutes using a disperser IKA Ultra-Turrax ® T 18 DIGITAL, then salt of platinum was added to obtain a correct homogenization. This solution was heating up to the boiling point of DEG, held at boiling for 3 hours to ensure complete reduction of the platinum salt. A three-necked flask of 250ml PYREX ® was used and rotary agitation to maintain the solution in stir during the reaction time. Subsequently the catalyst was filtered and washed with ethanol to remove excess of DEG. Finally the sample was treated thermally (TT) at 500 ° C for one hour in a tube furnace.





Figure 3. Equipment used for the synthesis by the polyol method

2.2 Exfoliation treatment of carbon nanotubes

Exfoliated carbon nanotubes (ex-CNT) were prepared by dispersing 0.25g in 15 mL of concentrated H_2SO_4 , the solution was kept stirred for 1 hr and brought to 50°C . Then carefully added 1.5 g of KMnO_4 and are allowed to react. When all the KMnO_4 was consumed 30 mL of deionized water and 3 mL of 30% H_2O_2 were added. The NTC-former were extracted by means of a centrifuge, which was operated at 2500 rpm for 20 min to separate the nanotubes from the liquid, to remove excess of oxidizing solvent washes were performed with deionized water.

2.3 Electrochemical study

For electrochemical analysis of the samples a Pyrex three electrode double-walled cell was used the working electrode RDE0008 commercial glassy carbon electrode with a 0.196 cm^2 area with teflon support was used using the reference electrode as sulfates $\text{Hg} / \text{Hg}_2\text{SO}_4$ (ES), whose standard potential is $E = 0.680\text{ V}$ with respect to the normal hydrogen electrode (NHE) as the counter electrode and platinum titanium mesh was used with a geometric area greater than 10 cm^2 . The potentials are reported with respect to the standard hydrogen electrode, NHE and 0.5M H_2SO_4 solution is used as electrolyte, the currents are referenced with respect to the geometric area of the working electrode.

For preparation of the working electrode, a glassy carbon surface exposed with a sandpaper # 600, until a flat surface together with Teflon to support the thin film of ink to adhere to the glassy carbon is then cleaned ethyl the surface to remove impurities on the surface are alcohol. The catalyst inks were prepared in a vial weighing 1 mg of catalyst were added 60 μL of ethyl alcohol as a diluent and 8 μL of Nafion[®] liquid (5% weight of ethanol) as adhesion to the electrode, the mixture was homogenized in a bath ultrasound for 15 minutes to form a homogeneous suspension called "catalyst ink." Of the catalyst ink 8 μL taken with a micropipette and deposited in the center of the electrode covering the entire geometric area of the glassy carbon. Allowed to dry the ink at room temperature for 15 minutes to observe a thin and homogeneous film on the surface. The working electrode was attached to a rotor Pine, controlled for different speeds of rotation, connected to a Potentiostat/Galvanostat Autolab whose response was analyzed with the software Autolab NOVA.

Before linear voltammetry studies cyclic voltammetry technique, which aims to enable the working electrode to remove surface oxides and adsorbed oxygen during the preparation of the electrode is used. The reduction-oxidation process of the surface increases the electrocatalytic properties of the materials analyzed, besides that there is restructuring of the surface at atomic catalytic stabilizing compounds. This technique in addition to activating the surface of the catalysts can also be used to analyze the signals redox characteristics that are carried out in certain metals, such as platinum which is being studied in this work. Argon was bubbled to deoxygenate the electrolyte for 15 min. Was conducted 10 cyclic sweeps over a range of potential of 0 V to 1.2 V (NHE) at a scan rate of 100 mV s^{-1} for cleaning the electrode and 2 swept at a speed of 50 mV s^{-1} , in the same range of potential to analyze the distribution of active sites and the redox processes occurring at the electrode surface.



Once activated the linear electrode are made voltammetries different rotation speeds for the study of the RRO. The electrolyte solution was bubbled with oxygen for 15 minutes to saturate the electrolyte solution, reaching a open circuit potential, E_{ca} , in this technique this is a very important parameter, you must monitor and verify each experimental run linear voltammetry at different rotational speeds of the electrode is analyzed if it is stable and the time it takes to reach the expected value, you should also take care to always reach the same value, if the voltage between each run of the first run is not reached is an indicator of catalyst instability. The sweep rate was 5 mV s^{-1} . The potential range was used to open circuit voltage (OCV). The speeds used for runs of different catalysts were: 100, 200, 400, 900, 1600 and 2500 rpm, starting from maximum to minimum. Between each scan the system is allowed to reach the initial OCV bubbling oxygen for 5 min, after reaching the potential flow of oxygen is removed from the electrolyte to prevent noise in the electrochemical response, but is left on the surface of the solution to ensure saturation of the solution.

3. Results and discussion

Figure 4 shows the last 2 cycles performed at a speed of 50 mV s^{-1} from 0 to 1.23 V/NHE of the media used for the synthesis of electrocatalyst Pt/C, can also exhibit the curves generated by the vulcan carbon because it serves as commercial support for this type of catalysts and included for comparison, further behavior of CNTs is shown with 10 wt% of WO_x to know if could have a role as co-support.

Carbon nanotubes with exfoliation treatment exhibit greater capacitance regarding carbon nanotubes without exfoliate, in this case the surface area corresponding to the capacitance as it has no faradaic process, indicating that the NTC-former have better properties due its top surface area.

It is noted that treatment of exfoliation in carbon nanotubes produced an increase in the interfacial activity of the NTC-ex. These signals, in both the anodic and cathodic sweep, appear at the same potential, so that these processes are attributed to the phenomena of adsorption/desorption of species of functional groups, thus exfoliation treatment has given functional groups on the "open" pipes surfaces.

The increase in capacitance is attributed to exfoliation treatment product functional groups, these functional groups also favour the nucleation of particles of platinum on the surface of carbon nanotubes.

Table 1. Carbon supports capacitance

Support	Capacitance
MWCNT	278.37
e-MWCNT	11762.00
Carbon Vulcan	1048.50
Mass Pt	40



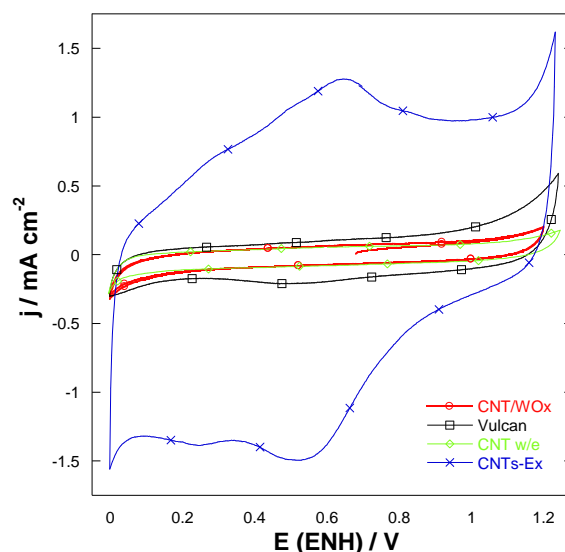


Figure 4. Comparison of Cyclic voltammery at 50 mV s⁻¹ catalyst supports Pt/C

Figure 5 shows the cyclic voltammograms catalysts synthesized by the polyol method. The area of adsorption and desorption of protons, lies between 0 and 0.3 V/ENH, continuing the anodic oxide formation sweep begins at 0.5 V/ENH and ends at 1.2 V / ENH. In the cathodic scan signal is reduced at a potential of 0.75 V/NHE and the double layer area between 0.3 and 0.5 V/ENH. Platinum response characteristic only in the sample with ex NTC and treated thermally (TT) is observed. Similar current density in the catalyst 10% Pt/90% NTC-former with TT and the Pt-Etek wide potential range is observed, this indicates a similar distribution of active sites on these samples as opposed to the other without or thermal exfoliation treatment, this indicates a greater distribution of active sites and larger surface area due to oxidation treatment.

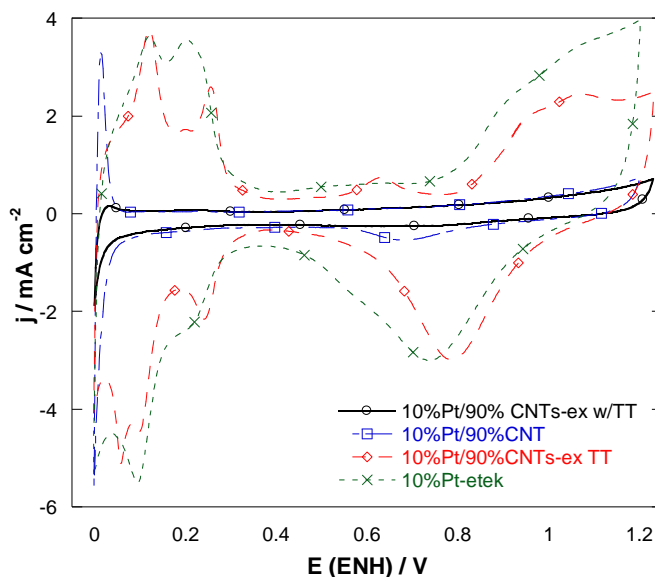


Figure 5. Cyclic voltammeteries at 50 mV s⁻¹ of 10% Pt/90%CNT catalysts.



Figure 6 shows the polarization curves of the samples tested at 900 rpm of electrocatalysts with Pt/CNTC. Three zones of the response characteristics of rotating disk electrode, a low overpotential one between 0.95 and 0.85 V/NHE, where electron transfer is the rate determining step of the reaction is observed as the current density, j , is clearly independent of the rotational speed of the electrode, ω and low current densities are observed. Control diffusional area of 0.7 V is observed up to 0.2 V, the current depends on the rotation speed of the electrode was observed almost horizontal plateau, indicating that the reaction is carried out at sufficient speed that allows a diffusion controlling at more cathodic potentials. Finally the mixed zone where the two phenomena are present, the first one is the transfer of electrons (contributes to increasing current) and the mass transport (transport of oxygen to the electrode surface via diffusion). Both processes influence the reaction rate.

Higher catalytic activity in the catalyst with carbon nanotubes cleaved and heat treated gender as higher current density (-3.2 mA cm^{-2}) is observed at 500°C and present a better definition in the control region that diffusional is in the range of 0.5 to 0.2V/ENH, of treating the catalyst without exfoliation good response is observed in the reduction of oxygen but higher potential applied to start the reduction in the range of plus potential is primarily required is a phenomenon of charge transfer, it has slow kinetics for this catalyst.

For determining step of the reaction speed is necessary to determine the Tafel slope, transfer coefficient and the exchange current. In Figure 7, the Tafel slope represented as a semi-logarithmic relationship of current density against the potential for different catalysts Pt/C is observed They are obtained outstanding polarization curves of Figure 6, eliminating the contribution to the total current density of mass transport, showing only the kinetic contribution. It is observed that the catalyst with heat treatment at current density of 0.1 mA cm^{-2} generates a potential difference greater than the catalyst with carbon nanotubes exfoliate and even Pt-etek.

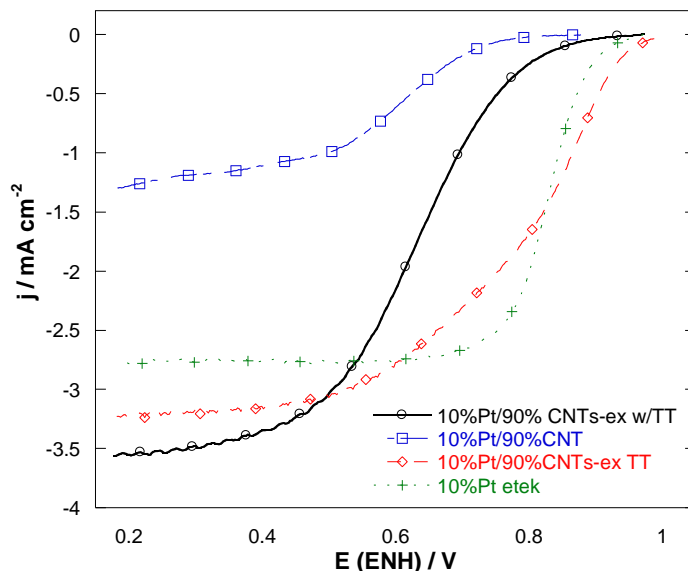


Figura 6. Comparison of linear voltammeteries at 900 rpm of 10%Pt/90%NTC catalyst.

The kinetic parameters that were deduced from Tafel slopes of Figure 6 are shown in Table 2. The kinetic Tafel slope information provides an electrochemical reaction of a Tafel slope of about 60 mV dec^{-1} to 120 mV dec^{-1} corresponds to a first-order kinetics, with the transfer of the first electron electrocatalyst for oxygen chemisorbed molecule on the electrode surface.



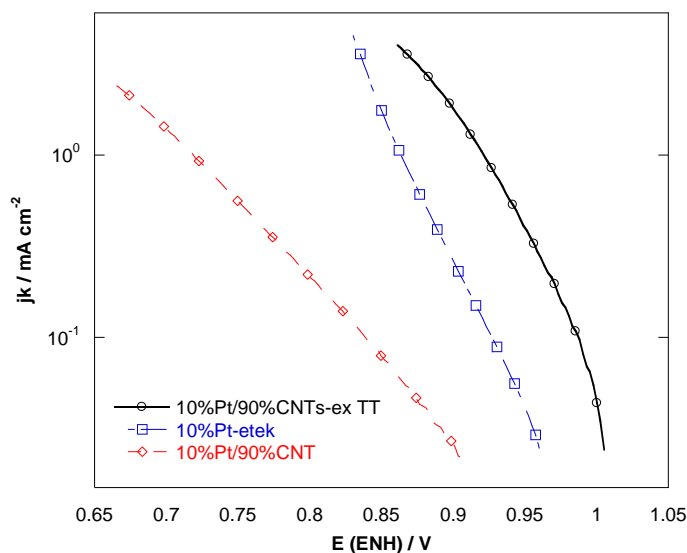


Figure 7. Tafel slope of 10%Pt/90%CNT catalysts

Table 2. Kinetic parameters obtained from the RRO

Catalyst	E_{ca} V / ENH	$-b$ mV dec ⁻¹	α	J_o mA cm ⁻²	Potential / j J=0.1 mA cm ⁻²
10%Pt/90%CNT	0.9	120.6	0.4832	6.4906×10^{-5}	0.84
10%Pt/90%CNTs-ex TT	1.01	59.74	0.991	8.2578×10^{-6}	0.99
10%Pt/C (E-tek)	0.98	62.95	0.9866	9.6858×10^{-7}	0.93

From the results in the table shows that catalyst with NTC-former has higher open circuit potential, smaller slope of Tafel and higher transfer coefficient, this can be attributed to that the catalyst has greater capacity to absorb oxygen because of its greater surface area.



4. Summary and perspectives

When performing the exfoliation treatment CNTs higher capacitance is obtained on support, which in no faradaic processes results in surface area and beneficiary distribution of active sites to obtain higher catalytic activity. Additionally it was observed that heat treatment is necessary to obtain higher catalytic activity, apparently because heat treatment induces a more uniform distribution over the support, which is checked by scanning electron microscopy but can also be observed in cyclic voltammetry.

Acknowledgements

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