Development Of Free-Metal Electrocatalyst From Inexpensive Sources Of Carbon: A Novel Electrode Material for Cathode Reaction in PEM Fuel Cells

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Recently, free noble metal electrocatalysts have been obtained, which are capable of carrying out the oxygen reduction reaction (ORR) with comparable performance to Pt. These novel electrocatalysts are doped nanostructured carbon (ej. nitrogen doped carbon nanotubes N-NTC and nitrogen doped reduced graphene, N-rG). Nowadays, the synthesis of these nanostructured materials has several technological challenges, because it production is still expensive and has a significant environmental impact. In this work, we have obtained novel metal-free electrocatalysts from two different inexpensive carbon source: i) an organic waste and ii) mineral coal from Sabinas region in Coahuila Mexico. These electrocatalysts have a significantly lower cost than conventional platinum-based electrocatalysts or than nanostructured carbon free-metal catalyst. The results show that these electrocatalysts are an inexpensive, environmental friendly and promising alternative for use as cathodes in PEMFC.

Introduction

Fuel cells are considered as a clean and efficient alternative for power generation. However, large-scale production has been limited because noble metals are used as electrocatalysts, which are expensive and scarce. Recently, it has been reported that carbon doped with nitrogen has electrocatalytic activity for fuel cell cathode (1), which opens a significant area of opportunity for the large-scale production of fuel cells. Currently few studies have explored the possibility of using biomass as a source of carbon and nitrogen for the production of electrocatalysts. Li and coworkers (2) reported the use of sponge for electrocatalyst preparation. The sponge was subjected to a heat treatment in ammonia atmosphere. Electrocatalysts obtained have promising properties; however, the use of ammonia has severe environmental implications. Another interesting work is the report by Chaudhari et. al. (3), who used his own urine for obtaining a novel electrocatalysts for this application. After removing water from urine ($\approx$ 95% vol.), the remaining material was subjected to heat treatment and cleaning. However, despite the

novelty of the material obtained by Chaudhari et.al. reporting yields are very low. Moreover, there are numerous reports of carbon nanotubes (4), graphene (5) or ordered mesoporous (6) carbon doped with nitrogen, which have electrocatalytic properties, in some cases, with superior performance to that platinum conventional electrocatalyst. However, the process of obtaining these materials is still expensive and in most cases, the processes are not environmentally friendly.

In this paper, we are use study the use two different inexpensive carbon source: i) an organic waste and ii) mineral coal as carbon and nitrogen source for electrocatalysts fabrication. These carbons were subjected separately at simple thermochemical treatments, in order to obtain a low cost and friendly environmental electrocatalyst.

Experimental procedure

Two inexpensive carbon source were treated in order to obtain self-doped electrocatalyst: mineral carbon (MC) and leather at the end of its useful life (OW). Both materials were carbonized so as received. Carbonization of MC and OW materials was conducted in a tubular furnace; 5 g of raw material was carbonized at 800°C for 90 minutes with the heating rate of 10 °C /min in N_2 atmosphere. The pyrolyzed materials were tagged as PMC800 and POW800 for the mineral carbon and leather respectively. Subsequently, these samples was subjected at activation treatment in order to increase their superficial area. PMC800 and POW800 were mixed separately with potassium hydroxide (Sigma-Aldrich 90%) at a mass ratio of 1 to 2. The samples were heating at 750°C for 90 minutes with a heating rate of 8 °C /min in N_2 atmosphere. After activation, the sample was washed with 1 M of hydrochloric acid solution (Sigma-Aldrich 37%)) to remove the residual alkaline. Finally, the powder obtained was dried at 80°C overnight. This sample were tagged as AMC800 and AOW800.

Morphology and elemental composition were characterized by scanning electron microscopy (SEM, Philips XL30 ESEM, equipped with EDAX detector for elemental analysis). The Raman spectrometry was performed with one Micro Raman Horiba Labranhr Vis 633 with a He-Ne laser source. Textural properties of electrocatalyst carbon materials were measured with Autosorb-1C Quantacrome, USA, at 77 K. Prior to analysis, all samples were degassed at 350 °C during 3 h. ORR electroactivity measurements were performed using a Bipotentiostat of Pine Instrument Company model AFCBP1, by rotating disc electrode technique (RDE) rotator model MSRX.A conventional three-electrode cell was used at 25 °C. The work electrode was prepared deposited 20 µL of a ink previously prepared, 20 mg of powder electrocatalyst were dispersed in 1mL of ethanol and 30 µL of liquid Nafion (Aldrich 5% Nafion) during 40 min in ultrasonic bath. The working electrode was polished and rinsed with ethanol before each measurement. A platinum wire was used as counter electrode and an electrode of Ag/AgCl (KCl sat) was used as reference electrode. The electrolyte media was a solution of 0.5 M of KOH (potassium hydroxide). Linear sweep voltamogramms were performance at 300 RPM using oxygen saturated 0.5 M KOH electrolyte. Measurements potential rate was from 0.2 to -1.0 V vs. Ag /AgCl reference electrode at a scan rate of 5 mVs^{-1}. For comparison, commercial 20% Pt/C (20% Pt/C BASF) was evaluated under the same conditions. XPS analysis was performed in Thermo Scientific equipment K-Alpha model.

Results and discussion

Leather is an organic material with high nitrogen content (10% wt), after carbonization and activation treatments, 15% wt of remaining material was obtained. In addition, mineral carbon was a yield of 39.4%. Figure 1 shows two secondary electron images. The sample AOW800 show a three dimensional structure with macropores larger than 5 μm. Pores formation is due to the release of gases from the thermal cracking during pyrolysis treatment. Moreover, in Figure 1 a micrography of AMC800 is observed. The damage on the surface of this sample is evident after the alkali treatment. However, the presence of macropores is not so evident in this sample.
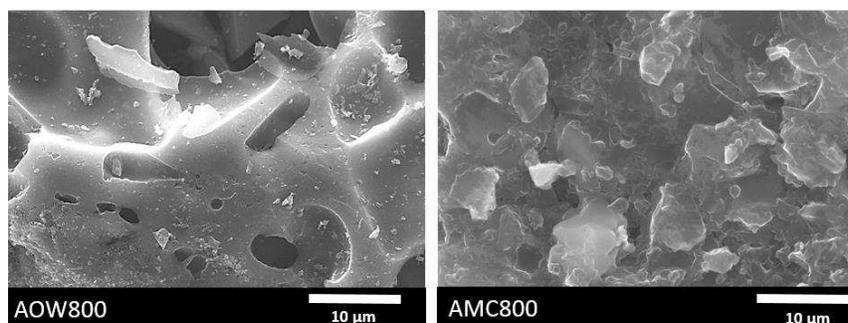

Figure 1. SEM images of two self-doped electrocatalyst. Left) Leather morphology after carbonization and activation treatment. Right) Mineral carbon after activation treatment.

Structural composition was determinate by Raman Figure 2 shows Raman spectra obtained for the two electrocatalysts. The samples show bands D (1350 cm-1) and G (1580 cm-1), these bands are characteristic of carbon materials with graphitic structure, and the relationship between the intensity of these bands gives information about its structural composition. In terms of their vibrational behavior, G band is caused by stretching of all pairs of sp^2 bond, in both chains and rings. Usually, D band is due a forbidden transition mode, but in presence of disorder, defect or broken symmetries in the graphitic network caused by doping, these transition states are allowed (7). So that the ratio of intensities between these two bands (I_D/I_G) can obtain information about the number of defects. Table 1 shows that I_D/I_G ratio is very close to 1for the sample AMC800, indicating that the proportion of defects and order in the structure of the electrocatalysts are in the same proportion. However, for the sample AOW800 the I_D/I_G ratio was of 1.4. This result indicates that this sample has more defects in its lattice than AMC800 sample.
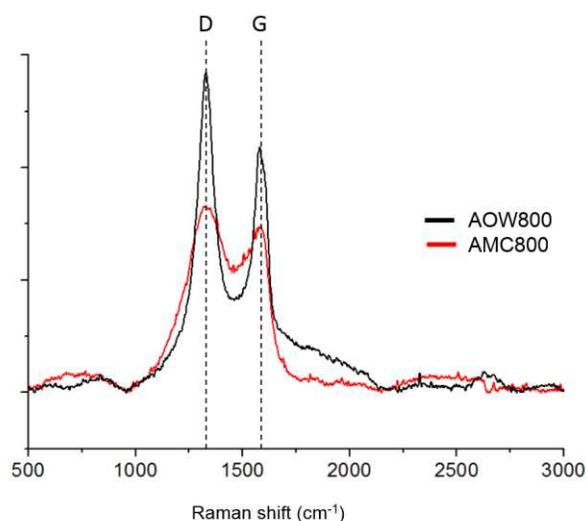
Figure 2. Raman spectra of two self-doped electrocatalyst. Black) Leather spectra after carbonization and activation treatment. Red) Mineral carbon after activation treatment.

Moreover, the chemical composition and molecular structure was determined by XPS, the nitrogen content and nitrogen-carbon bond types are summarized in Table 1. Is evident that pyrolysis treatment modify the nitrogen-carbon chemical bonds in the leather and mineral carbon. Moreover, atomic percent of nitrogen in AOW800 is about 1.45% at. While, AMC800 has a nitrogen content fo 2.64 % at. Specific areas calculated by BET method were of 1768 and 1118 m^2/g for AOW800 and AMC800 samples respectively (Table 1).

TABLE I.   Physical and chemical properties of two self-doped electrocatalyst obtained from inexpensive carbon sources.

Code	I_D/I_G	S_{BET} (m^2/g)	Elemental composition by XPS (% at.)				Binding energies (eV)/ relative atomic concentration (%)			
			C1	O1	N1	S	N1 Pyridinic	N2 Pyrrolic	N3 Quaternary	N4 Pyridinic-N-oxide
AOW800	1.40	1768	89.5	8.44	1.45	0.54	398.6 (21.9)	399.6 (44.7)	400.6 (27.5)	401.9 (5.9)
AMC800	1.09	1118	69.9	25.0	2.64	2.29	- -	399.5 (7.3)	400.2 (64.8)	401.8 (27.9)

Figure 3c shows LVS of two electrocatalyst performed at 300 RPM compared with a commercial platinum electrocatalyst (20% Pt / C). The AMC800 material even show activity for ORR, with on-set potential ≈-270 mV and current density lower than platinum. Moreover, AOW800 sample has an on-set potential very close at -220 mV, more close compared with Pt/C (-115 mV). The current density of the sample AOW80 is also higher than of platinum. However, no limit current can been determinate at this potential window. The increase in electrocatalytic activity for this sample can be attributed to the increased surface area and the presence of more pyridinic and quaternary

bonds (8). In addition, AOW800 sample has less oxygen bonds; it is help to improve its electrocatalytic activity. The presence of defects corroborated by Raman, in combination with high electrode-electrolyte interface provide to AOW800 of high activity for the ORR.
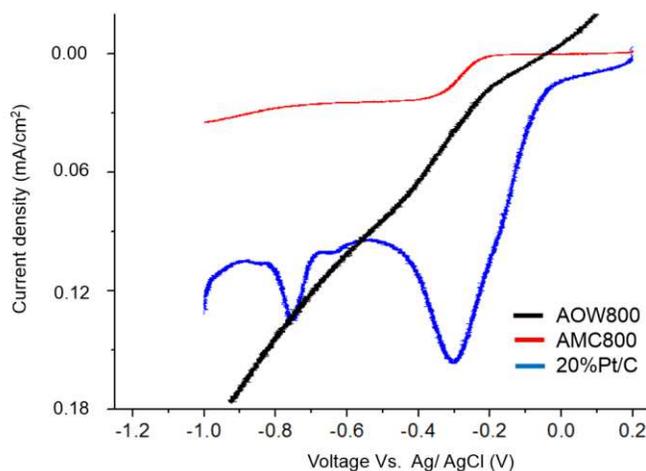

Figure 1. LSV-curves of two self-doped electrocatalyst compared with conventional platinum electrocatalyst. The test was performed in alkali media with 0.5 M of KOH as electrolyte, at scan rate of 5 mV/s.

Conclusions

Electrocatalysts were obtained from single thermochemical treatments using as raw material leather scrap and mineral carbon. The physicochemical characterization allowed determining the features of these materials, which reinforced the explanation about their high electrocatalytic activity. The results show that after the pyrolysis and activation treatment, leather and mineral carbon bonds are modified, while the relative carbon content increases, which gives to the materials properties of electrical conduction. Carbon-nitrogen bonds were modified, forming mostly quaternary and pyridinic bonds in AOW800 sample. Both materials showed electrocatalytic activity for ORR. However, the sample has AOW800 electrochemical properties that make it an attractive and promising material to be used as electrocatalyst for the application proposed here. Besides having the advantage that it can get from a domestic waste, adding value to get a free-platinum electrocatalyst, of lower cost and more environmentally friendly.

Acknowledgments

References

1. K. Gong et. al. *Science* **323**,760 (2009).
2. J. Li et. al. *Electrochem. Acta*. **149**, 56 (2014).
3. N. K. Chaudhari and M. Y. Song. *Scientific Reports*. **4**, 5221 (2013).
4. J. Wei et. al. *Physica E* **40**, 462 (2008).
5. S. Y. Yang et. al. Electrochemistry Communications **14**, 39 (2012).
6. H. W. Liang et. al. *J. Am. Chem. Soc*., **135**, 16002 (2013).
7. Y. Wang et. al. *Chem. Mater*. 1990, **2**, 557 (1990).
8. H. Wang, *ACS Catal*. **2**, 781 (2012).