Student Prize: Nitrogen doped activated carbons as electrocatalysts for the oxygen reduction reaction

María José Mostazo-López[1], Ramiro Ruiz-Rosas[1], David Salinas-Torres[2], Emilia Morallón[3], Diego Cazorla-Amorós[1].

[1] *Instituto Universitario de Materiales, Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, 03080-Alicante, Spain*

[2] *División of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Siuta, Osaka 565-0871*

[3] *Instituto Universitario de Materiales, Departamento de Química Física, Universidad de Alicante, Apartado 99, 03080-Alicante, Spain*

Introduction

One of the main challenges for the development of fuel cells is the generation of new catalysts for the oxygen reduction reaction (ORR) that takes place in the cathode. The most common materials are based on platinum and other noble metals, but they show drawbacks, such as their high cost, low availability and vulnerability to CO-poisoning, that strongly affects the durability of the device. An alternative to the current state-of-the-art catalysts is the use of metal-free carbon materials doped with different heteroatoms, such as nitrogen, since its presence can modify the electron-donor properties of the carbon and provide a redistribution of electronic density, producing an increase of the electrocatalytic activity for the ORR. However, the role of the different nitrogen functional groups is not still well understood.

In this work, N-doped activated carbons have been prepared by chemical polymerization of aniline over activated carbons with well-developed microporosity followed by thermal post-treatments of the polyaniline/activated carbon composites at different temperatures. The role of surface chemistry on their electroactivity towards ORR has been extensively studied.

Materials and Methods

Activated carbon (AC) was produced by chemical activation of anthracite with KOH as activating agent (4:1 ratio) at 750ºC for 2 hours. PANI/AC composite was prepared by chemical polymerisation of aniline (70mM) with ammonium persulfate solution in 1M HCl. The obtained PANI/AC composite was submitted to thermal treatments at a heating rate of 5ºC/min up to 600 and 800 ºC under N_2 atmosphere (200mL/min, 1h) to produce N-doped activated carbons, named as N-AC_600 and N-AC_800. Porous texture of the samples was characterized by N_2 adsorption/desorption at -196 ºC. XPS analyses were performed in a VG-Microtech Multilab 3000 spectrometer (Al anode). TPD experiments were carried in a TGA-DSC instrument (TA Instruments, SDT Q600 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers, BSC 200).

The electroactivity of the materials for the ORR was evaluated by using a rotating-disk electrode, equipped with a glassy carbon disk (5.61 mm diameter) and a platinum ring electrode, in alkaline electrolyte (0.1 M KOH). A platinum wire was used as counter electrode and a reversible hydrogen electrode (RHE) immersed in the same electrolyte as reference electrode. The catalyst was deposited on the glassy carbon disk by using a dispersion of each carbon material in ethanol and Nafion. The materials were characterized by linear sweep voltammetry in O_2 saturated 0.1 M KOH electrolyte at different rotation rates (400 – 2025 rpm) and at a scan rate of 5mV/s. The potential of the ring electrode was kept constant at 1.5 V (vs RHE) during all measurements.

Results and Discussion

Table 1 summarizes the main physicochemical properties related to the surface chemistry and porous texture of the samples. The polymerization of aniline over AC produces the attachment of nitrogen (mainly amines) and oxygen functionalities (CO and CO_2 evolving groups), as well as a decrease of the apparent surface area and micropore volume. The thermal treatments produce the decrease of nitrogen and oxygen groups due to the elimination of surface functionalities. Moreover, the nitrogen groups in the PANI/AC composite are selectively converted into pyridones/pyrroles and pyridines (Figure 1a) as consequence of carbonization of polyaniline through cross-linking and condensation reactions[1]. In addition, some part of the microporosity of the pristine carbon material is recovered after the heat treatments because of the removal of surface functional groups. Thus, two different activated carbons with high microporosity but different surface chemistry are obtained.

The role of the nitrogen groups on the ORR was thoroughly analysed in alkaline medium. Figure 1b shows the LSV curves obtained for the pristine carbon material (AC) and N-doped activated carbon at 800ºC (N-AC_800) and Table 1 compiles the *onset* potential (E_{onset}) and the number of electrons involved in the ORR for all samples. The chemical modification of the carbon material AC produces some changes in the electrocatalytic activity of the samples. The formation of polyaniline over AC decreases the electroactivity because of the generation of detrimental surface functionalities. However, some beneficial effects are observed for the heat-treated N-doped activated carbons (N-AC_600 and N-AC_800). First, an increase of the number of electrons involved in the reaction was detected for both heat-treated carbons due to the presence of nitrogen groups, such as pyridones, that favors the 4e$^-$ pathway for the production of H_2O. The best performance was found for the activated carbon heat treated at 800 ºC, which also evidences an improvement on the E_{onset} up to 0.90 V.

These improvements are mainly consequence of the formation of nitrogen groups with high electroactivity at this temperature[2] along with an increase of conductivity.

Sample	N_{XPS} (At. %)	CO_2 TPD ($\mu mol/g$)	CO TPD ($\mu mol/g$)	S_{BET} (m^2/g)	V_{DR}^{N2} (cm^3/g)	E_{onset} (V vs RHE)	n (at 0.3 V)
AC	0.3	520	2400	3460	1.19	0.81	2.9
PANI/AC	6.0	1320	3560	1460	0.54	0.78	2.6
N-AC_600	4.7	380	1860	2290	1.03	0.80	3.3
N-AC_800	2.0	210	740	2330	1.04	0.90	3.4

Table 1. Physicochemical and electrochemical properties of the samples.
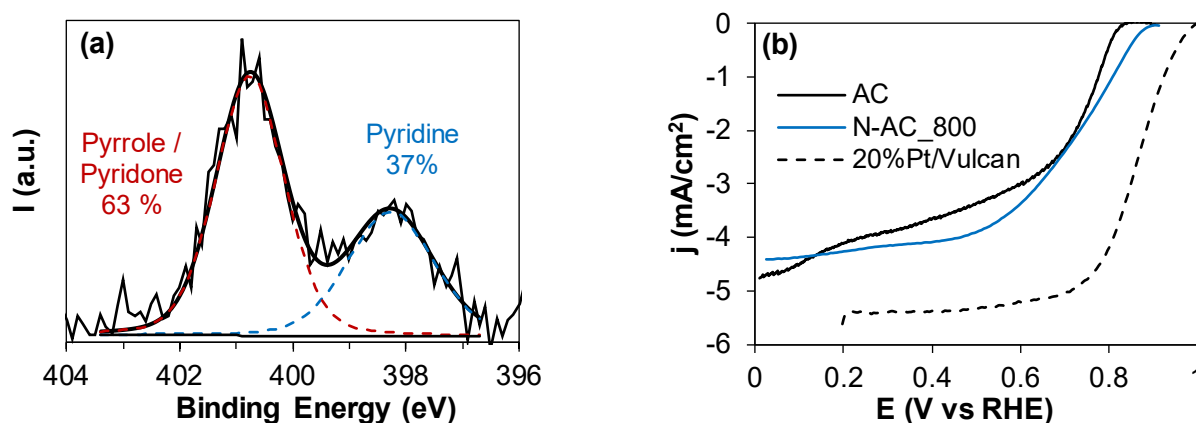

Figure 1. (a) N1s XPS spectrum obtained for N-AC_800, (b) LSV profiles obtained for AC (black), N-AC_800 (blue) and Pt/Vulcan (dashed line) at 1600 rpm. 5 mV/s.

Conclusions

Carbon-based electrocatalysts with high apparent surface area and different nitrogen content were prepared by polymerisation of aniline and post-heat treatments. Their performance towards ORR evidenced an improvement of the electrocatalytic activity towards ORR related to the generation of nitrogen groups at high temperatures (pyrroles, pyridones, etc.).

Acknowledgment

References

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