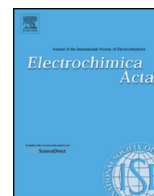




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## Chemical and Electrochemical Stability of Nitrogen and Sulphur Doped Mesoporous Carbons

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### ABSTRACT

Mesoporous carbons (MCs) are porous materials with high surface area and superior mass transport efficiency than traditional carbon materials that make them attractive to electrocatalytic applications. Doped carbons are particularly interesting due to their possible use as metal-free catalysts for oxygen reduction reaction (ORR) or as electrode support for Pt based catalysts. One of the key points to address for the doped MCs implementation in electrochemical devices, subjected to strong electrochemical stresses, is to determine their durability. In this paper we investigate the chemical modification in nitrogen and sulfur doped or co-doped MCs after *ex situ* accelerated degradation test (ADT) consisting in ten thousand voltammetric cycles in a potential window of  $-0.25/+1.0$  V vs. SCE, in Ar saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>, 0.1 M HClO<sub>4</sub> or 0.1 M KOH electrolytes. The morphological, chemical and electrochemical properties of doped MCs before and after ADT were evaluated by scanning electron microscopy, thermal gravimetric analysis, Raman and X-ray photoemission spectroscopies, cyclic and linear sweep voltammeteries. The carbon materials have proved to keep the porous structure after the ADT, without evident structural collapse. It was found that in acidic and in a lower degree in alkaline electrolytes, pyridinic and pyrrolic functional groups can be oxidized to nitrogen oxide groups, whereas N-graphitic and thiophenic like groups are less affected by the electrochemical oxidation. After ADT, nitrogen doped MCs and, to a lesser extent, sulfur doped MCs resulted to partially lose their catalytic activity towards ORR.

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### 1. Introduction

Carbon materials are common electrode supports to be used in several technological fields including sensors, electrolyzers, metal-air batteries, supercapacitors and fuel cells [1–4]. Two of the most important properties of carbon materials are the pore structure and the pore dimension, which determine the surface area, the electrical conductivity and the mass transport capability inside the material. However, these two properties oppose each other so that a reasonable balance is found in mesoporous carbons (MCs), which are typically preferred, because they provide high surface area and at the same time efficient mass transport [5–7].

MCs like most carbons are hydrophobic and inert in nature, however, their surface modification with heteroatoms such as

nitrogen and sulfur can promote properties such as wettability, chemical interaction and electrochemical activity [8–16]. MCs doped with nitrogen or sulfur heteroatoms have shown to catalyze the oxygen reduction reaction (ORR) [17–20] so that, they are promoted as metal-free and cost-effective electrocatalysts. Furthermore, it was found, that depending on the type of functional groups [21], doped carbon materials can be selective towards the 2e<sup>-</sup> pathway leading to H<sub>2</sub>O<sub>2</sub> [22] or the 4e<sup>-</sup> pathway, leading directly to H<sub>2</sub>O [23].

Despite the widespread use of carbon materials in electrochemical devices and in proton exchange membrane fuel cell (PEMFC) in particular, it is known that carbon undergoes electrochemical oxidation to oxidized carbon and eventually to CO<sub>2</sub>, when it is subject to high acidity, high potential, high humidity and high temperature ( $\sim 80$  °C) [24–27]. The carbon corrosion brings to the detachment of noble metal nanoparticles from the electrode or to the ripening to larger aggregates. Oxidation of carbon support can also lead to changes in surface

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hydrophobicity that can cause gas transport difficulties. Therefore, the main issue to be addressed, for a successful commercialization of PEMFC and other electrochemical devices, is to disentangle and fix the aspects ruling the carbon support oxidation and degradation under operational condition. Doped MCs are widely investigated as possible metal free electrocatalysts or as innovative carbon support for Pt nanocatalyst to be used in PEMFC. In fact, chemical defects are supposed to promote a stronger bonding between a metal nanoparticle and the carbon support [28–30], which can lead to an increased charge transfer from the substrate, accompanied by a substantial downshift of the d-band center of the Pt cluster [5,31,32]. However, to our knowledge, there is no work reporting the extent of surface oxidation of heterogroups either at low-temperature or at PEM fuel cells conditions.

*In situ* accelerated degradation test (ADT) methods typically involve manufacture of a membrane electrode assembly and the control of a huge number of variables including temperature, pressure, humidity etc. and even though they are undoubtedly the most preferable methods they are still relatively expensive [24,27]. An alternative approach useful for the fundamental understanding of the degradation processes is the *ex situ* ADTs conducted in a three-electrode electrochemical half cells. These tests typically consist in the electrochemical oxidation of the carbon material by using either voltammetric cycles [33], chronoamperometry [32] or potential pulse perturbation [34]. In this paper we investigate the chemical modifications occurring on nitrogen and sulfur doped MCs under oxidizing condition at ambient temperature in both acidic and alkaline electrolytes. ADTs conducted on nitrogen and sulfur doped or co-doped MC consist in ten thousand voltammetric cycles, between  $-0.25$  and  $1$  V vs. SCE in a three electrode configuration cell. The influence of ADTs on the electrocatalytic activity of doped MCs for ORR in  $0.5$  M  $H_2SO_4$  and  $0.5$  M KOH is also investigated.

## 2. Experimental

### 2.1. Chemicals

Mesoporous Silica (200 nm particle size, 4 nm pore size), phenanthrene (>98%), 1,10 phenanthroline (>99.5%), phenothiazine (>98%), carbazole (>95%), dibenzothiophene (>98%), indigo

carmine (>98%), were purchased from Sigma-Aldrich and used as received without further purification. Other employed chemicals are: Ethanol (Fluka HPLC, >99.8%), Nafion (Sigma Aldrich, 5 ww% in a mixture of lower aliphatic alcohols and water), acetone (Sigma Aldrich, >99.5%),  $H_2SO_4$  (Fluka,  $\geq 95\%$ , TraceSELECT<sup>®</sup>),  $HClO_4$  (Aldrich,  $\geq 67\%$ , TraceSELECT<sup>®</sup>), NaOH (VWR, >99%). The commercial mesoporous carbon (c-MC) purchased from Sigma Aldrich (<500 nm particle size, 99.95%) and used as received.

### 2.2. Material Synthesis

The synthesis and characterization of doped MCs is exhaustively reported in a previous paper [22]. Briefly, the preparative procedure consists in the dissolution of 1 g of silica and 1 g of organic precursor in 15 mL of acetone or ethanol depending on the precursor solubility in the medium. 200–300  $\mu$ L  $H_2SO_4$  were also added to facilitate the oligomerization of the precursors during the impregnation process. The solution is dried in an oven for 1 h at  $100^\circ C$  and the resulting powder is heated in a quartz tube at  $750^\circ C$  for 2 h. The templating agent is subsequently removed by treating it with a liquid solution of 20 mL of NaOH and 20 mL of ethanol. The precipitated MCs are then washed and separated by vacuum filtration on a nylon nanometric filter (GVS, nylon 0.2  $\mu$ m, 47 mm membrane diameter). The adopted precursors are listed in Fig. 1, and the corresponding MCs have been labeled as N-MC-1 (1,10 phenanthroline), N-MC-2 (carbazole), N,S-MC-1 (phenothiazine), S-MC-1 (dibenzothiophene), N,S-MC-2 (indigo carmine) and MC (phenanthrene).

### 2.3. Physico-chemical characterization

All the electrochemical measurements were conducted in a thermostated ( $25^\circ C$ ) three-electrode electrochemical cell including a saturated calomel reference electrode ( $Hg|Hg_2Cl_2|Cl^-_{(sat)}$ ; SCE) and a Pt wire counter electrode. A salt bridge was employed to avoid chloride contamination. The working electrode was a rotating disk electrode tip (Metrohm, 3 mm diameter), which was employed in static conditions or under controlled rotation, depending on the technique. The working electrode was prepared by drop-casting the ink on the glassy carbon disk. The catalyst inks were prepared by finely grinding MCs in a mortar in order to obtain

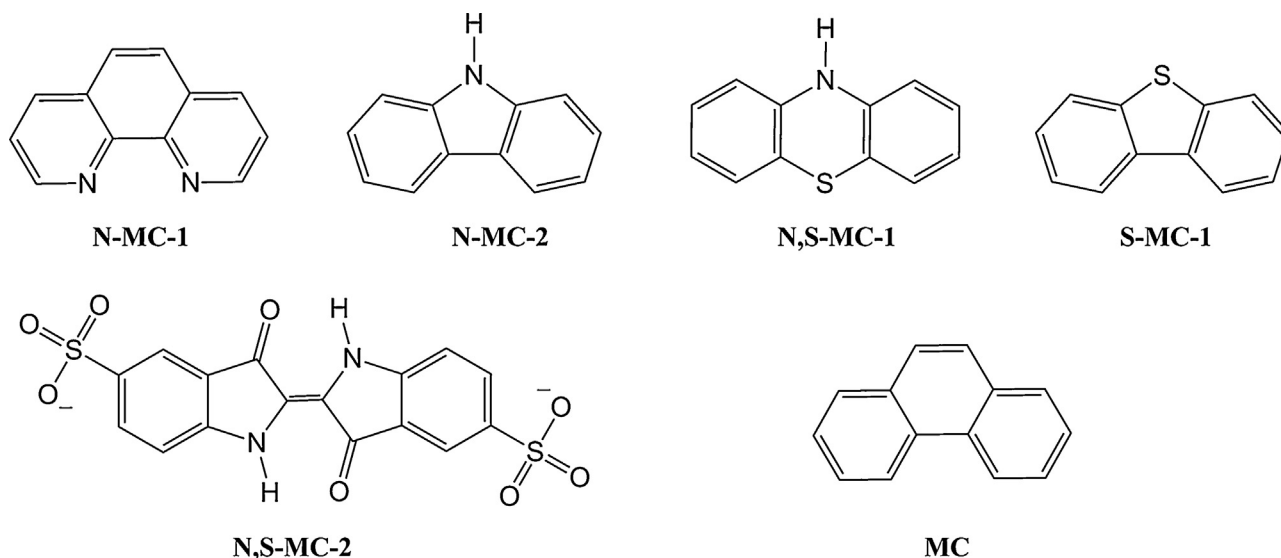


Fig. 1. Condensed aromatic heterocycles employed in the synthesis of the doped MC.

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