



Stability and catalytic properties of nanostructured carbons in electrochemical environments



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ABSTRACT

This work reports a study of the electrocatalytic properties and stability of nanostructured carbon electrodes by on-line differential electrochemical mass spectrometry (DEMS). A wide electrochemical characterization in 0.1 M NaHCO₃ involving anodic (carbon corrosion and oxygen evolution reaction, OER) and cathodic (CO₂ reduction and hydrogen evolution reaction, HER) key reactions in energy-conversion devices was performed. DEMS studies showed that the faradaic current from 1.3 to 1.6 V vs. RHE of carbons was only associated to CO₂ formation by corrosion and not to OER, the stability being improved by the graphitic character of carbon. H₂ evolution was also enhanced with graphitic carbon nanofilaments, even though metal traces might positively influence their catalytic activity. By comparison of the faradaic currents and the H₂ formation signals, in the absence and presence of CO₂, a high inhibition of the HER was established for all carbon electrodes due to the species adsorption from CO₂ reduction.

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1. Introduction

Noble metals or metal oxides supported on carbon materials are conventionally used as catalysts in renewable energy conversion and storage devices, for example in polymer electrolyte membrane (PEM) fuel cells and metal-air batteries [1–7].

The commercial carbon black Vulcan XC-72R (supplied by Cabot) is the most commonly used material in the field of electrocatalysis because of their adequate mesoporous distribution and good electrical properties [4,8]. However, much research effort has been made using advanced nanostructured carbon materials (NCMs) over the last decades, such as graphenes [1], carbon nanotubes (CNTs) [3,9,10], carbon nanofibers (CNFs) [3,11], carbon nanocoils (CNCs) [12,13], carbon xerogels (CXs) [14,15], carbon nanocages [5] and ordered mesoporous carbons (OMCs) [2]. These materials offer optimal textural and chemical features which lead to an enhanced performance. For example, OMCs and CXs provide a high surface area and a developed mesoporosity which is essential for achieving a good dispersion of metal nanoparticles and to favour the diffusion of reactants and by-products. Another key specification is the stability of the carbon material since carbon-support corrosion is considered to be one of the main problems facing the performance of fuel cells [16–20]. Also, a high electrical

conductivity is required to facilitate electron transfer [3,4,14]. In order to solve these issues, more graphitic carbons (e.g., CNTs and CNFs) have been used [3,9,10].

Carbon-supported catalysts have been also used in the electrochemical reduction of CO₂ obtaining promising results [21–25]. An enhanced activity was reached on these carbon-based electrocatalysts in comparison to massive metal electrodes, which may be explained by a better distribution of CO₂ on the active surface. However, few efforts have been made involving advanced NCMs [26–28].

On the other hand, the use of carbon electrodes for electrochemical energy conversion and storage applications has received special attention during the last years [6,24,29–37]. In this context, Zhang and coworkers [6] obtained good electrocatalytic properties for both oxygen reduction and evolution reactions on a N,P-doped mesoporous carbon foam. On the other hand, Wu et al. [36] reported high Faradaic efficiencies (up to 90%) for CO₂ reduction to ethylene and ethanol on nanometre-size N-doped graphene quantum dots. Finally, the hydrogen evolution reaction (HER) has been also recently studied on carbon electrodes obtaining promising results [32,37].

The electrochemical behaviour of carbon materials for energy-conversion applications has been evaluated in detail using conventional electrochemical techniques, as cyclic voltammetry or chronoamperometry [1,8,20,37–42]. However, these measurements do not allow distinguishing between the current signals

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associated with the production of different species at the electrode surface in the same potential region. For example, oxygen evolution reaction (OER) by water oxidation takes place at potentials above 1.23 V vs. RHE, and consequently, it is accompanied by carbon corrosion. In contrast, the hydrogen formation is a competitive reaction, which occurs during the CO₂ reduction in aqueous electrolytes. This limitation can be resolved by using differential electrochemical mass spectrometry (DEMS), coupling on-line an electrochemical cell to a mass spectrometer. In this way, DEMS allows simultaneously following the electrochemical properties of electrodes and the volatile and gaseous species generated on the electroactive surface, with excellent sensitivity and under potential control. Therefore, DEMS is a powerful in situ tool to investigate the electrochemical behaviour of carbon materials and to elucidate the reaction pathways taking place [16,17,21,43,44]. But this technique is not commercial and the DEMS configuration has to be adapted for every application.

In this work, the electrochemical stability and catalytic behaviour of various nanostructured carbons has been established by DEMS. In particular, OMCs, two types of graphitic carbons, CNFs and CNCs, and the commercial carbon black Vulcan XC-72R, have been used. Different cathodic and anodic electrochemical processes have been studied: capacitive properties, tolerance to corrosion and activity toward HER and OER. Furthermore, carbons have been tested in the electrochemical reduction of CO₂. To the best of our knowledge, it is the first work reporting an extensive study of the electrochemical properties and stability of different nanostructured carbons by in-situ electrochemical mass spectrometry.

2. Experimental

2.1. Synthesis of nanostructured carbon materials

OMCs were prepared by the nanocasting technique using a mesoporous silica (SBA-15) as template and a furan resin/acetone as carbon precursor. Finally, OMCs were washed with 1.1 M NaOH in order to remove the silica particles [22,45].

CNFs were synthesized by methane decomposition at 700 °C over a NiCuAl₂O₃ (atomic ratio 78:6:16) catalyst. After CNF synthesis, the metal particles were removed by means of an oxidation treatment with concentrated nitric acid (65 wt%, Panreac) at room temperature for 2 h [11,22].

CNCs were prepared by the catalytic graphitization method using Ni and Co nitrates as graphitization catalysts, a mixture of resorcinol and formaldehyde as the carbon precursor and silica sol to generate mesoporosity. Obtained CNCs were first washed with 1.1 M NaOH (98 wt%, Panreac) solution to remove the silica particles, and subsequently treated with concentrated nitric acid (65 wt%, Panreac) at room temperature for 2 h for eliminating the metal content [22,46].

In addition to the removal of metal nanoparticles, the treatment with nitric acid led to the creation of a low concentration of oxygen functionalities on CNFs and CNCs, especially carbonyl/quinone groups (see Supporting Information; Tables S1 and S2). The treatment at low temperature was selected to preserve the original structure of nanofibers and nanocoils while removing the non-encapsulated metal [46–48].

2.2. Physicochemical characterization

Transmission electron microscopy (TEM) micrographs of the NCMs were obtained using a JEOL-2000 FXII microscope equipped with a LaB6 gun at 200 kV and with a spatial resolution of 0.28 nm. To obtain the micrographs, the samples were finely grinded and ultrasonically dispersed in ethanol. A drop of the resultant

dispersion was deposited and dried onto a standard copper grid coated with Lacey carbon.

X-ray diffraction (XRD) patterns of the materials were recorded using a Bruker AXS D8 Advance diffractometer with a θ - θ configuration and with Cu K α radiation.

N₂ adsorption–desorption isotherms of the NCMs were measured at –196 °C using a Micromeritics ASAP 2020. The total surface area was calculated from BET (Brunauer, Emmett and Teller) equation and the total pore volume was determined using the single point method at P/P₀ = 0.99. V_{meso} and average pore sizes (D_p) were obtained from the analysis of the desorption branch of the N₂ isotherm using the BJH (Barrett, Joyner and Halenda) method.

Thermogravimetric analyses (TGA) were carried out on a thermogravimetric SETARAM Setsys Evolution under air atmosphere. The temperature was varied between room temperature and 950 °C with a heating rate of 5 °C min⁻¹.

Temperature programmed desorption (TPD) experiments were carried out in an AutoChem II 2920 apparatus to determine the amount of surface oxygen groups on carbon materials. The profiles of desorbed CO and CO₂ were obtained in a quartz reactor heated under a constant flow of Ar (50 mL min⁻¹) at a heating rate of 10 °C min⁻¹ up to 1000 °C. The amounts of CO and CO₂ desorbed from the carbon samples were analyzed online by mass spectroscopy. The total amount of CO and CO₂ released was calculated by integrating the area under the flow rate versus time curve. Furthermore, the ratio CO/CO₂ was obtained as a measure of the surface acidity. The deconvolution of TPD profiles was performed using a multiple Gaussian function and a non-linear least-squared optimization procedure based on the Levenberg-Marquardt algorithm using the software Fytik and assigning as initial estimate distinct desorption temperatures for each group [49,50]. The CO and CO₂ evolution and the deconvoluted TPD profiles are shown in the Supporting Information (see Figs. S1 and S2).

X-ray photoelectron spectroscopy (XPS) analyses were carried out with an ESCAPlus OMICRON system equipped with a hemispherical electron energy analyser. The spectrometer operated at 150 W (15 mA, 10 kV), using a non-monochromatized MgK α (1253.6 eV) anode and under vacuum (<5 · 10⁻⁹) over an area of sample of 1.75 × 2.75 mm. A survey scan (1sweep/200 ms dwell) was acquired between 0 and 1100 eV, at 0.5 eV step, 0.2 s dwell and 50 eV pass energy. Detailed scans for C 1s and O 1s were obtained at 0.1 eV step, 0.5 s dwell and 20 eV pass energy. For calibration purposes, the C 1s binding energy of the graphitic peak (BE) was referenced at 284.6 eV. C and O content was calculated from the corresponding peak areas divided by the appropriate sensitive factors (1.00 for C 1s and 2.85 for O 1s) using the CASAXPS software after Shirley background subtraction. Fig. S3 shows the survey XPS spectra and C1s and O1s regions for a selected sample: Vulcan XC-72R.

Elemental analysis (EA) of carbon materials were performed in a CHNS-O Analyzer Thermo FlashEA 1112.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) were performed on a Jobin Yvon 2000 spectrometer to determine the silica and metal residues in the carbon matrixes (Table S3).

2.3. Electrochemical and spectro-electrochemical characterization

Spectro-electrochemical measurements were carried out at room temperature and atmospheric pressure in a three electrodes electrochemical cell directly attached to a mass spectrometer (Balzers Omnistar quadrupole mass spectrometer), with a Faraday cup detector. The potentiostat–galvanostat was an Autolab PGSTAT302 (Ecochemie). Further details about DEMS set-up can be found elsewhere [51]. A high surface area carbon rod was used as counter electrode, whereas an Ag/AgCl/3M KCl electrode

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