DEMS strategy for the determination of the difference in surface acidity of carbon materials

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Abstract

Differential electrochemical mass spectrometry (DEMS) was used to establish the difference of surface acidity of the commercial carbon black (Vulcan) and the chemically modified Vulcan with concentrated nitric acid (VulcanO) in a specific surrounding (sulfuric acid solution). The mass signal for the $m/z = 2$ associated to the H_2 formation was observed to be under the influence of functional groups at the carbon surfaces. Analysis of the mass spectra with the help of the Nernst equation allowed us to quantitatively find the difference in surface pH between both carbon-based materials in acid media. The elevated concentration of functional groups at the VulcanO surface induces a decrease of the surface local acidity at these conditions (0.5 M H_2SO_4), and consequently, the hydrogen evolution reaction (HER) is delayed.

Keywords: DEMS, HER, Surface chemical oxidation, Electrocatalysis, Carbon, pH

1. Introduction

Carbon material applications generally involve interface interactions where specific atoms, molecules or ions access to the carbon surface. These applications are strongly influenced by the carbon surface chemistry.

In general, carbons present amphoteric nature with acid and basic sites coexisting on the surface [1]. A variety of surface functional groups containing different heteroatoms (i.e. oxygen, nitrogen, hydrogen and sulfur) may contribute to carbon surface acidity/basicity. Among these surface functionalities, oxygen-containing groups are the most common. Traditionally, carboxyl, lactone and phenol groups have been identified as acidic surface sites [1, 2]. However, the nature and strength of basic groups are controversial since can be attributed to basic-oxygen-containing groups (such as quinones, pyrones and ketones) and/or delocalized π -electrons of the basal planes, which can also act effectively as proton-binding sites [2, 3]. The overall acidity/basicity of the carbon depends on the surface concentration of these functional groups and their strength as acids or bases. Surface chemistry of carbons have been evaluated in the literature by different analytical techniques, such as temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) or Fourier transformed infrared spectroscopy (FTIR), as well as potentiometric titrations and measurements of the pH of the point zero charge (pH_{PZC}) [4, 5].

Additionally, a variety of chemical oxidizing agents either in solution (NaClO_4 , HNO_3 or H_2O_2) or in the gas phase (CO_2 , O_3 or O_2) can be used to modify the surface chemistry of carbons by the introduction of oxygen-containing-groups. These treatments result in an increase of the surface acidity of carbons, decreasing the pH_{PZC} [5].

On the other hand, the pH of the surrounding media plays also an important role on the interfacial interactions. Acid sites release protons, especially in basic media, whereas basic groups adsorb protons in basic solutions. All these criteria must be considered when carbon surfaces are used in catalysis.

In this work we propose a strategy to estimate the difference in surface acidity between two carbons with different surface chemistry in a specific media, using on-line differential electrochemical mass spectrometry (DEMS). Selected carbons were commercial carbon black Vulcan XC-72R and the later carbon subjected to an oxidation treatment with nitric acid. The procedure is based on the determination of the onset potential for the hydrogen evolution reaction (HER) in acid media (0.5 M H₂SO₄). By means of the Nernst equation, the difference in [H⁺] between both carbon surfaces in 0.5 M H₂SO₄, and thus, the ΔpH can be obtained.

2. Experimental

2.1 Functionalization of Vulcan XC-72R

The surface of the commercial carbon black Vulcan XC-72R (supplied by Cabot) was chemically modified with concentrated HNO₃ (65%, Panreac) at 120 °C during 120 min. After the oxidation treatment, the carbon was filtered, thoroughly washed with ultrapure water and dried at 60 °C. The resulting material was denoted as VulcanO.

2.2 Physicochemical characterization

TPD experiments were obtained in an AutoChem II 2920 analyzer. Carbon materials were heated at 10 °C min⁻¹ up to 1000 °C in a quartz reactor under Ar atmosphere (50 mLmin⁻¹). The CO and CO₂ amounts were monitored online by mass spectrometry. The TPD deconvolution was performed adjusting the experimental profiles to a multiple Gaussian function [6, 7].

Elemental analyses (EA) were obtained in a Thermo FlashEA 1112 analyzer.

N₂ adsorption-desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2020. The total surface area (S_{BET}) was calculated from Brunauer, Emmett and Teller equation and the total pore volume (V_{T}) was determined using the single point method at $P/P_0 = 0.99$. The mesopore volume (V_{meso}) and average pore sizes (D_{p}) were obtained from the analysis of the desorption branch of the N₂ isotherm using the Barrett, Joyner and Halenda method.

XPS spectra were performed in an ESCAPlus OMICRON system operating at 150 W (15 mA, 10 kV) using a non-monochromatized MgK α (1253.6 eV) anode [6, 7].

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

Transmission electron microscopy (TEM) micrographs of the carbons were obtained using a JEOL-2000 FXII microscope equipped with a LaB6 gun at 200 kV.

2.3. Preparation of working electrodes

Gas diffusion electrodes (GDEs) were used as working electrodes (7 mm of diameter). The working electrodes were prepared depositing a layer of the carbon catalyst ink onto one side of a commercial gas diffusion layer (GDL), provided by E-TEK, which consists on a carbon cloth with a microporous carbon layer onto one side with a Teflon content of 20%. The total thickness of the GDL is about 250 μm .

Catalyst inks were prepared by mixing 2 mg of carbon, 12 μL of Nafion dispersion (5 wt%, Sigma-Aldrich) and 20 μL of ultrapure water. Final metal loading of the working electrodes was 3 mg cm⁻² electrode.

2.4. DEMS studies

Spectro-electrochemical measurements were carried out in a three electrodes electrochemical cell directly attached to a mass spectrometer (Balzers QMG112) with a

Faraday cup detector. The potentiostat-galvanostat was an Autolab PGSTAT302. A high surface area carbon rod was used as a counter electrode, whereas an Ag/AgCl/3M KCl electrode (0.21 V vs. normal hydrogen electrode, NHE) placed inside a Luggin capillary was employed as reference. All potentials in the text are referred to this electrode.

The working electrode was fixed between a PTFE membrane (Scimat) and a carbon glassy rod, which also keeps the electric contact. The working electrode was immersed into 0.5 M H₂SO₄ (Merck, p.a.) electrolyte solution, previously deaerated with argon (N50). The catalyst layer was placed against the membrane in order to prevent the material depletion by the formation of bubbles during the electrochemical experiments. Further details of the DEMS set-up can be found elsewhere [8].

3. Results

3.1 Physicochemical characterization of carbons

The physiochemical features of the carbons have been already described in a recent work [6]. The total oxygen content was obtained by TPD (O_{TPD}) and EA (O_{EA}), while the surface oxygen amount (O_{XPS}) was determined by XPS. O_{TPD} and O_{EA} results correlate quite well, while O_{XPS} values are higher for both carbons indicating that the surface is enriched with oxygen. The three techniques evidenced that the oxidation treatment substantially increased the amount of oxygenated species (Table 1).

The oxygen functional groups distribution was determined by deconvolution of TPD profiles according to [6]. Table 1 summarizes the main results. Briefly, the chemical oxidation treatment with nitric acid led to an important increase of organic functional groups (carboxylic acid, anhydride, lactone, phenol and carbonyl+quinone), which resulted in a decrease of the hydrophobic character of carbon materials [6].

The textural parameters obtained from N₂ adsorption-desorption isotherms are displayed in Table 1. Chemical oxidation led to a decrease of the S_{BET} and an increase of the D_p ascribed to the creation of oxygen groups [9]. On the other hand, V_T and V_{meso} remain similar after the oxidation treatment.

TEM images (not shown) evidenced that both carbons were formed by spherical nanoparticles composed of small crystallites [6, 7, 10]. Similar diffractions patterns were evidenced for both carbons [6]. From the graphite (002) peak, the crystallite sizes (L_c) of carbons were calculated using the Scherrer's equation [6, 10]. Identical values of L_c (1.7 Å) were obtained, indicating that the original carbon Vulcan preserved their structure and morphology upon chemical oxidation.

3.2 Cyclic voltammetry (CV) and mass spectrometric cyclic voltammetry (MSCV)

Figure 1 shows the blank cyclic voltammograms (BCVs) for both carbon-based materials in the supporting electrolyte. Vulcan (black line) reveals the typical profile of carbon black electrodes, i.e., a capacitive current in the potential range investigated [11]. The oxidation treatment of Vulcan strongly enhances the capacitive current and the reversible peaks at ca. 0.35 V associated to the quinone/hydroquinone redox pair (red line) [12, 13]. The last is related to the creation of functional groups into the carbon surface structure since the physical parameters remain similar after the chemical modification of Vulcan (Table 1).

Figure 2 shows the first positive going potential linear scan (PLS) and the corresponding mass linear scan (MSLS) for the $m/z = 2$ (H_2^{++}) signal for both materials recorded in 0.5 M sulfuric acid solution at 0.01 V s^{-1} . It is observed that the faradaic current (upper panel) decreases, meanwhile the ionic current increases (bottom panel). Noteworthy that faradaic current can be associated to several electrochemical reactions, while ionic currents are only related to the formation of molecular hydrogen. Therefore,

a precise onset potential (E_o) for the hydrogen evolution reaction (HER) can be achieved by DEMS. In this regard, it is clearly discerned from the $m/z = 2$ signal that the onset potential for the HER at Vulcan ($E_o \approx -0.4$ V) is about 0.2 V more negative than at VulcanO ($E_o \approx -0.6$ V). The last indicates that the oxidation treatment, which produce organic functional groups at the carbon surface, increase the overpotential for the HER in the present conditions.

The experimental results can be understood with the help of the acidity constant of the functional groups ($pK_a = 2-5$ for carboxylic acids, 6-7 for lactones and carboxylic anhydride groups, 8-11 for phenolic and carbonyl groups and > 11 for protonated basic structures [14]), the Nernst equation and pH of the medium. In the current conditions (pH = 0) the HER should occur at 0.0 V if there are no kinetics limitations, which are the main responsible for the high overvoltage observed at both carbon electrodes. However, a great difference at the onset potential (~ 0.2 V) for the HER between both carbon-based materials is discerned. As we stated before, this result should be understood as consequence of different surface acidity caused by the diverse quantity and nature of functional groups at the surface of both electrodes. Indeed, the quantity of oxygen functional groups at VulcanO is much higher than at Vulcan material and the strength of each one in solution can be found with their respective acidity constant (K_a). In this regard, the deprotonation of oxygen functionalities at the carbon surfaces is quite low in the experimental conditions (pH = 0) and the contribution of the functional groups responsible for the alkalinity becomes more important (see above the pK_a for each functional group). VulcanO presents a higher content of carbonyl and quinone groups (Table 1), as can be seen in the increase of the quinone/hydroquinone redox pair at ca. 0.35 V (Figure 1), which are considered proton-binding sites. These basic sites tend to accept protons in the acid media, increasing the local pH. Therefore, a higher

surface acidity is expected at Vulcan in comparison to VulcanO in highly acidic media. In spite of this, an easy and accurate way to obtain surface acidity degree at carbon-based materials is quite challenging.

The potential at the electrode surface (E) is directly related to the proton concentration $[H^+]$, and thus to the pH at the electrode surface, according to the Nernst equation:

$$E = E_{H_2|H^+}^0 + 0.05916 [V] \cdot \log[H^+] = E_{H_2|H^+}^0 - 0.05916 \cdot \text{pH} [V]$$

where $E_{H_2|H^+}^0$ is the standard potential for the HER. Thus, an elegant and facile way to estimate the difference in surface acidity between both carbons in a reaction media with a specific pH and without account of the number and type of functional groups is to use the onset potentials achieved by DEMS and the Nernst equation:

$$\Delta E = 0.05916 [V] \cdot \log \frac{[H^+]_a}{[H^+]_b} = -0.05916 [V] \cdot \Delta \text{pH}$$

where, ΔE is the difference in the onset potential for the HER at both electrodes, and $[H^+]_a$ and $[H^+]_b$ are the surface acidity at Vulcan and VulcanO, respectively. After that, it is conceivable in a very facile way to achieve the difference of surface acidity ($\Delta \text{pH} = 3.4$) between these electrodes.

4. Conclusions

A sophisticated strategy to estimate the difference in surface acidity of carbons in an electrochemical media has been proposed using on-line electrochemical mass spectrometry. Two carbons with different surface chemistry were studied: carbon black Vulcan and chemically oxidized Vulcan with concentrated nitric acid. DEMS was used to monitor the hydrogen evolution reaction at both carbon surfaces in 0.5 M H_2SO_4 . Interestingly, the HER was influenced by the surface oxygen-containing groups, being

the onset potential around 0.2 V more negative in the oxidized carbon.

By means of the Nernst equation, differences in the surface pH of both carbon materials in 0.5 M H₂SO₄ were obtained. In this context, the deprotonation of functional groups is quite low in this media (pH = 0), and thus, the adsorption of protons at basic sites becomes more important. VulcanO with a high concentration of functional groups (including proton-binding species, such as carbonyls and quinones) induced an increase of the surface basicity in comparison to Vulcan ($\Delta\text{pH} = 3.4$) in highly acid media, and consequently, a shift in the onset potential for the HER was recorded.

Finally, the proposed methodology to estimate the difference in surface acidity of materials takes into account the role of the surrounding media on the surface interactions, which is an important issue to consider in the design of catalysts.

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272 **Figure captions**

273 **Figure 1.** Blank cyclic voltammograms for Vulcan (black line) and VulcanO (redline)
274 materials recorded in 0.5 M H₂SO₄ at 0.01 V s⁻¹.

275 **Figure 2.** PLS and MLS for Vulcan (black line) and VulcanO (redline) materials
276 recorded in 0.5 M H₂SO₄ at 0.01 V s⁻¹.

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278 **Table captions**

279 **Table 1.** Oxygen content of carbons from TPD, EA and XPS, deconvolution of TPD
280 profiles and textural parameters from N₂ adsorption-desorption isotherms of carbon
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Figure 1. Blank cyclic voltammograms for Vulcan (black line) and VulcanO (redline) materials recorded in 0.5 M H₂SO₄ at 0.01 V s⁻¹.

Figure 2. PLS (top panel) and MLS (bottom panel) for Vulcan (black line) and VulcanO (redline) materials recorded in 0.5 M H₂SO₄ at 0.01 V s⁻¹. Inset: zoom of the MLS revealing the onset potential for the HER.

Table 1. Oxygen content of carbons from TPD, EA and XPS, deconvolution of TPD profiles and textural parameters from N₂ adsorption-desorption isotherms of carbon materials.

Sample	<i>O</i>_{TPD}	<i>O</i>_{EA}	<i>O</i>_{XPS}	<i>C</i>_a	<i>A</i>	<i>L</i>	<i>Ph</i>	<i>C+Q</i>	<i>S</i>_{BET}	<i>V</i>_T	<i>V</i>_{meso}	<i>D</i>_p
	wt%			μmol g ⁻¹					m ² g ⁻¹	cm ³ g ⁻¹		nm
Vulcan	0.6	0.4	2.3	39	6	20	5	25	238	0.38	0.31	10.4
VulcanO	5.6	7.0	12.0	478	369	99	325	682	181	0.38	0.33	14.0

C_a: carboxylic acid, *A*: anhydride, *L*: Lactone, *Ph*: Phenol, *C+Q*: carbonyl+quinone.