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Electrochemical behavior of the carbon black Vulcan XC-72R: Influence of the surface chemistry

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ABSTRACT

The effect of chemical surface oxidation of the carbon black Vulcan XC-72R on the capacitance, tolerance to corrosion and electrochemical activity toward the hydrogen evolution reaction (HER) has been studied in 0.1 M NaHCO₃. Acid treatments with HNO₃ or a HNO₃–H₂SO₄ mixture resulted in a progressive introduction of oxygen-containing groups which led to a strong increase of the capacitance and a higher tendency to carbon corrosion. In contrast, an inhibition of the hydrogen evolution current (at potentials more negative than –1.0 V) was observed for oxidized samples in comparison to the un-treated material. HER was also tested in the presence of dissolved CO₂ to study the influence of the surface chemistry on the CO₂ electroreduction. An inhibition of the H₂ evolution current was evidenced in the CO₂ saturated electrolyte due to the adsorption of species from CO₂ reduction. A strong hydrogen current decrease (65–78%), and thus a higher tendency to adsorb (CO₂)_{red} species, was obtained on the original Vulcan and the HNO₃-treated samples, in comparison to the carbon oxidized with HNO₃–H₂SO₄ (15%), which could be related to the highest content of basic groups of the last carbon.

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Introduction

Carbon blacks have been extensively used in the field of electrochemistry owing to their high mesoporous distribution, good electrical properties, as well as their low cost and high availability since they are usually obtained by thermal decomposition of hydrocarbons derived from petroleum sources [1–4]. Different carbon blacks, such as acetylene black, Ketjen Black, Black Pearl or Vulcan XC-72, have been used as electrodes in supercapacitors or catalyst supports in electrochemical applications [1–8]. Among them, Vulcan XC-

72R (industrially produced by Cabot Corporation) has attracted special attention due to its good compromise between adequate surface area (~250 m² g⁻¹) and high electric conductivity (~2.77 Scm⁻¹) [1,9].

In general, carbon applications involve interfacial interactions, where different reactants and ions access to the carbon surface. As a result, a great effort has been devoted to study the effect of surface chemical properties of carbons (including carbon blacks) on the electrochemical performance for energy-conversion and storage devices, such as supercapacitors, polymer electrolyte membrane fuel cells (PEMFC) and electrolyzers [3,10–15]. Particularly, the chemical

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introduction of oxygen-containing species on the carbon structure has been extensively investigated [3,10,16–21]. Different chemical oxidation procedures have been studied using oxidizing solutions (such as NaClO, HNO₃ or H₂O₂) or gases (e.g. CO₂, O₃, O₂, NO, etc.) [5,22,23], which result in the generation of different oxygen functionalities on carbon surfaces, such as carboxyls, carbonyls, phenols, quinones or lactones.

These oxygen functionalities has been found to play an important role on the electrochemical behavior of carbon-based electrodes and their activity toward main reactions involved in PEMFC and electrolyzers [3,10,16–21]. Particularly, the introduction of oxygen-containing species has been reported to be advantageous for attaining a better dispersion and anchoring of the electrocatalytic active phase onto the carbon surface [5,24,25]. In addition, oxygen functionalities decrease the hydrophobic character of carbons, enhancing the capacitance, and thus the accessible electrochemical area [21,26–29].

In contrast to the advantages of improved capacitance or good dispersion of the active phase, the introduction of oxygen functional groups may promote the carbon electrochemical corrosion, which is one of the main problems facing the PEMFC efficiency [26,30]. During the electrooxidation of the carbon support, oxygen species are progressively adsorbed on the carbon surface which are converted to CO₂ at high overpotentials, resulting in a substantial decrease of the active surface area of the catalyst, and consequently a severe loss of the PEMFC performance [26,30,31]. It has been found that the presence of oxygen functionalities onto the carbon surface may facilitate the gasification of the carbon support [26,30]. These studies generally involve the progressive electrochemical oxidation of carbon-supported catalysts [11,21,26,32]. However, to our best knowledge, there are still few studies dealing with both the influence of previous chemical oxidation of carbon blacks (not only by the electrochemical route) and the corrosion resistance of metal-free carbon electrodes [33].

On the other hand, few efforts have been made in the role of oxygen-functionalized carbons on the electrochemical activity toward the hydrogen evolution reaction (HER) [20,34], which is the cathodic half reaction in electrochemical water splitting. In this context, Bleda-Martínez et al. [20] found an improved hydrogen storage capacity in carbons with a low content in surface oxygen complexes. On the other hand, a previous work showed that carbon electrooxidation might decrease the active sites and hence, inhibit the hydrogen formation [34]. Nevertheless, the effect of the chemical introduction of oxygen species on carbon surfaces on the activity for the HER remain largely unknown.

Electrocatalysts supported on carbon materials have been also used for other electrochemical applications, such as the hydrogenation of CO₂ into energy-rich products [35–44]. In this context, Hossain et al. have recently showed the effective reduction of CO₂ to CO, HCOOH and CH₄ with a faradaic efficiency of 76.6% in a CO₂ saturated NaHCO₃ solution on a nanocomposite consisting of Cu nanoparticles deposited on reduced graphene oxide [41]. Interestingly, high efficiencies to the formation of hydrocarbons and oxygenates have been recently reported on metal-free N-doped carbon electrodes

[45–49]. However, scarce studies about the effect of the oxygen functionalization on the electrocatalytic activity toward the CO₂ conversion can be found in the literature [35,42,48]. In addition, these studies usually involve metal-base electrodes or trace metals and the role of the support has not been stated.

A recent report has evidenced that the presence of oxygen functionalities may play an important role on the capacitance and on the corrosion tolerance of carbon materials, as well as on the electrocatalytic activity toward H₂ evolution and CO₂ reduction reactions [34]. However, carbons of different nature with different morphology, structure, textural properties and surface chemistry were considered in this previous work [34], making difficult to clarify the role of surface oxygen-containing species. The current report addresses this issue by gradually introducing oxygen functional groups on the carbon surface of Vulcan XC-72R. Different chemical oxidation treatments with concentrated nitric acid or a nitric-sulphuric acid mixture over a prolonged period of time (from 0.5 to 2 h) at 30 or 120 °C were used. The electrochemical behavior of the original and oxidized carbon samples was studied by cyclic voltammetry in aqueous 0.1 M NaHCO₃. The obtained results are discussed in terms of the capacitance, tolerance to corrosion and activity toward the HER, which are key issues on energy-conversion devices. The study is extended to the evaluation of the performance of carbons for the CO₂ electrochemical reduction.

Experimental

Functionalization of Vulcan XC-72R

Functional groups were generated on Vulcan XC-72R (supplied by Cabot) surface by using concentrated HNO₃ (65%, Panreac) or a HNO₃/H₂SO₄ (95%, Sigma Aldrich) mixture 1:1 (v/v) as oxidizing agents. Three different chemical oxidation procedures were employed: (i) oxidation with HNO₃–H₂SO₄ at 30 °C for 30 min; (ii) oxidation with HNO₃ at 120 °C during 30 min and (iii) oxidation with HNO₃ at 120 °C during 120 min. The resulting oxidized samples were denoted as Vulcan-O1, Vulcan-O2 and Vulcan-O3, respectively. After the oxidation treatments, carbons were filtered, thoroughly washed and dried at 60 °C.

Physicochemical characterization

Temperature programmed desorption (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 an Ar atmosphere (50 mL min⁻¹). The CO and CO₂ amounts were monitored on-line by mass spectrometry. The TPD deconvolution was performed adjusting the experimental profiles to a multiple Gaussian function using the Fytk software [5,34,50]. The CO and CO₂ evolutions and the deconvoluted profiles are displayed in Figs. S1 and S2.

X-ray photoelectron spectroscopy (XPS) spectra were performed in an ESCAPlus OMICRON system operating at 150 W (15 mA, 10 kV) under vacuum (<5·10⁻⁹), using a non-monochromatized MgK α (1253.6 eV) anode. Survey scans (1sweep/200 ms dwell) were recorded at 0.5 eV step size, 0.2 s

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