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Sugar-based catalysts for oxygen reduction reaction. Effects of the functionalization of the nitrogen precursors on the electrocatalytic activity

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ABSTRACT

Non-noble metal catalysts for the electrochemical reduction of oxygen (ORR) in acidic and alkaline solutions have been produced by pyrolysis of a silica gel containing fructose, as a carbon source, and derivatives of guanidine, as nitrogen compounds. The importance of the formation of iron complexes with nitrogen precursors to obtain good oxygen reduction reaction (ORR) catalysts has been investigated by varying the functionalization of guanidine derivatives. The presence of secondary or tertiary amines on guanidine limits or hinders the formation of iron complexes and, as a result, the produced materials are not very active. Conversely, the presence of primary amines promotes the formation of iron complexes, and, during the pyrolysis, of iron nanoparticles and ordered graphitic planes, making the final material very active for ORR. An explanation of this behavior in terms of surface and bulk composition has been proposed. An attempt to find the ORR rate determining step for the samples in both alkaline and acidic solutions has been done.

1. Introduction

The reduction reaction of oxygen (ORR) is the most essential reaction in life processes, *e.g.* biological respiration, and in energy-converting systems, *e.g.* zinc/air batteries and low-temperature fuel cells, in which ORR is the cathodic reaction. As observed in all energy converting systems, the overall energy efficiency strongly depends on the kinetics of the two electrodes processes of which the most kinetically hindered is the oxygen reduction reaction [1]. To cope with typical power requirements, ORR requires efficient and active catalysts, such as platinum and platinum alloys nano-dispersed on active carbon, which have been considered so far the most active [2–4]. Nevertheless, platinum cost, natural scarcity, and technological drawbacks (*e.g.* oxidation, dissolution and migration) hamper the commercialization of such energy converting systems [5–8]. In recent years, these "obstacles" spawned development of cheaper but as-effective Pt substitutes and nowadays ORR catalysts with low Pt percentage or, even better, Pt-free materials are valuable alternatives to catalysts based on noble metal nanoparticles. Such noble-metal-free catalysts are actively searched for by worldwide investigation [9–12]. Since the first demonstration of ORR activity of metal substituted-phthalocyanines [13] several works about Pt-free catalysts followed [14–26]. Research on metal-nitrogen macrocycles significantly widened, showing a relationship between ORR catalytic activity and carbon-bonded N_4-Me and N_2-Me moieties [11,17,27–30]. However, because of precursors cost and chemical instability, research shifted toward simpler nitrogen-containing precursors and preparation procedures.

The ORR-promoting role of nitrogen in carbon has been experimentally evidenced and theoretically confirmed by many research groups, with the result of relating ORR activity with substitutional nitrogen atoms at a few specific positions of graphene layers [21,29,31]. In fact, "aromatic" nitrogen, *e.g.* pyridinic, pyrrolic and quaternary nitrogen in the graphene layer could act as an n-type dopant of carbon and form disordered carbon nanostructures or donate electrons to carbon, in either case enhancing the ORR activity [32]. An impressive improvement in electrocatalytical properties and faradaic efficiency of water production is obtained by adding iron to nitrogen-modified carbon. Although several works have speculated about the

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relevance and the role of iron in the ORR active site [21,33–35], several authoritative groups proved both experimentally and theoretically the synergy between N and Fe atoms underlying the catalytic activity of Fe(II) cations coordinated by pyridinic nitrogen, which forms Fe-N_x centres embedded in the π-electron-deficient ligand environment of graphitic carbon [21,36,37]. Moreover, combined electrochemical and spectroscopic measurements have led to a proposed ORR mechanistic pathway based on such active centres both in alkaline and in acidic conditions; in the latter case, this mechanism also relied on the role of iron nanoparticles [21].

In the literature [21,29,38] nitrogen-based polymers (polyamine, polypyridine derivatives) as well as nitrogen aromatic/aliphatic compounds typically acted as precursors for both nitrogen and carbon. In order to reduce the amount of nitrogen compounds used in the synthesis, it could be useful to introduce a carbon source that is cheap and rich in carbon atoms, such as monosaccharides. In this work we present some data obtained on iron-doped electrocatalysts prepared using fructose as a carbon source and derivatives of guanidine as nitrogen compounds in the presence of silica as templating agent. The importance of the formation of iron complexes with nitrogen precursors to obtain good ORR catalysts was highlighted by the choice of guanidine derivatives in view of their lone-pair availability and steric hindrance, thus, of their tendency to form these complexes.

2. Experimental

2.1. Materials

All the chemicals and reagents were used as received without further purification. *D*-(-)-fructose, guanidine acetate, 2-guanidinobenzimidazole, 1,1,3,3-tetramethylguanidine, iron(II) acetate, glacial acetic acid, Nafion® (5 wt. % EtOH solution), 37% hydrochloric acid, concentrated sulfuric acid, and ethanol were purchased from Sigma Aldrich. 60% $HClO_4$ solution was purchased from Merck. KOH from Fluka was used to prepare a 0.1 mol dm^{-3} solution. A Pt-based commercial catalyst (EC20, 20% Pt onto carbon) was tested and used as a reference material.

2.2. Synthesis

The following method has been previously reported in the literature [39]. Briefly, 10 mL of an aqueous solution of *D*-(-)-fructose, a nitrogen compound (molar ratio glucose:nitrogen compound = 1:1), glacial acetic acid, equimolar to nitrogen compound, and iron acetate (0.96 wt % Fe calculated on the total mass of fructose and nitrogen compound) were added to silica powder to obtain a silica gel (2.3 mL/SiO_2 g). This gel underwent a first heating step of 1 hour at 600 °C under a N_2 flow (100 cm^3 min^{-1}). After ball-milling (5 min, 10 Hz) the product was lixiviated in boiling NaOH (3 mol dm^{-3}) and washed in order to remove silica. The resulting carbon was dried in nitrogen (100 °C, 24 h) and finally ball-milled (5 minutes, 10 Hz). A second heating step (900 °C, 3 h, under a N_2 flow) was performed to activate the catalytic sites. Because the used nitrogen compounds were guanidine acetate, 2-guanidinobenzimidazole, 1,1,3,3-tetramethylguanidine (Scheme 1), the resulting materials will be labelled FGA, FGB, and FTG, respectively.

2.3. Characterization

2.3.1. BET surface area and Porosity Distribution

The Brunauer-Emmett-Teller (BET) specific surface area was obtained from N_2 adsorption/desorption isotherms at 77 K using a Micromeritics Tristar II apparatus (Tristar II 3020). Measurements were performed many times to assess isotherms reproducibility and accuracy. Surface area and porosity distribution were calculated from nitrogen isotherms by B.E.T. and B.J.H equations., respectively, using the instrumental software (Version 1.03). Prior to measuring, sample powders were heat-treated at 150 °C for 4 h under a N_2 flow to remove adsorbed foreign species.

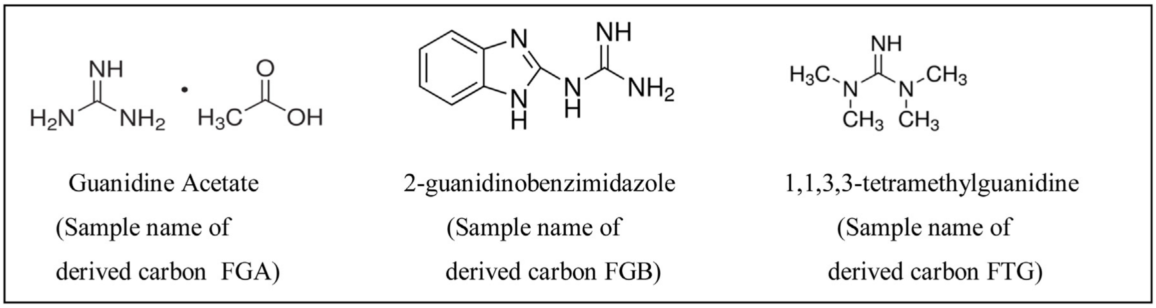
2.3.2. Transmission Electronic Microscopy

Transmission Electronic Microscopy (TEM) images were obtained by a Zeiss EFTEM LEO 912AB (120 kV) microscope. To obtain average characteristics many different sample areas were analysed.

2.3.3. X-Ray Powder Diffraction

X-Ray Powder Diffraction (XRPD) data were collected at the ID22 beamline of the European Synchrotron (ESRF) in Grenoble, France. The powder samples were loaded into 1.0 mm diameter Kapton® capillaries and mounted parallel to the axis of the diffractometer. An empty Kapton® capillary was measured for background scattering subtraction. Data on all the samples were collected at room temperature using $\lambda = 0.017704(3)$ nm and a 2D CCD detector (Perkin Elmer XRD 1611CP3) with 100 × 100 mm^2 pixel size. Wavelength, sample-detector distance (379.3 mm), and azimuthal integration parameters were calibrated on a CeO_2 reference that was sintered for 4 hours at 1400 C. The detector mask was created with the program FIT2D [40]; calibration and azimuthal integration were all done using the program pyFAI [41]. In addition, high-Q resolution data were collected on the FGA sample using an X-ray wavelength $\lambda = 0.032635(6)$ nm and a 9-element detector array.

Peak fitting, phase analysis, and structural refinement on the XRPD data in reciprocal space were all carried out using the program TOPAS (v.4.2, 2007, Bruker-AXS, Germany). Analysis of the interatomic distances made use of the reduced Pair Distribution Function (PDF), G(*r*), which is the product of the sine Fourier



Scheme 1. Nitrogen Compounds used in the carbon synthesis.