Journal of Electroanalytical Chemistry 775 (2016) 350–355

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Templating induced behavior of platinum-free carbons for oxygen reduction reaction

Stefania Marzorati, Mariangela Longhi *

Università degli Studi di Milano, Dipartimento di Chimica, Via Golgi 19, 20133 Milano, Italy

ARTICLE INFO

Article history:
Received 19 April 2016
Received in revised form 17 June 2016
Accepted 23 June 2016
Available online 24 June 2016

Keywords:
Oxygen reduction reaction
Pt-free carbons
Templating effects
Pore size
Pore shape

ABSTRACT

The aim of this work is to investigate the effect that pore shape and morphology may introduce in the behavior of some platinum free catalysts for the oxygen reduction reaction (ORR). Samples of the catalyst are obtained heat-treating a reactant mixture with constant composition and using a variety of templating procedures, *i.e.* shape-imprinting materials (like high surface area silica and Black Pearls 2000), and some self-templating processes (freeze-drying and in-situ generation of gas bubbles). Reaction products are characterized by XPS, BET and electrochemical methods. Analysis of results shows that the ORR catalyst activity depends in a complex manner on structural and morphological features, being not only affected, as expected, by surface area and pore width, but also by the pore shape. In a detailed examination a relation in fact emerges between ORR activity and relative abundance of micro- and mesopores of different size and pore shape.

1. Introduction

For decades scientific research has been studying a better way to develop efficient systems to produce electrical energy by fuel cells. The current scientific and technological knowledge seemingly allows a near forecast for the use of such devices on a large consumer scale. However, despite remarkable recent improvements [1,2], cost, durability and technological aspects make the fuel cells engineering one of the greatest challenges of the present time [3,4].

The overall energy efficiency in fuel cells is deeply affected by the kinetics of the two electrodes processes of which the most kinetically hindered is the oxygen reduction reaction (ORR) at the cathode. In order to cope with variable and peak power automotive requirements this reaction needs effective catalysts to proceed as fast as possible. Among existing catalysts, platinum and platinum alloys are nowadays best credited, even though their cost and availability are strong drawbacks [5]. Moreover, under fuel cell working conditions, platinum efficiency is reduced because it undergoes oxidation, dissolution and migration, and loss of active surface area. To overcome these “barriers” to fuel cells commercialization, effective Pt substitutes have to be developed. Today, efforts are addressed to development and synthesis of new ORR catalysts with low Pt percentage or, even better, Pt-free materials. Such noble-metal-free catalysts are actively searched for by worldwide investigation [6–9]. Several relevant papers have been published after a first report by Jasinski [10] in 1964 demonstrating the ORR activity of metal substituted-phthalocyanines. Then, research on metal-nitrogen macrocycles significantly expanded, leading to the picture that ORR catalytic activity can be related to carbon-bonded N_4-Me and N_2-Me moieties. However, for precursor cost and unsatisfactory lifetime, research was steered towards more simple nitrogen-containing reactants and preparation procedures. The ORR-promoting role of nitrogen in carbon was independently demonstrated both theoretically and experimentally with the outcome that ORR-promotion depends on substitutional nitrogen at a few, specific, peripheral positions of graphene layers in well-ordered carbon nanostructures [11–13]. Significant steps in this direction were obtained by Dodelet *et al.* who demonstrated that ORR overpotentials almost linearly decrease with increasing nitrogen content in carbon. Positive results were also obtained on a series of samples prepared by high temperature treatment of carbon precursors in $NH_3/H_2/N_2$ mixtures; moreover, doping these modified carbons with iron rather than cobalt was shown to be preferable for better ORR efficiency, even though still lower than that of platinum [14–21].

Besides the above composition-dependent factors, catalyst activity also depends on structural and morphological carbon features. An optimized porosity of carbon is beneficial for an easy access of reacting oxygen to the catalyst layer in contact with the proton exchange electrolyte membrane RM = Mixture Reaction [22,23]. Many works have been published about the best and most useful porosity range for ORR application, even though with controversial results. Dodelet and co-authors highlighted the importance of micropores to improve ORR activity [18,19] proposing that an increase in micropore area promotes ORR activity because of formation of a catalytic molecular assembly bridging two pore walls at a specific distance corresponding to the micropore diameter [17]. However, this is contrasted by a picture in which mesoporosity is only useful to improve the ORR performance,

---

* Corresponding author.
E-mail address: mariangela.longhi@unimi.it (M. Longhi).

http://dx.doi.org/10.1016/j.jelechem.2016.06.032
1572-6657/

this porosity allowing efficient mass transport of reactants/products to/from the electrode, respectively, and ensuring a better metal dispersion in the catalytic material [24,25]. Since electronic interactions between catalyst and molecular oxygen may be tuned to achieve different structural and textural carbon features, this work is aimed at investigating any morphological effect that different templating methods may exert on the ORR behavior of end catalyst products; in this the focus is not only to gain control on pore size, but also, more specifically, on pore shape. The starting point of this work is a hard templating method, in which organic precursors are reacted at high temperature in the presence of silica gel [26]. Though effective, the method is laborious and time consuming so that faster and more simple methods were developed, tested and reported presently.

2. Experimental

2.1. Synthesis

All chemicals and reagents were used as received without further purification. D-glucose, L-histidine, iron(II) acetate, glacial acetic acid, Nafion® (5 wt.% EtOH solution), 37% hydrochloric acid, concentrated sulfuric acid and ethanol were purchased from Sigma Aldrich. Silica (70–230 mesh) and 60% $HClO_4$ solution was from Merck. A Pt-based commercial catalyst (EC20, 20% Pt onto carbon) was tested and used as a reference material.

A constant composition reactant mixture (RM), comprising D-glucose, L-histidine (molar ratio glucose:histidine = 10:1) and iron acetate (0.96 wt.% Fe calculated on the total mass of glucose and histidine) was heat-treated adopting many templating procedures. Glacial acetic acid, equimolar to histidine, was always added to dissolve the *N*-containing compound.

2.1.1. Silica wet templating

This method was previously reported in the literature [26]. Briefly, 10 mL of an aqueous RM solution was added to silica powder to obtain a silica gel (2.3 RM mL g^{-1} SiO_2). The gel was treated by a first heating step (H1) of 1 h 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 to remove silica. The resulting carbon was dried in nitrogen (100 °C, 24 h) and finally ball-milled (5 min, 10 Hz). A second heating step (H2) was performed (900 °C, 3 h, under a N_2 flow), to activate catalytic sites. The resulting material will be labelled C/Si in the following.

2.1.2. Incipient Wetting of Black Pearls 2000

An active carbon (0.5 g, Black Pearls 2000, Cabot) was impregnated by "Incipient Wetting" with RM solution volumes such as to completely fill the carbon pore volume. Small quantities of RM solution were added dropwise under stirring to carbon to let the solution enter into the pores by capillarity, until the liquid volume was enough (ca. 4.7 mL g^{-1} of carbon) to fully wet the catalyst with no liquid excess.

The mixture underwent the same two heating steps H1 and H2 of the previous templating technique (see Section 2.1.1). The resulting material will be labelled C/BP in the following.

2.1.3. Freeze-drying

Freeze-drying was set up by freezing an RM solution under reduced pressure for 24 h. The freeze-dried mixture was heat-treated using the above two heating steps H1 and H2 (see Section 2.1.1). The resulting material will be labelled C/Lio in the following.

2.1.4. Thermal decomposition of a gas-evolving reactant

Promotion of pore formation was achieved by *in-situ* generation of gas bubbles, arising from thermal decomposition of a fragile molecule like oxalic acid. A semi-solid mixture of glucose (2 g), histidine (0.173 g), iron acetate (0.069 g) and glacial acetic acid was mechanically blended with oxalic acid (0.5 g) and ball-milled (15 min, 10 Hz). This mixture was put in a closed tube and heat-treated at 140 °C for 1 h. The resulting brown-yellowish mass, with a strongly expanded overall volume, underwent the same two heating steps H1 and H2 (see Section 2.1.1). The end material will be labelled C/Gas in the following.

2.2. Characterization

2.2.1. BET surface area

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. Specific surface area was determined by the instrumental software. Porosity distribution was evaluated for each sample by using Density Functional Theory (DFT) method applied to the N_2 adsorption data. Before measurements, sample powders were heat-treated at 150 °C for 4 h under a N_2 flow to remove adsorbed foreign species.

2.2.2. Electrochemical measurements

Electrochemical characterization was performed in 0.1 mol dm^{-3} $HClO_4$ by the Thin Film Rotating Disk Electrode method using Cyclic Voltammetry (CV). Catalyst aliquots (10 mg) were dispersed in water (1.0 mL), added with Nafion® (5 μL), sonicated 5 min, ball-milled (20 min, 10 Hz) and finally sonicated 5 min; 7 μL of this mixture were pipetted onto the graphite tip (geometric surface area: $A = 0.07$ cm^2) of a rotating disk electrode (EDI 101, Radiometer) and dried in a bottom-up position over a tungsten lamp (100 W). Electrocatalyst loading was 1 mg cm^{-2}.

A two-compartment cell with a graphite counter electrode (Amel 201/S-016) and a AgCl/Ag external reference electrode (Amel) in 3 mol dm^{-3} NaCl was used. The potentiostat was Amel mod. 7050. Before CV recording, the electrode was conditioned by cycling 45 min in N_2 saturated 0.1 mol dm^{-3} $HClO_4$ within the potential range $E = -0.275$ / $+0.800$ V, followed by 100 min cycling in O_2 saturated solution ($v = 5$ mV s^{-1}, $\omega = 1600$ rpm). CVs in O_2 were recorded in the same conditions at different rotation rates. To verify electrode stability and internal reproducibility several CVs at $\omega = 1600$ rpm were recorded in each run. After measurements in O_2, CVs were again recorded in N_2 to obtain background faradaic currents for O_2 reduction data correction.

2.2.3. X-ray photoelectron spectroscopy measurements

XPS measurements were performed with an M-Probe Instrument (SSI) equipped with a monochromatic Al Kα source (1486.6 eV) with a spot size of 200 × 750 μm and a pass energy of 25 eV, providing a resolution of 0.74 eV. The energy scale was calibrated with reference to the $4f_{7/2}$ level of a freshly evaporated gold sample (84.00 ± 0.1 eV) and to the $2p_{3/2}$ and 3 s levels of copper (932.47 ± 0.1 and 122.39 ± 0.15 eV, respectively). An electron flood gun was used to compensate for the build-up of positive charge on insulating samples: a value of 5 eV was selected. Quantitative data were carefully checked and reproduced several times. Uncertainty in spectral decomposition is estimated to be 1%.

3. Results and discussion

The final surface samples composition was determined by XPS and is constant for all the samples (C ~95–96%; N ~1–1.5%, O ~1.5–3%, Fe < 1%).

Fig. 1 shows CV cathodic ORR polarization curves of all prepared catalysts recorded at $\omega = 1600$ rpm in 0.1 mol dm^{-3} $HClO_4$. For comparison a similar CV curve is also reported for a commercial Pt-based catalyst, EC20 (labelled as Pt EC20).

Except for the Pt sample, a limiting current is not clearly detected for the synthesized carbons. The best onset potential is observed for C/BP and C/Si, displaced by 200 mV at more cathodic potentials than the reference Pt EC20 (Table 1).