Iron and Copper Containing Oxygen Reduction Catalysts from Templated Glucose-Histidine.

Ivano Galbiati, Claudia Letizia Bianchi, Mariangela Longhi, Leonardo Formaro

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Pore Size Distributions at different temperatures. GluHistFe75.
338x238mm (96 x 96 DPI)

Pore Size Distributions at various Glu/Hist molar ratios (T= 600°C).
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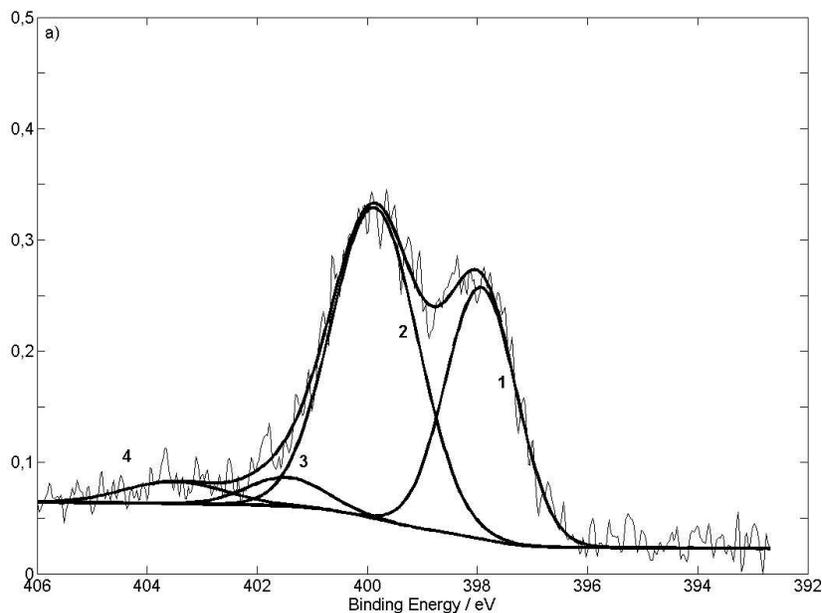
High resolution Nitrogen (1s) Spectra of GluHist: a) T= 600°C; 1) pyridinic N (N6) (B.E. 398 -398.4 eV); 2) pyrrolic-N in five member ring and or pyridonic-N (N5) (B.E. 400-400.5 eV); 3) quaternary-N (NQ), e.g. N in graphene structure (B.E. 401.5-402.2 eV); 4) pyridinic-N-oxide (NX) (B.E. 403.5-404.8 eV) B.E. are from [45-48].
338x232mm (96 x 96 DPI)
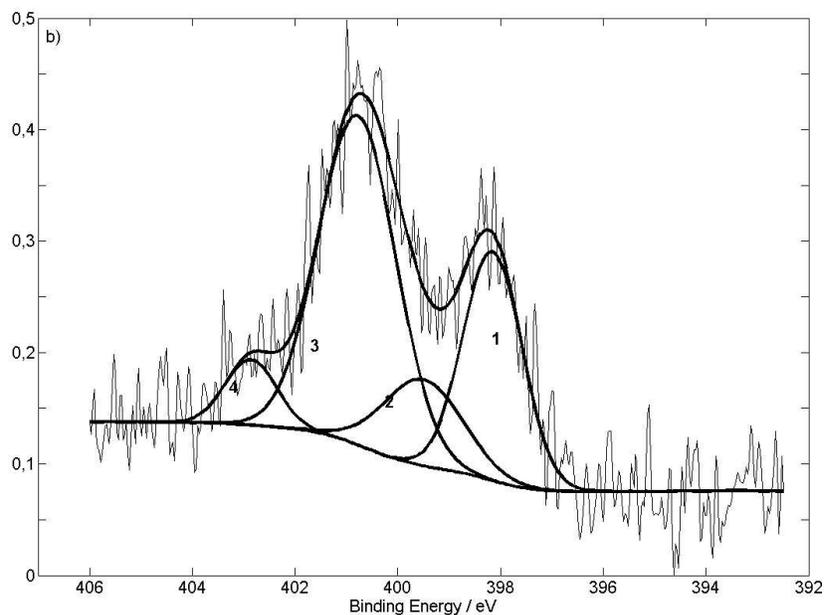
High resolution Nitrogen (1s) Spectra of GluHist: b) T= 900°C. 1) pyridinic N (N6) (B.E. 398 -398.4 eV); 2) pyrrolic-N in five member ring and or pyridonic-N (N5) (B.E. 400-400.5 eV); 3) quaternary-N (NQ), e.g. N in graphene structure (B.E. 401.5-402.2 eV); 4) pyridinic-N-oxide (NX) (B.E. 403.5-404.8 eV) B.E. are from [45-48].
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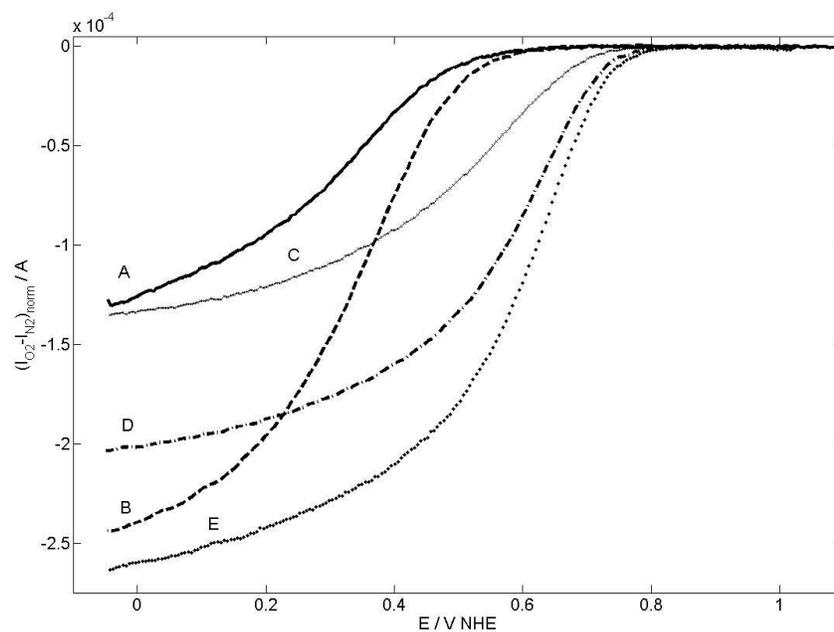
Voltammograms in oxygen-saturated 0.1M HClO4. A) GluHist; B) GluHistFe0; C) GluHistFe25; D) GluHist75; E) GluHistFe100. (T=25°C; scan rate 5 mV s-1; rotation rate 700 rpm).
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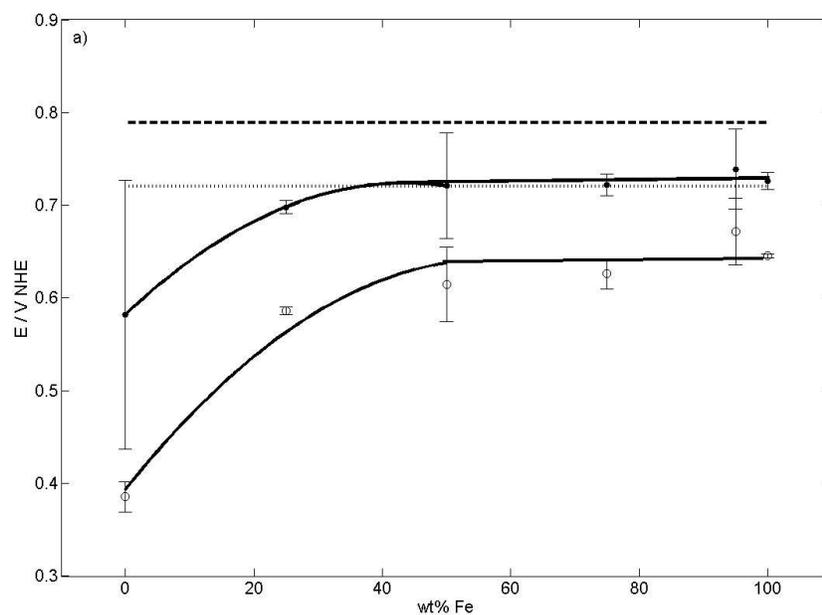
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a) Incipient oxygen reduction potentials at different Fe wt %: ● and --- (heavy dashes) potentials at the intersection points in Fig. 5; ○ and --- (light dashes) peak potentials of cathodic maxima at $\omega=0$ rpm. Dashes are for EC-20 Pt catalyst, open and closed points are for home made carbons.
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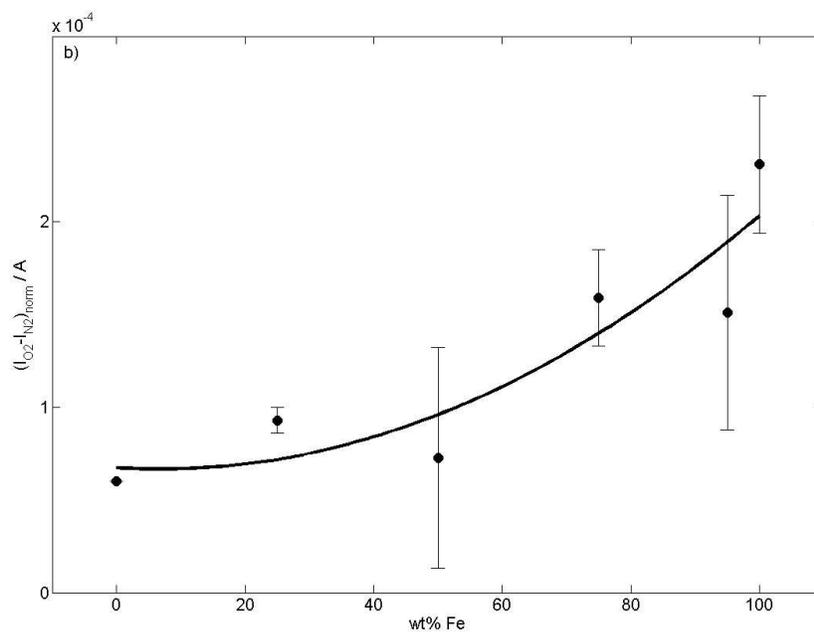
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b) Currents at E=+0.420 V NHE at different wt % Fe.
Lines are a guide to the eye. Error bars represent standard deviation of experimental data. (0.1M HClO4, scan rate 5 mV s-1, rotation rate 700 rpm, T= 25°C.)

338x232mm (96 x 96 DPI)

Iron and Copper Containing Oxygen Reduction Catalysts from Templated Glucose-Histidine.

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Abstract

Nitrogen doped carbons loaded with non-precious transition metals are currently investigated as substitutes of Pt-based catalysts for oxygen reduction in Polymer Electrolyte Fuel Cells (PEMFC's). This paper reports the preparation of one kind of such catalysts using glucose/histidine mixtures added with Fe and Cu salts in the presence of silica gels as hard templating agent to increase carbon surface area. The resulting carbons contain nitrogen in amounts that depend on heating temperature (T=600 and T=900°C) on the glucose/histidine molar ratio and, more weakly, on the relative Fe/Cu amount. Surface areas are a function of reactant concentration and heating temperature, whereas pore size and pore size distribution only depend on glucose-histidine molar ratio. Cyclic voltammetry results on oxygen reduction depend on Fe/Cu ratio, the best result both in terms of incipient oxygen reduction potentials and currents being observed on samples only containing Fe, with no Cu added.

Keywords: Oxygen Reduction Reaction, Platinum-free Catalysts, C/N/Me centers, Iron-Copper, Hard Templating,

1. Introduction

Fuel cells, and more specifically PEMFC's, represent promising power systems to the world economy, with many applications and low environmental impact. A most important aspect concerning their widespread implementation is the cost of both polymeric membranes and catalytic electrode materials which are necessary to promote electrode reactions thus increasing fuel cell energy efficiency. This is especially true for the cathodic oxygen reaction (ORR), the best catalyst being at present based on the very expensive platinum metal or Pt-alloys (about 2250 $/oz [1]). Therefore, a decrease in Pt amount (from 1.1 to 0.2 g/KW in 2015, DOE data [2]) or its replacement with non-precious materials having comparable performance is necessary. Research on this subject started in the '60s [3] with a notable turning point from Yeager's work at the end of '80s [4], and became a worldwide continuing issue with contributions from many authoritative research groups.

Among various materials, nitrogen modified carbons also containing non-precious transition metals (Fe and Co) are considered interesting because of their ORR activity and reliability as confirmed by results from independent groups [5-15]. Several preparative methods are reported: 1) carbon impregnation with metal organosalts or cyanoderivatives, followed by thermal activation in the presence of e.g. ammonia gas [5]; 2) thermal treatment of nitrogen-containing metal complexes adsorbed onto carbon [16-36]; 3) polymerization of aromatic compounds, e.g. pyrrole [37,38], onto carbon surface followed by metal ion adsorption (Co^{2+}) to obtain porphyrine-like structures; 4) thermal treatment of mixed precursors from a carbon and nitrogen source, respectively, e.g. glucose and an amino acid, added with transition metal salts (Fe,Cu) [9,14]. These latter materials are considered interesting because of the ease and flexibility of the

synthetic route and, moreover, of the catalytic activity, with incipient oxygen reduction potentials closely approaching (by ~40 mV) those of commercial Pt catalysts [14]. Unfortunately, however, they are reported with low stability [14].

Recently, thermodynamic criteria were put forward to model the catalytic activity of Pt-free bimetallic alloys [39] permitting to evaluate what metal, or combination of metals, may be most effective in ORR. As a result Fe^{2+}/Cu^+ ions were shown most favourable. Interestingly these ions are also present in natural enzymatic systems like cytochrome C oxidase, an effective and selective catalyst in the reduction of oxygen to H_2O, based on a cooperative effect of the two ions.

Improving catalyst activity is not only a matter of varying composition but also involves morphological/textural aspects. By reference to carbon supported Pt catalysts, carbon origin, surface area, porosity and pore size distribution reportedly affect end material performances. Reviewing these aspects, Antolini [40] has recently shown that besides good electrical conductivity, carbon supports have to be characterized by high surface areas and high fractional pore percentage in the mesoporosity region (2-50 nm) in order to favour reactant mass transport to and from catalytic centers, the more so if the catalytic sites are preferentially located at inner positions of the carbon structure, in the micropore size region as reported by [41].

Histidine was chosen as the nitrogen-bearing precursor, because it contains both an imidazolic ring and a carboxyl group that, if retained in end products upon thermal activation, may presumably contribute to ORR activity [40-42]. In the attempt of increasing carbon surface area and at the same time controlling porosity in the mesoporosity range a hard template method was adopted using silica gel suspensions in

water. Also, Fe^{2+} and Cu^{2+} in variable ratios were used to explore the entire composition

range as suggested by the theoretical examination in [39].

2. Experimental

2.1. Reagents

Glucose, histidine, Fe(II) acetate, Cu(II) acetate, glacial acetic acid and Nafion (5 wt %

solution) were purchased from Aldrich and used as received. Silica (Silica Gel 60 HR)

and $HClO_4$ (60 wt %) were from Merck and Fluka, respectively. High purity water from

a MilliQ system (Millipore) was used throughout. Nitrogen and oxygen (Sapio, 5nines)

were used.

2.2. Preparation of the catalytic materials

A glucose (Glu in the following) solution in water (1.68 mol dm^{-3}) was added with

histidine (Hist) in variable molar ratios: Glu/Hist=1/1 is indicated as GluHist in the

following; Glu/Hist=2/1 as GluHist0.5; Glu/Hist=4/1 as GluHist0.25; Glu/Hist=10/1 as

GluHist0.1. Adding equimolar glacial acetic was found necessary to dissolve histidine.

10 ml of this solution were stirred with 4.3 g of silica for 5 min to form a gel, and stirred

again 5 min after 15 min standing. The gel was loaded in a quartz reactor, degassed with

N_2 (100 cm^3 min^{-1}) for about 5 min and inserted in a preheated vertical oven at

T=600°C in order to carbonize as fast as possible the precursors, preserving the ordered

room temperature gel structure in the final products. Heating was continued for 1 h

under continuous N_2 purging (100 cm^3 min^{-1}). Then the tube was rapidly quenched in

air. Silica was removed in 3M boiling NaOH followed by repeated carbon

washing/filtering (MilliQ water, 0.45 μm Durapore filters) until water conductivity

became lower than 4 μS. Products were dried in nitrogen (100 °C, 24 h) and finally

ground in an agate mortar. Metal containing catalysts were prepared by the same

procedure but for the addition of acetate metal salts (Fe and Cu ions at 1 wt % total with

respect to glucose+histidine, at variable ratios between them). The ratio of iron and

copper salts was varied in a range from 0% to 100% iron: GluHistFe0: 0% Fe/100 %

Cu; GluHistFe25: 25% Fe/75 % Cu; GluHistFe50: 50% Fe/50 % Cu; GluHistFe75: 75%

Fe/25 % Cu; GluHistFe95: 95% Fe/5 % Cu; GluHistFe100: 100% Fe/0 % Cu.

All materials were heat-activated in a second step at T=900°C under constant N_2 flow

$(100 \text{ cm}^3 \text{ min}^{-1})$ in the following conditions: 30 min room temperature purging, ramping

at 6°C min^{-1} and 3 h standing at T= 900°C, fast quenching to room temperature.

2.3. Characterisation of materials

X-ray Photoelectron Spectroscopy (XPS).

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 4f7/2 level of a freshly evaporated gold sample $(84.00 \pm 0.1 \text{ eV})$

and to the 2p3/2 and 3s levels of copper $(932.47 \pm 0.1$ and 122.39 ± 0.15 eV,

respectively). An electron flood gun was used to compensate for the buildup of positive

charge on insulating samples: a value of 5 eV was selected. For all samples, the C 1s

peak level was taken as the internal reference at 284.6 eV. Accuracy of reported binding

energies (BEs) is approximately ± 0.2 eV. Quantitative data were carefully checked and

reproduced several times. Uncertainty in spectral decomposition is estimated to be $\pm 1\%$.

Specific Surface Area.

Surface area and porosity were determined by low temperature B.E.T. N_2 adsorption

using an SA3100 Coulter apparatus. Before measurement, samples were outgassed at

T= 80 °C for 3 h. Surface area and porosity were calculated from nitrogen isotherms

using the instrumental software (Version 2.12).

TEM images were obtained by a Zeiss EFTEM LEO 912AB (120 kV) microscope

2.4. Electrode and catalyst layer preparation

Electrochemical characterisation was performed by the Thin Film Rotating Disk

Electrode (TFRDE) method immobilizing small catalyst amounts onto the graphite tip

(geometric surface area: A=0.0491 cm^2) of a rotating disk electrode (EDI 101,

Radiometer). Before use the tip was gently cleaned with soft sandpaper, polished by

diamond powder (Aldrich) and finally degreased with ethanol. Catalyst aliquots (8 mg)

were dispersed in water added with Nafion (1.5 ml water, 4 μl Nafion) and sonicated for

30 min; 7 μl of this mixture were pipetted onto the electrode tip and dried in a bottom-

up position above a tungsten lamp.

2.5. Electrochemical measurements

A two compartment cell with a graphite counterelectrode (Amel 201/S-016) and a

AgCl/Ag external reference electrode (Amel) in 3M NaCl was used. The reference was

connected to the cell by a salt bridge filled with the working electrolyte (0.1 M $HClO_4$).

Before each experimental run all glassware was washed by concentrated H_2SO_4 and

rinsed in MilliQ water. The counterelectrode was cleaned with filter paper. The

potentiostat was AMEL mod. 7050. Measurements were performed by an accurately

reproducible procedure. Before CV recording, the electrode was conditioned cycling 45

min in N_2 in the potential range E=-0.275 – +0.800 V, followed by 100 min cycling in

O_2 saturated solution (5 mV/s, ω=1600 rpm). Then O_2 reduction results were recorded

in the same conditions at different electrode rotation rates. To verify electrode stability

and internal reproducibility several CVs at ω= 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. Background charge values were also

obtained by integration of N_2 curves and used as a measure of real electrode surface

area, normalizing the many investigated materials with respect to Glu (T=900°C) that

was assumed as an internal, arbitrary reference.

3. Results and Discussion.

In the presence of silica gel as a templating agent, carbon materials with expanded,

sponge-like overall morphology are obtained as shown in Fig. 1 for a plain glucose

sample heated at T=600 °C. These effects are more quantitatively observed in the first

two entry lines of Tab. 1 where the sample obtained in the presence of silica shows a

tremendous increase of BET surface area (1100 m^2/g) instead of a few square meters/g

of the corresponding glucose-only sample. Though in the absence of comparison data

without added silica, Tab. 1 shows that similarly high BET areas are obtained for all the

samples. Interestingly, besides depending on silica, surface areas are a function of the

used reactant, reactant concentration and heating temperature. Most relevant effects are

due to histidine that, at even the lowest used molar ratio with respect to glucose (see

GluHist0.1 in Tab. 1), causes a surface area decrease of ~200 m^2/g, with a further

decreasing trend taking place with increasing histidine/glucose molar ratio. Though

moderate, opposite effects arise from metal ion addition, with surface areas in any case

greater than the metal-free reference (sample GluHist) and also weakly increasing with

increasing the Fe^{2+}/Cu^{2+} ratio. As expected on general grounds, and in accordance with

some matter loss visually observed as brownish gas emitted during the second heating at

T=900 °C, surface areas decrease with increasing temperature. This decrease is in some

relation with surface areas from the previous heating at T=600 °C. As a fact, the last

column in Tab. 1 shows that surface areas at T=900 and T=600 °C are in a ca. constant

ratio of 0.75-0.9. In a further aspect of this thermal behaviour, BET fractional pore

volume distributions of many samples were found essentially independent of heating

temperature. This is shown as an example in Fig. 2 for sample GluHistFe75. Then, the

above surface area ratio and the lack of variation in pore volume distribution appear

related, and jointly suggest that textural sample features are mostly established during

the first heating in the presence of silica, followed by lesser rearrangements taking place

at higher temperature after silica removal, these readjustments in their turn causing a

moderate decrease of previous surface areas while leaving essentially unchanged

porosity distribution.

Reactant composition effects on porosity are reported for the more extensively available

results at T=600 °C. In Fig. 3 histidine addition causes readjustments of the pristine

glucose porosity, especially relevant at both the extremes of the accessible pore size

range. In the low size region, pores 6-8 nm in size undergo a first redistribution in

favour of the smaller ones (6 nm). Though with irregular variations, pores with these

latter size are a large fractional value regardless of increasing histidine amounts. At the

other extreme of size, increasing histidine causes the 20-80 nm pore size to become

gradually more abundant, up to ~35% of the overall sample porosity. Adding Fe^{2+} and

Cu^{2+} ions in variable relative amounts has no apparent effect (not reported) on the

porosity distribution of a number of carbons with constant Glu/Hist ratio

(Glu/Hist=1/1). Histidine is therefore most effective to promote pore size increase. This is at variance with Maruyama's results [9] on similar glucose/adenine carbons from a "dry" procedure without templates.

XPS survey results are shown in Tab. 2. Cu and Fe are undetected even for the lower used heating temperature. This situation is frequently observed, and unresolved, in the literature with the baffling outcome that, though undetected in outermost surface layers, added metals are indeed effective in promoting electrochemical ORR carbon behaviour. As also representative of the present results, we mention that Fe was undetected by both XPS and UPS [43] in spite of wide variation in added amounts, the maximum Fe value reaching 5.5 wt % with respect to the graphite oxide that was used in that case. Moreover, in [44] it is reported that "after carbonization, the content of copper decreases as the copper ions are reduced into metallic copper nanoparticles. These nanoparticles are difficult to detect by XPS because they are coated by a thin carbon layer and migrate into the carbon matrix". As observed in Tab. 2 for samples heated at both T=600 and 900 °C, the relative abundance of C1s and N1s signals is moreover only weakly affected by metal addition.

Tab. 2 shows that N1s signals of GluHist (T=600 °C) are initially very high (14%) and decrease with both increasing temperature (7%, T=900 °C) and decreasing the histidine amount adopted in preparation (4%, Glu/Hist0.10). Notably, the temperature-dependent nitrogen decrease is accompanied by increasing C1s signals (from 82 to 91%) showing that nitrogen removal also induces chemical carbon readjustments. Fig. 4 and Tab. 3 evidence that different nitrogen forms are present (Fig. 4a) with variable and temperature-dependent relative amounts (Fig. 4b). In GluHist for T=600 °C two main

contributions are due to pyridinic (N6) and pyrrolic/pyridonic (N5) forms, in relative amounts of 36 and 55 atomic %, respectively. Minor contributions are due to quaternary-N (NQ, ~5%), and pyridinic-N-oxide (NX, 4%) (Relevant binding energies, B.E., are reported in the caption to Fig. 4 [45-48]). All these nitrogen forms undergo extensive redistribution upon heating to T=900 °C, with N6 that decreases by ~25%, N5 by ~75%, such variations being counteracted by an extraordinary, tenfold increase of NQ, and doubling of NX. These readjustments are in accordance with literature data [48] by which N5 and N6 are thermally unstable with respect to NQ. This latter NQ represents a class of compounds in which substitutional nitrogen in graphene layers is theoretically advocated [49, 50] as active for ORR on metal-free catalysts.

However, results in Tab. 3 show that adding metals (Fe, Cu) to glucose-histidine precursors surprisingly does not cause a decrease in N5 and N6 signals with the increasing heating temperature, which would be expected from all the above literature data. This behaviour may be attributed to the formation of metal complexes from N5 and N6 groups, which indirectly corresponds to their thermal stabilization. In support of this hypothesis, it can be mentioned that in a recent paper [51] the signal at 399.3 eV, which is consistent with the present N5 and N6 species, was attributed to iron-associated pyridinic nitrogen species. This evidence can be considered as an indirect proof of the presence of metals onto the carbon surface, even though they are not directly determined by XPS.

Electrochemical results are collectively reported in Fig. 5 to permit comparison of the many materials obtained with variable relative Fe/Cu weight amounts and a constant, equimolar Glu/Hist ratio. Results only concern T=900 °C given that weak or no activity

was observed for T=600 °C. All curves are net oxygen reduction currents, corrections

for background residual currents and surface area normalization having been applied as

described in the Experimental. Metal addition affects both incipient oxygen reduction

potentials and currents. Notably enough, currents at first sharply increase by addition of

Cu only (curve B) to the metal-free reference (curve A), and approach a limiting current

behaviour at most negative potentials. Substituting a fractional Fe amount (25%) for Cu

(curve C) causes the incipient oxygen reduction potential to shift anodic by ~0.2 V at

the expense however of a decrease in current that becomes comparable to those of the

Glu/Hist blank. Thereafter, any increase in fractional Fe amount is accompanied by

gradually increasing currents, better approaching a diffusion mass transport behaviour,

with some, though limited, further increase in incipient reduction potentials. Figs. 6a, 6b

are an overview outlining the observed metal dependence of oxygen reduction currents

and incipient reduction potentials (at ω=700 rpm, constant) in comparison with similar

values recorded on a commercial Pt catalyst (EC-20). In Fig. 6a two series of incipient

potential data are used, a first set of values being rather qualitatively based on "kink"

potentials at the cross-over point between a first, generally flat, and a second rising part

of each I/E curve; the second set relying instead more quantitatively on the peak

potential of a characteristic current maximum recorded at ω=0 rpm [52] (such results

are not reported for brevity). In Fig. 6a incipient potentials increase with increasing

fractional Fe amount and reach well defined, limiting high values for Fe/Cu greater than

~50 wt %, lower than the corresponding Pt values by ~40-50 mV. A similar increasing

trend occurs for currents (Fig. 6b), without however any plateau and a maximum value

at 100 wt % Fe.

Then, we are left with open conclusions. On the one side, ORR behaviour improves

with increasing Fe/Cu ratio, reaching however a maximum in the presence of Fe only,

in the absence of a second metal (Cu), thus making uncertain that both metals are

essential to catalytic ORR activity. Given the above XPS results, in both instances the

question arises if Fe metal, possibly buried in the carbon matrix and/or complexed with

nitrogen groups, is accessible, and to what extent, to the outside solution in order to

form catalytically effective centres. Problems also arise concerning electrode durability

given the limited amount of metal present as such or in ionic form.

Acknowledgements

References

[1] http://platinumprice.org/platinum-price-history.html

[2] http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

[3] R. Jasinski, *Nature* **1964**, *201*, 1212.

[4] S. Gupta, D. Tryk, I. Bae, W. Aldred, E. Yeager, *J. Appl. Electrochem.* **1989**, *19*, 19.

[5] M. Lefèvre, E. Proietti, F. Jaouen, J.-P. Dodelet, *Science* **2009**, *324*, 71.

[6] M. Yuasa, A. Yamaguchi, H. Itsuki, K. Tanaka, M. Yamamoto, K. Oyaizu, *Chem. Mater.* **2005**, *17*, 4278.

[7] N. P. Subramanian, S.P. Kumaraguru, H. Colon-Mercado, H. Kim, B. N. Popov, T. Black, D. A. Chen, *J. Power Sources* **2006**, *157*, 56.

[8] E. B. Easton, A. Bonakdarpour, R. Yang, D. A. Stevens, J. R. Dahn, *J. Electrochem. Soc.* **2008**, *155*, B547.

[9] J. Maruyama, I. Abe, *Chem. Commun.* **2007**, *2007*, 2879.

[10] T. E. Wood, Z. Tan, A. K. Schmoeckel, D. O'Neill, R. Atanasoski, *J. Power Sources* **2008**, *178*, 510.

[11] A. Garsuch, K. MacIntyre, X. Michaud, D. A. Stevens, J. R. Dahn, *J. Electrochem. Soc.* **2008**, *155*, B953.

[12] T. Schilling, M. Bron, *Electrochim. Acta* **2008**, *53*, 5379.

[13] A. H. C. Sirk, S. A. Campbell, V. I. Birss, *J. Electrochem. Soc.* **2008**, *155*, B592.

[14] J. Maruyama, N. Fukui, M. Kawaguchi, I. Abe, *J. Power Sources* **2008**, *182*, 489.

[15] V. Nallathambi, J.-W. Lee, S. P. Kumaraguru, G. Wu, B. N. Popov, *J. Power Sources* **2008**, *183*, 34.

[16] O. Ikeda, H. Fukuda, H. Tamura, *J. Chem. Soc., Faraday Trans.* **1986**, *82***,** 1561.

[17] R. Holze, I. Vogel, W. Vielstich, *J. Electroanal. Chem.*, **1986**, *210*, 277.

[18] S. Dong and R. Jiang, *Ber. Bunsenges. Phys. Chem.* **1987**, *91*, 479.

[19] T. Sawaguchi, T. Itabashi, T. Matsue, I. Uchida, *J. Electroanal. Chem.* **1990**, *279*, 219.

[20] A. Widelöv, R. Lasson, *Electrochim. Acta* **1992**, *37*, 187.

[21] A. Widelöv, *Electrochim. Acta* **1993**, *38*, 2493.

[22] B. Bittins-Cattaneo, S. Wasmus, B. Lopez-Mishima, V. Vielstiech, *J. Appl. Electrochem.* **1993**, 23, 625.

[23] G. Faubert, G. Lalande, R. Côté, D. Guay, J.P. Dodelet, L.T. Weng, P. Bertrand, G. Dénès, *Electrochim. Acta* **1996**, *41*, 1689.

[24] G. Faubert, R. Côté, D. Guay, J.P. Dodelet, G. Dénès, P. Bertrand, *Electrochim. Acta* **1998,** *43,* 341.

[25] A.L. Bouwkamp-Wijnoltz, W. Visscher and J.A.R. van Veen, *Electrochim. Acta* **1998,** *43,* 3141.

[26] S.L. Gojković, S. Gupta, R.F. Savinell, *J. Electroanal. Chem.* **1999**, *462*, 63.

[27] R. Jiang, D. Chu, *J. Electrochem. Soc.* **2000**, *147*, 4605.

[28] M. Lefèvre, J.P. Dodelet, P. Bertrand, *J. Phys. Chem. B* **2000**, *104*, 11238.

[29] M. Lefèvre, J.P. Dodelet, P. Bertrand, *J. Phys. Chem. B* **2002**, *106*, 8705.

[30] A.L. Boukamp-Wijnoltz, W. Visscher, J.A.R. van Veen, E. Boellaard, A.M. van der Kraan, S.C. Tang, *J. Phys. Chem. B* **2002**, *106*, 12993.

[31] M. Lefèvre, J.P. Dodelet, *Electrochim. Acta* **2003**, *48*, 2749.

[32] H. Schulenburg, S. Stankov, V. Schu1nemann, J. Radnik, I. Dorbandt, S. Fiechter, P. Bogdanoff, H. Tributsch, *J. Phys. Chem. B* **2003**, *107*, 9034.

[33] J.A.R. van Veen, H.A. Colijn, J.F. van Baar, *Electrochim. Acta* **1988,** *33,* 801.

[34] G. Lalande, G. Faubert, R. Côté, D. Guay, J.P. Dodelet, L.T. Weng, P. Bertrand, *J. Power Sources* **1996**, *61*, 227.

[35] M. Bron, J. Radnik, M. Fieber-Erdmann, P. Bogdanoff, S. Fiechter, *J. Electroanal. Chem.* **2002**, *535*, 113.

[36] K. Sawai, N. Suzuki, *J. Electrochem. Soc.* **2004**, *151*, A2132.

[37] R. Bashyam, P. Zelenay, *Nature* **2006**, *443*, 63.

[38] K. Lee, L. Zhang, H. Lui, R. Hui, Z. Shi, J. Zhang, *Electrochim. Acta* **2009,** *54,* 4704.

[39] Y. Ma, P. B. Balbuena, *Chem. Phys. Lett.* **2007**, *440*, 130.

[40] E. Antolini, *Appl. Catal. B* **2009**, *88*, 1.

[41] J. Herranz, M. Lefèvre, J.-P. Dodelet, *J. Electrochem. Soc.* **2009**, *156*, B593.

[42] C. W. B. Bezerra, L. Zhang, K. Lee, H. Liu, A. L. B. Marques, E. P. Marques, H. Wang, J. Zhang, *Electrochim. Acta* **2008**, *53*, 4937.

[43] P. Wang, Z. Wang, L. Jia, Z. Xiao *Phys. Chem. Chem. Phys.* **2009**, *11*, 2730.

[44] R. Fu, N. Yoshizawa, M. S. Dresselhaus, G. Dresselhaus, J. H. Satcher Jr., T. F. Baumann, *Langmuir* **2002**, *18*, 10100.

[45] D. Hulicova-Jurcakova, M. Seredych, G.Q. Lu, T. J. Bandosz *Adv. Funct. Mater.* **2009**, *19*, 438.

[46] S. Biniak, G. Szymański, J. Siedlewski, A. Światkowski, *Carbon* **1997**, *35*, 1799.

[47] D. Long, J. Zhang, J. Yang, Z. Hu, G. Cheng, X. Liu, R. Zhang, L. Zhan, W. Qiao, L. Ling, *Carbon* **2008**, *46*, 1253.

[48] J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, K. M. Thomas, *Carbon* **1995**, *33*, 1641.

[49] R. A. Sidik, A. B. Anderson, N. P. Subramanian, S. P. Kamaraguru, B. N. Popov, *J. Phys. Chem. B* **2006**, *110*, 1787.

[50] N. P. Subramanian, X. Li, V. Nallathambi, S. P. Kumaraguru, H. Colon-Mercado, G. Wu, J.-W. Lee, B. N. Popov, *J. Power Sources* **2009**, *188*, 38.

[51] R. Kothandaraman, V. Nallathambi, K. Artyushkova, S. Calabrese Barton, *Appl. Cat. B* **2009**, *92*, 209.

[52] F. Jaouen, S. Marcotte, J.-P. Dodelet, G. Lindbergh, *J. Phys. Chem. B* **2003**, *107*, 1376.

Figure Captions

Figure 1. TEM image of Glu sample (T= 600°C).

Figure 2. Pore Size Distributions at different temperatures. GluHistFe75.

Figure 3. Pore Size Distributions at various Glu/Hist molar ratios (T= 600°C).

Figure 4. High resolution Nitrogen (N1s) Spectra of GluHist: a) T=600°C; b) T=900°C. 1) pyridinic N (N6) (B.E. 398-398.4 eV); 2) pyrrolic-N in five member ring and/or pyridonic-N (N5) (B.E. 400-400.5 eV); 3) quaternary-N (NQ), *e.g.* N in graphene structure (B.E. 401.5-402.2 eV); 4) pyridinic-N-oxide (NX) (B.E. 403.5-404.8 eV) B.E. are from [45-48].

Figure 5. Voltammograms in oxygen-saturated 0.1M $HClO_4$. A) GluHist; B) GluHistFe0; C) GluHistFe25; D) GluHist75; E) GluHistFe100. (T=25°C; scan rate 5 mV s^{-1}; rotation rate 700 rpm).

Figure 6. a) Incipient oxygen reduction potentials at different Fe wt %: ● and **---** (heavy dashes) potentials at the intersection points in Fig. 5; ○ and ⋯ (light dashes) peak potentials of cathodic maxima at ω=0 rpm. Dashes are for EC-20 Pt catalyst, open and closed points are for home made carbons.
b) Currents at E=+0.420 V NHE at different wt % Fe.
Lines are a guide to the eye. Error bars represent standard deviation of experimental data. (0.1M $HClO_4$; scan rate 5 mV s^{-1}; rotation rate 700 rpm; T=25°C.)

Tables

Table 1. Specific Surface Area ($m^2 g^{-1}$)

	Glu/Hist Molar Ratio	Fe/Cu wt%	Surface Area (m^2g^{-1}) (T= 600°C)	Surface Area (m^2g^{-1}) (T= 900°C)	S_{900}/S_{600}
Glu no silica	1/0	-	25	-	-
Glu	1/0	-	1143	-	-
GluHist0.1	1/0.10	-	950	714	0.75
GluHist0.25	1/0.25	-	728	700	0.96
GluHist0.50	1/0.50	-	813	-	-
GluHist	1/1	-	603	541	0.90
GluHistFe0	1/1	0 / 100	670	564	0.84
GluHistFe25	1/1	25 / 75	-	555	-
GluHistFe50	1/1	50 / 50	696	559	0.80
GluHistFe75	1/1	75 / 25	665	589	0.88
GluHistFe100	1/1	100 / 0	698	587	0.84

Table 2. Atomic C, O, N Percent Sample Compositions

	N 1s%		O 1s%		C 1s %	
	T= 600°C	T= 900°C	T= 600°C	T= 900°C	T= 600°C	T= 900°C
Glu	-	-	6	-	94	-
GluHist	14	7	4	2	82	91
GluHist0.10	4	4	5	2	91	94
GluHistFe0	14	-	4	-	82	-
GluHistFe50	13	7	5	2	82	91
GluHistFe75	13	8	5	2	83	90

Table 3. Atomic N Percent Sample Compositions

	B.E. eV	Description	GluHist		GluHistFe50		GluHistFe75	
			T= 600°C	T= 900°C	T= 600°C	T= 900°C	T= 600°C	T= 900°C
N6*	398.0-398.4	pyridinic N	36	27	39	37	38	36
N5*	400.0-400.5	pyrrolic-N in five member ring and or pyridonic-N	55	14	48	48	51	45
NQ*	401.5-402.2	quaternary-N	5	52	4	5	8	16
NX*	403.5-404.8	pyridinic-N-oxide	4	7	9	10	3	3

* Specification in the text
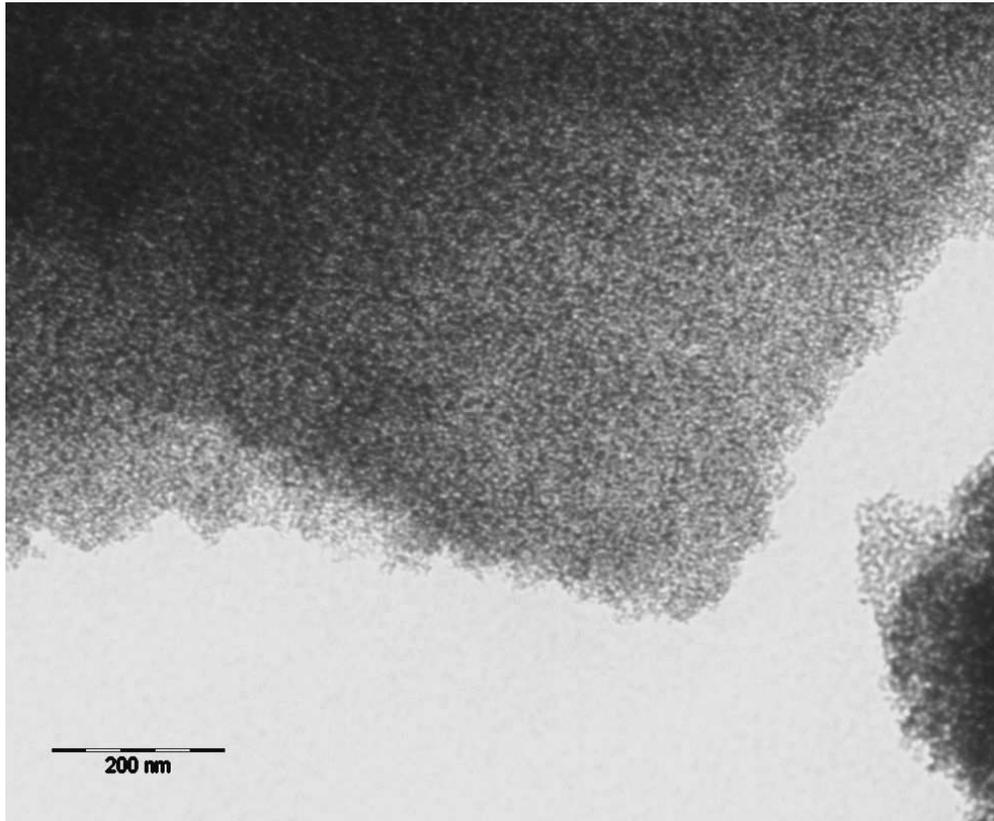
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TEM image of Glu sample (T= 600°C).
349x288mm (72 x 72 DPI)