

Short communication

Saccharide-based graphitic carbon nanocoils as supports for PtRu nanoparticles for methanol electrooxidation

Marta Sevilla^a, Grzegorz Lota^b, Antonio B. Fuenes^{a,*}

^a Instituto Nacional del Carbón (CSIC), P.O. Box 73, 33080 Oviedo, Spain

^b Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, 60-965 Poznan, ul. Piotrowo 3, Poland

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Abstract

Highly graphitic carbon nanocoils were synthesised from the catalytic graphitization of carbon spherules obtained by the hydrothermal treatment of different saccharides (sucrose, glucose and starch). This nanostructured carbon was characterized by X-ray power diffraction, N₂ adsorption and microscopy techniques (SEM and TEM). The carbon nanocoils were used as a support for PtRu nanoparticles, which were well-dispersed over the carbon surface. This catalytic system was investigated for use as an electrocatalyst for methanol electrooxidation in an acid medium. The experiments were carried out at two working temperatures (25 °C and 60 °C). It was found that the carbon nanocoils supporting PtRu nanoparticles exhibit a high catalytic activity, which is even higher than that of conventional carbon supports (Vulcan XC-72R). We believe that the high electrocatalytic activity of the carbon nanocoils presented here is due to the combination of a good electrical conductivity, derived from their graphitic structure, and a wide porosity that allows the diffusional resistances of reactants/products to be minimized.

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1. Introduction

The synthesis of nanostructured graphitic carbon materials (i.e. nanofibers, nanotubes, nanocoils, nanoparticles, nanocapsules, etc.) has recently generated a great deal of attention due to their possible applications in areas such as electron field emitters, hydrogen storage, electrical double layer capacitors, catalytic supports, etc. [1–6]. More specifically, the application of graphitic carbon nanostructures as supports for noble metal nanoparticles in the electrodes of direct methanol fuel cells (DMFC) is important because they have the properties suited to this application [6–12]. Indeed, the carbons to be used as electrocatalytic supports in DMFC must exhibit a good electronic conductivity, a high resistance to corrosion and a relatively large porosity made up of wide pores. However, it is difficult to synthesise low-cost carbon materials that combine all of these characteristics. Most nanostructured graphitic carbons that are

suitable for this application (i.e. carbon nanotubes, graphitic carbon nanofibers, etc.) require complex and expensive production steps (i.e. laser evaporation, arc discharge, thermal CVD, etc.). It is essential therefore to develop simple and low-cost synthetic methods in order to produce nanostructured graphitic carbons suitable for use as electrocatalytic supports in DMFC systems. Hyeon et al. recently reported a procedure to prepare nanostructured carbons for application as electrocatalytic supports [6–8]. They used a resorcinol-formaldehyde gel doped with transition metals as a precursor to obtain nanostructures of graphitic carbon and, in addition, they demonstrated that these materials are excellent supports for the electrodes of direct methanol fuel cells.

Recently we developed a novel and simple synthetic strategy for fabricating carbon nanostructures of high crystallinity (unpublished results). This synthetic method is based on the use of low-cost and widely available saccharides (i.e. glucose, sucrose and starch) as a carbon precursor and the use of different metals as catalysts to produce, at relatively low temperatures (≤ 1000 °C), graphitic nanostructures identified as carbon nanocoils. Here, we investigate the performance of the PtRu nanoparticles deposited on the graphitic carbon nanocoils

* Corresponding author.

E-mail address: abefu@incar.csic.es (A.B. Fuenes).

in methanol electrooxidation. In order to evaluate their performance as electrocatalytic supports for carbon nanocoils, we compare the results obtained from these materials with those deduced from the employment of carbon black (Vulcan XC-72R).

2. Experimental

2.1. Synthesis and characterization of graphitic carbon nanostructures

As a first step in our synthetic scheme, carbon spherules were prepared by a hydrothermal method as reported by Wang et al. [13–15] by using as starting material various saccharides: (a) monosaccharide (D-glucose), (b) disaccharide (sucrose) or (c) polysaccharide (starch from potato). These saccharides were purchased from Aldrich. The preparation of graphitic carbon was carried out as follows. The saccharide (9 g glucose, 4.3 g starch or 9 g sucrose) was dissolved in water (50 mL) and the mixture was placed in a Teflon-lined autoclave and maintained at a temperature of: 240 °C for 30 min for glucose, 200 °C (5 h) for starch and 190 °C (4 h) for sucrose. The solid products obtained consist of carbon spherules, which were retrieved by centrifugation. This material was impregnated with a solution of nickel nitrate in ethanol (3 mmol Ni(g carbon)⁻¹) and then thermally treated under nitrogen up to 900 °C for 3 h. In order to eliminate the metal nanoparticles formed during the graphitization step, the carbonized material was treated with an acid (HCl, 20 wt%). Subsequently, in order to remove the amorphous carbon, the carbon sample was treated under reflux for 2 h with an oxidising mixture whose molar composition was H₂O:H₂SO₄:KMnO₄ = 1:0.01:0.003. Finally, the solid residue was separated by centrifugation, treated with HCl (20 wt%) to remove the MnO₂, rinsed with abundant water and oven-dried at 120 °C for 3 h. The obtained sample is almost exclusively made up of graphitic carbon. Depending on the saccharide used in the synthesis, the obtained graphitic carbons were denoted as: GC (glucose-based), SC (sucrose-based) and AC (starch-based).

Adsorption measurements of the graphitized materials were performed using a Micromeritics ASAP 2010 volumetric adsorption system. The BET surface area was deduced from the analysis of the isotherm in the relative pressure range of 0.04–0.20. X-ray diffraction (XRD) patterns were obtained on a Siemens D5000 instrument operating at 40 kV and 20 mA, using Cu K α radiation ($\lambda = 0.15406$ nm). Transmission electron micrographs (TEM) and selected area electron diffraction (SAED) patterns were taken on a JEOL (JEM-2000 FX) microscope operating at 200 kV. High resolution transmission electron micrographs (HRTEM) were taken on a JEOL (JEM-3000 F) microscope operating at 300 kV.

2.2. Preparation of Pt/Ru–C catalysts and electrochemical measurements

PtRu (50:50 at.%) nanoparticles purchased from Alfa Aesar Johnson Matthey were deposited on the carbon supports according to the suspension method described elsewhere [9]. The

catalyst was deposited in the same mass proportion for all carbon materials: GC (glucose-based), SC (sucrose-based), AC (starch-based) and XC 72R (Vulcan XC-72R) (90% carbon material–10% Pt/Ru). The final masses of all the samples were around 100 mg.

The electrochemical oxidation of methanol in an acidic medium (1 M CH₃OH + 1 M H₂SO₄) was investigated by the voltammetry method at a scan rate of 5 mV s⁻¹ using a three electrode cell. The counter electrode was platinum, whereas the reference electrode was mercury/mercurous sulphate (Hg/Hg₂SO₄) in 1 M H₂SO₄ (MMS). The working electrode had a geometrical area of 0.8 cm² and the electrode mass was 5 mg. Impedance spectroscopy measurements were performed with an amplitude of 10 mV in the frequency range of 10 kHz to 10 mHz at different potentials (from –0.25 V to 0.25 V versus MMS with step 0.125 V). All the results were obtained at 25 °C and at 60 °C. For all electrochemical measurements the potentiostat/galvanostat (AUTOLAB ECOCHEMIE BV-PGSTAT 30/FRA2) and ARBIN Instruments BT2000 were used.

3. Results and discussion

The hydrothermal treatment of saccharides at temperatures >160 °C produces via an emulsion polymerization mechanism carbon materials with a perfect spherical morphology and smooth surfaces [16]. As an example, Fig. 1a shows a typical SEM image of carbon spherules prepared by the hydrothermal treatment of starch at 200 °C. The carbon materials obtained by this technique contain abundant oxygen functional groups (–OH, –CO, –COOH, etc.) as deduced by FTIR spectroscopy (data not shown). This is important because these groups facilitate the impregnation and dispersion of the metallic salt (nickel nitrate) and also favour the formation of graphitic carbon [17]. The thermal treatment and removal of nickel nanoparticles give rise to a material composed of graphitic carbon nanostructures (formed around metal nanoparticles) embedded in a matrix of amorphous carbon. This amorphous carbon has a low crystallinity and a porosity made up of narrow pores. Such properties are undesirable in an electrocatalytic support. It is therefore necessary to selectively remove the amorphous carbon so that only the graphitic carbon is preserved. To achieve this objective, the carbon material is oxidised in liquid phase by KMnO₄ in the presence of H₂SO₄ under reflux [7]. Under these harsh oxidising conditions, the amorphous carbon is converted into soluble compounds whereas the graphitic carbon is retained almost unchanged. The insoluble fraction recovered after removal of the amorphous carbon is composed exclusively of carbon nanostructures as deduced by electron microscopy (SEM and TEM). Thus, Fig. 1b shows that the solid carbon residue obtained after the oxidation step consists of agglomerates made up of elongated nanoparticles of around 100 nm. TEM examination of these nanoparticles reveals that they are carbon nanocoils, as is clearly illustrated in Fig. 1c. These carbon nanocoils have diameters in the 80–120 nm range. They exhibit a high crystallinity as can be deduced from the SAED pattern (Fig. 1d) which shows diffraction rings that are consistent with the presence of

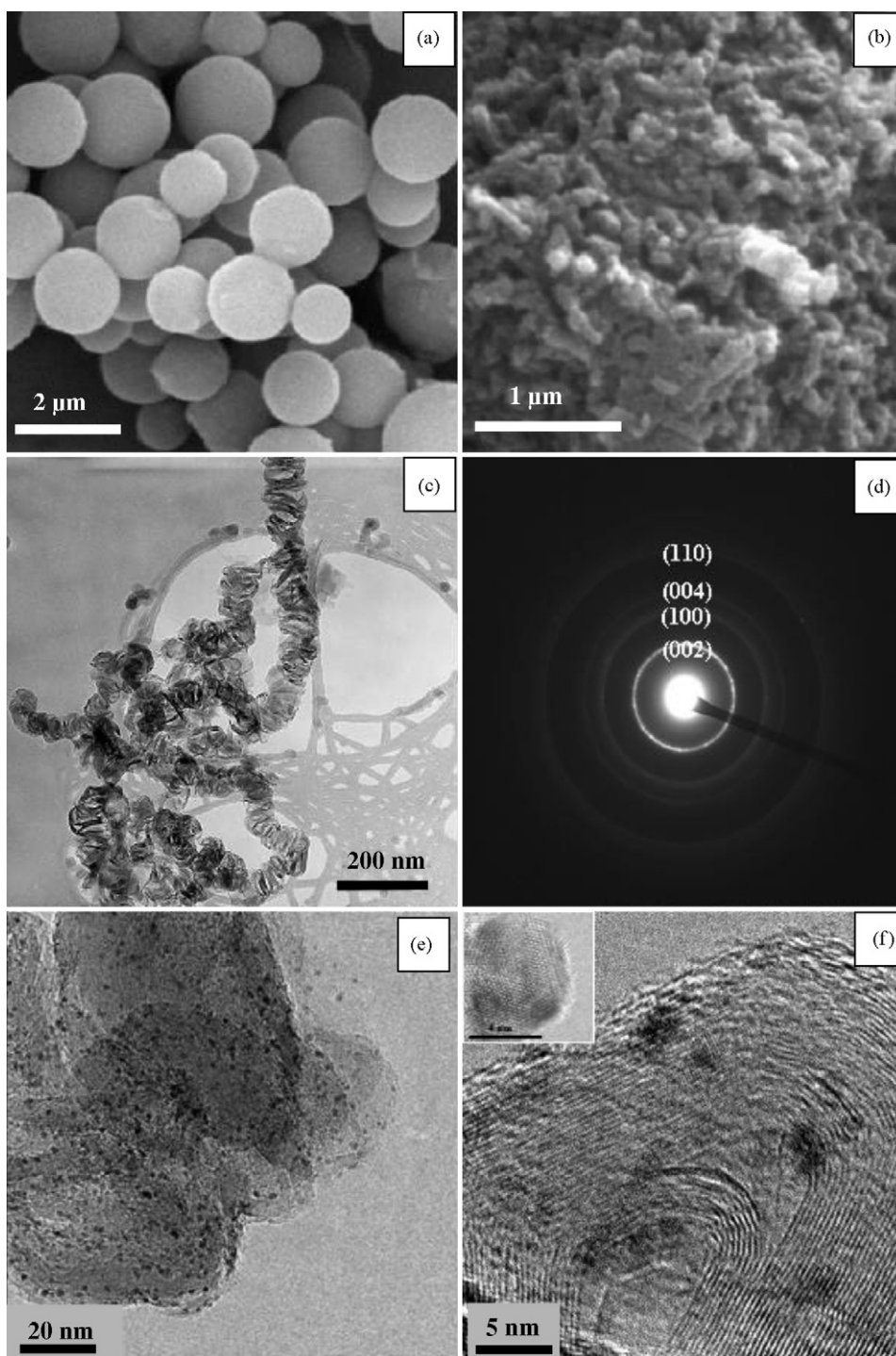


Fig. 1. SEM images of: (a) carbon microspheres obtained from starch through a hydrothermal route, (b) carbon nanostructures obtained from starch by catalytic graphitization and subsequent oxidation. TEM images of (c) carbon nanocoils obtained from sucrose, (d) selected area electron diffraction of carbon nanocoils obtained from sucrose, (e) PtRu nanoparticles (dark points) dispersed over the sucrose-based carbon support. (f) HRTEM image of graphitic carbon nanostructures (sucrose-based) with deposited catalyst nanoparticles (dark points) (inset, detail of PtRu nanoparticle showing the cubic structure).

a graphitic structure. The high crystallinity of the synthesised nanostructures is also evidenced from the HRTEM image shown in Fig. 1e which reveals well-defined (002) lattice fringes. The XRD diffraction pattern obtained for the sucrose-based carbon (Fig. 2) confirms that these nanostructures are well-graphitized as can be inferred from the very narrow peak at $2\theta = 26.1^\circ$ corre-

sponding to the (002) reflection (d_{002} -spacing of 0.340 nm and a crystallite size perpendicular to the basal plane L_c of 12 nm). These graphitic materials have a relatively large BET surface area of around $150 \text{ m}^2 \text{ g}^{-1}$. In Fig. 2b is represented the nitrogen sorption isotherm for the glucose-based nanocoils. It exhibits a large adsorption uptake for relative pressures >0.9 , which is

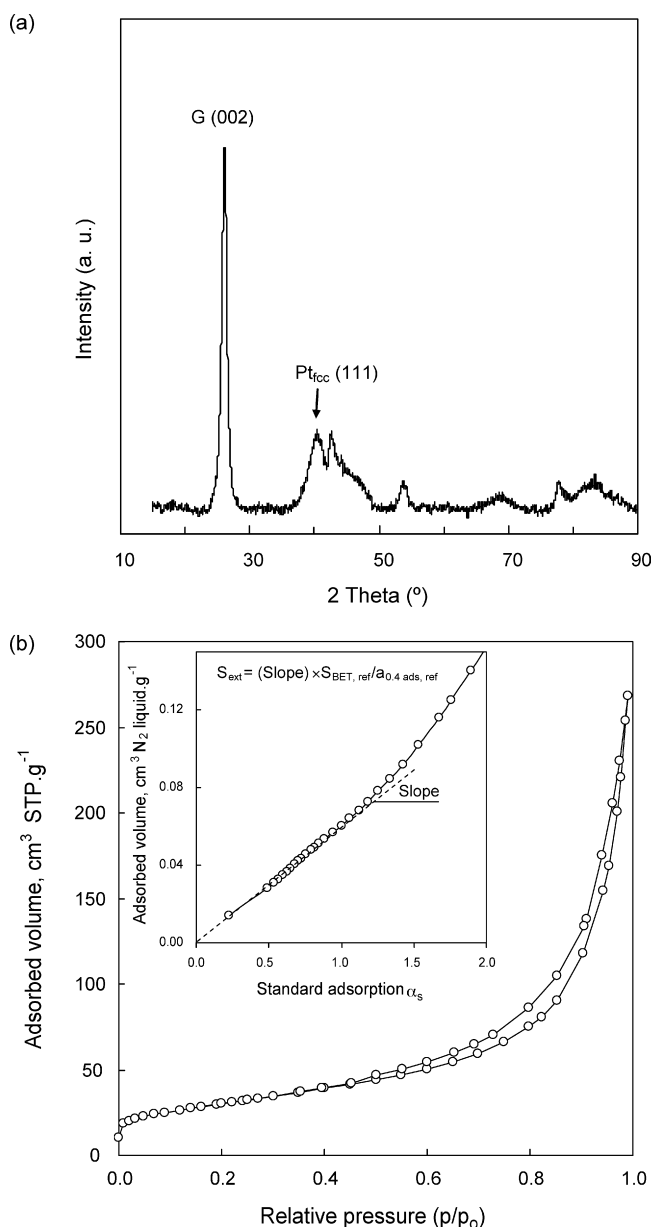


Fig. 2. (a) XRD pattern of the carbon nanocoils (sucrose-based) supporting the catalyst nanoparticles (PtRu) and (b) nitrogen adsorption isotherm of the glucose-based carbon nanocoils. Inset in (b): α_s plot obtained for the isotherm. In this figure is illustrated the method employed for the calculation of the external surface area. $S_{BET,ref}$ is the BET surface area of material used as reference and $a_{0.4ads,ref}$ is the amount of nitrogen (cm³ N₂ liquid g⁻¹) adsorbed by the reference solid at a relative pressure of 0.4. For details see [22].

typical for nanosized materials that do not contain framework-confined pores. This is coherent with the morphology observed by TEM inspection for the carbon nanocoils (see Fig. 1c). The α_s -plot analysis of the N₂ adsorption branch (Fig. 2a, inset) reveals that this material does not contain micropores. Moreover, the external surface area calculated from the α_s -plot method as indicated in Fig. 2b (inset) (~ 140 m² g⁻¹) match to the BET surface area (~ 150 m² g⁻¹), which shows that this material does not contain framework-confined mesopores. The rest of the saccharide-based nanocoils have similar textural properties. These results indicate that the surface area of these materials con-

sists of the external surface area, which implies the mass transfer resistances of reactants/products involved in the electrooxidation of methanol are minimized. The electrical conductivity of these samples was measured at a pressure load of ~ 7 MPa and it was found that they have values in the 3–5 S cm⁻¹ range (the EC for Vulcan XC-72R at 7 MPa is ~ 8 S cm⁻¹).

The TEM image of the supported PtRu nanoparticles shows that they are highly dispersed over the carbon nanocoils (Fig. 1e). These PtRu nanoparticles have an average particle size in the 3–4 nm range (i.e. 3 nm, 3 nm and 4 nm for the GC, SC and AC supports, respectively) as estimated by means of the Scherrer equation applied to the Pt_{fcc}(1 1 1) XRD peak (Fig. 2). These values are in a good agreement with the results deduced from the HRTEM images (Fig. 1f). The high crystallinity of the deposited PtRu nanoparticles is evidenced by the HRTEM images (see Fig. 1f, inset).

The performance of the carbon nanocoils supporting the PtRu catalytic nanoparticles for methanol electrooxidation was examined by means of cyclic voltammetry experiments. Fig. 3a shows the curves obtained for the AC sample and for the reference material (Vulcan XC-72R) at two different working temperatures, 25 °C and 60 °C. The highest values for the current density

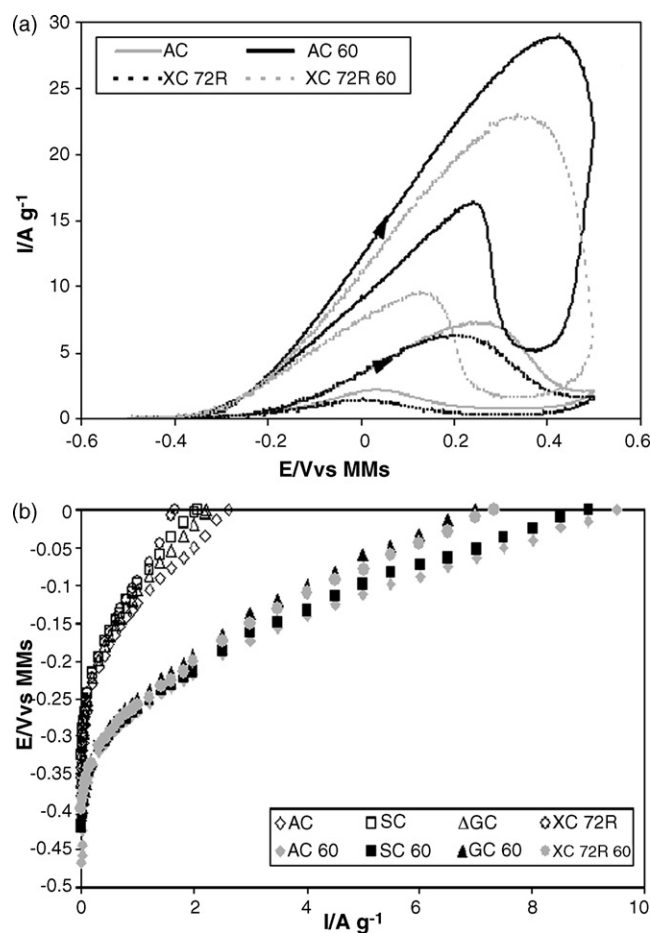
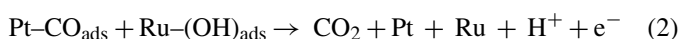
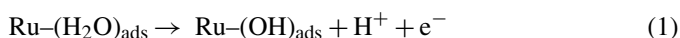


Fig. 3. (a) Cyclic voltammetry characteristics (5 mV s⁻¹) for the oxidation of methanol on Pt–Ru particles deposited on AC (starch-based) and XC 72R (Vulcan XC-72R) at 25 °C and at 60 °C. (b) Polarization characteristics for methanol oxidation at 25 °C and at 60 °C for different carbon materials.

are $\sim 6.7 \text{ A g}^{-1}$ at 25°C and $\sim 29 \text{ A g}^{-1}$ at 60°C . These data show that the change in working temperature from 25°C to 60°C dramatically increases (ca. by four times) the response of the current. The results shown in Fig. 3a also illustrate that at both temperatures, the AC–PtRu electrocatalyst shows a higher methanol oxidation current density compared to the reference material (Vulcan XC-72R). Significantly, although the Vulcan XC-72R has a greater BET surface area ($\sim 240 \text{ m}^2 \text{ g}^{-1}$) and a higher electrical conductivity (8 S cm^{-1}) compared to the AC sample ($160 \text{ m}^2 \text{ g}^{-1}$ and 3 S cm^{-1} , respectively), the measured current density is around 20% smaller. Similar results were obtained for the other saccharide-based carbon nanocoils. In our opinion this behaviour is due to the fact that the unique structural characteristics of carbon nanocoils here synthesised favour the mass transfer of reactants/products. In contrast, the Vulcan XC-72R contains a high fraction of micropores $< 2 \text{ nm}$ [18] which induce a poor PtRu utilization due to the resistance to the diffusion of methanol and products generated during electrooxidation process. This result is in agreement with those recently reported by Wu et al. [19], which showed that the Pt supported over carbon nanotubes exhibits better catalytic performance towards methanol oxidation compared to Pt/Vulcan XC-72R. In opinion of these authors, this result is because the carbon nanotubes possess a wider porosity compared to the carbon black that contains a high number of micropores, which are difficult to access by solvated ions. Similarly, Hyeon et al. [8] also suggested that the unique pore characteristics of the graphitic carbon nanostructures (synthesised by carbonization of a polymeric gel), which favour the diffusion of methanol and the removal of

the by-products, are responsible for the high electrocatalytic activity.

By analysing the change in current density with the applied potential it is possible to evaluate fuel cell performance. With this purpose we measured the polarization curves at 25°C and 60°C , for the different samples supporting the PtRu nanoparticles (Fig. 3b). The saccharide-based carbons exhibit, at both working temperatures, an excellent performance, which is superior to that of Vulcan XC-72R. The kinetics of methanol oxidation was studied by means of electrochemical impedance spectroscopy (EIS). Fig. 4 shows the EIS measurements obtained at 25°C (Fig. 4a) and at 60°C (Fig. 4b) for the AC sample at different potentials ranging from -250 mV to $+250 \text{ mV}$ versus MMS. The semicircles observed at high frequencies correspond to the electron transfer limited processes. It is known, that the mechanism of the methanol electrooxidation involves several reactions. Two of them depend on potential [20]:



As potential increases the diameter of semicircle decreases, indicating that the charge transfer resistance gets smaller. The smallest value of R reflects the optimum conditions for methanol oxidation. In other hand, when the potential reaches a limit value (0 V versus MMS), the rates of adsorption and oxidation of the methanol molecules became slower due to the coverage of the active sites of catalyst by the (OH) species [21]. In consequence, the semicircles are became larger (see Fig. 4a and b), which

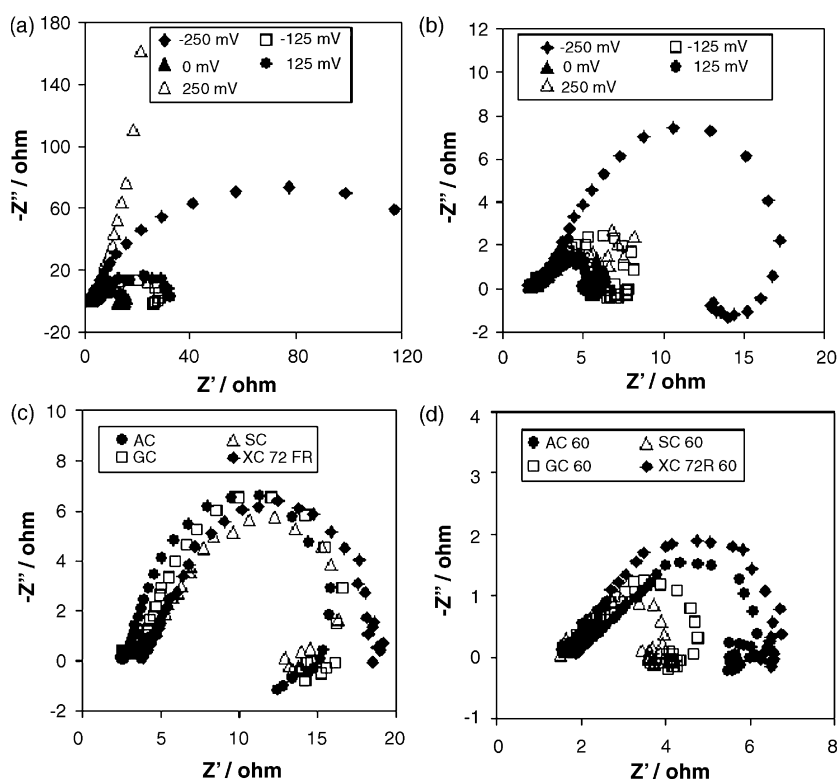


Fig. 4. Impedance spectroscopy plots for methanol electrooxidation: (a) for the AC sample at 25°C at different potentials; (b) for the AC sample at 60°C at different potentials; (c) for all the samples at 0 V (vs. MMS) and at 25°C ; (d) for all samples at 0 V (vs. MMS) and at 60°C .

reveals that the reaction rate of methanol electrooxidation is slower.

The comparison of the results shown in Fig. 4a and b reveals that an increase in working temperature from 25 °C to 60 °C leads to a notable improvement in the efficiency of methanol oxidation. This is a consequence of a reduction in the blockage of the surface of the electrocatalyst as the temperature increases. Fig. 4c and d provides a comparison of the EIS measurements obtained for all the samples at a constant selected potential (0 V versus MMS) and at the working temperatures of 25 °C (Fig. 4c) and 60 °C (Fig. 4d). The results obtained at 25 °C (Fig. 4c) indicate that samples exhibit a similar behaviour, the R values being in the 5.6–6.5 Ω range. In contrast, at a temperature of 60 °C (Fig. 4d) the GC and SC supports exhibit a better performance than the AC and Vulcan XC-72R samples. More specifically, the smallest resistance was found for the SC sample ($\sim 0.8 \Omega$).

4. Conclusions

In summary, highly graphitic carbon nanocoils were synthesised by the heat treatment (900 °C) of Ni impregnated carbon spherules obtained by the hydrothermal processing of saccharides (sucrose, glucose and starch). These carbon nanostructures have a high crystallinity with a d_{002} -spacing of 0.340 nm and a crystallite size perpendicular to the basal plane L_c of 12 nm. They exhibit a good electrical conductivity and a very open and accessible structure with a BET surface area of around 150 m² g⁻¹, which can be identified with the external surface area. These nanostructures are good supports for PtRu nanoparticles, which are widely dispersed over this material. This investigation of carbon nanocoils that support PtRu nanoparticles as electrocatalysts for the electrooxidation of methanol shows that this catalytic system exhibits an activity greater than that measured in the case of a conventional support (Vulcan XC-72R). We believe that this high electrocatalytic activity is a consequence of the fact that these carbon nanocoils display a good combination of electrical conductivity, derived from their graphitic structure with a large and widely accessible surface area that allows the diffusional resistances to be minimized. The fact that these electrocatalytic supports can be obtained from cheap and easily available precursors (saccharides) offers a novel low-cost route for preparing such materials on a large scale.

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