Nanocellulose-based carbon prepared by hydrothermal carbonization as support for PtRu nanoparticles for methanol electro-oxidation

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Introduction

Fuel cells employing alcohols as a fuel have been considered a promising power sources for portable applications. Methanol has been considered the most promising alcohol and the best results have been reached using carbon-supported PtRu nanoparticles (PtRu/C electrocatalyst), whose activity is strongly dependent on the method of preparation and the carbon support used [1]. Studies have been shown that the use of different carbon supports like nanotubes, mesoporous carbons and others nanostructured carbons could improve the performance of PtRu/C electrocatalysts for methanol electro-oxidation. Lately, the hydrothermal carbonization of saccharides at low temperatures (< 250 ºC) has provided carbonaceous materials with interesting morphologies and porosity [1]. In this work, nanocellulose-based carbon was prepared by hydrothermal carbonization and thermal treatment and it was used as support for PtRu nanoparticles for methanol electro-oxidation.

Experimental

Cellulose from residual textile fibers was used to prepare nanocellulose by acid hydrolysis [2]. Cellulose-based and nanocellulose-based carbons were prepared by hydrothermal carbonization in a Teflon-lined stainless steel autoclave at 200 ºC for 48 h [1]. The obtained carbonaceous materials were further treated under argon atmosphere at 900 ºC for 3 h. PtRu/C electrocatalysts (20 wt% metal loading and Pt:Ru atomic ratio of 50:50) were prepared by an alcohol-reduction process [3]. The X-ray diffraction analyses were performed using a Rigaku diffractometer model Miniflex II using Cu Kα radiation source. Scanning electron microscopy (SEM) was performed using a JEOL JMS-6701F electron microscope and transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV.

Results and Discussion

Cellulose and nanocelulose were initially subjected to hydrothermal carbonization at 200 ° C which is able to generate carbonaceous materials. In a next step, the carbonaceous materials were treated at 900^{o}C to improve their electrical conductivities [1]. X-ray diffractograms of the resulting carbon materials and the PtRu/C electrocatalysts are shown in Figure 1a. X-ray diffractograms of the carbon-based materials showed three broad peaks at about 2Θ = 10^{o}, 20^{o} e 45^{o} that are characteristic of amorphous carbon [1]. The resulting PtRu/C electrocatalysts besides the carbon peaks it was observed four peaks at about 2θ = 40º, 47º, 67º and 82º characteristic of the face-centered cubic (fcc) of Pt and Pt alloys[1]. The current-times curves for methanol electro-oxidation (Fig. 1b) showed that PtRu/nanocellulose-based carbon showed superior activity than PtRu/cellulose-based carbon and the commercial PtRu/C BASF.

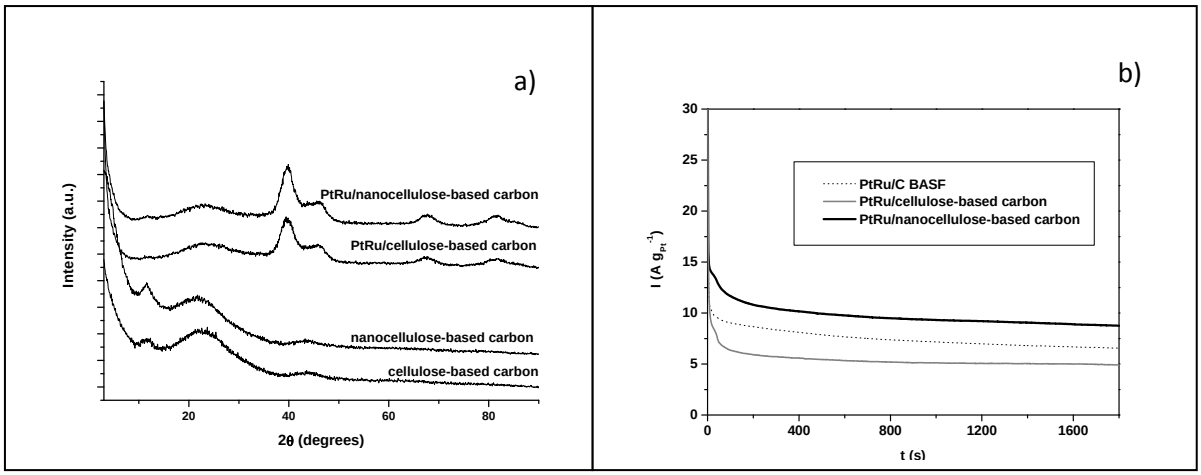

Figure 1: ***a)****X-ray diffratograms and* ***b)****current-time curves of the PtRu/C electrocatalysts in 1.0 mol* L^{-1} *in 0.5 mol* L^{-1} H_2SO_4 *at 0.5 V vs. RHE*

SEM and TEM micrographs of the obtained materials are shown in Figure 2a-d.

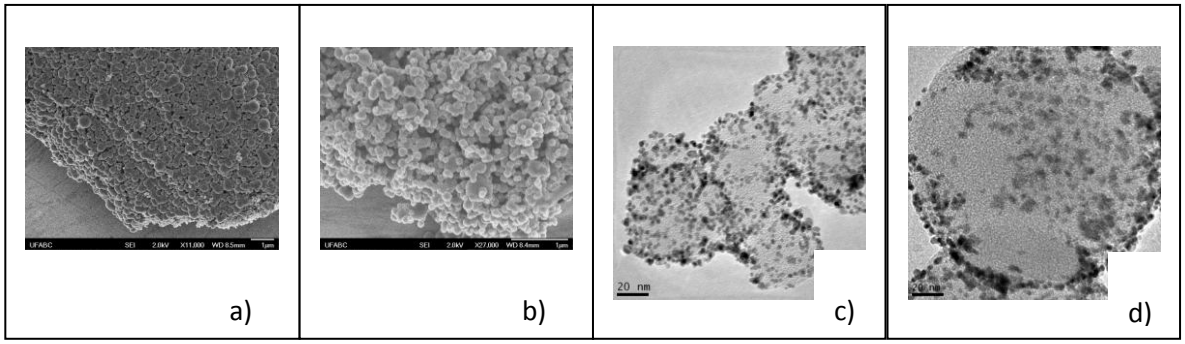

Figure 2: SEM micrographs (bar 1 µm) ***a)****cellulose-based carbon and* ***b)****nanocellulose-based carbon and TEM micrographs (bar 20 nm)* ***c)*** *PtRu/cellulose-based carbon and* ***d)****PtRu/nanocellulose-based carbon*

SEM micrographs showed that the cellulose-based and nanocellulose-based carbons have a morphology of spherical agglomerates, however nanocellulose has a high apparent porosity between the spheres. TEM micrographs showed the metal nanoparticles (2-5nm range) with a good distribution on the carbon supports.

Conclusions

Nanocellulose-based carbon prepared by hydrothermal carbonization and thermal treatment could be used as support for PtRu nanoparticles leading to active electrocatalysts for methanol electro-oxidation. The superior activity of nanocellulose-based carbon as support could be attributed to the increased surface area and/or pore volume that could contribute with the access of the reagents minimizing the diffusional resistance, however, it was necessary to characterize the materials using BET analysis.

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