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ELECTROSPINNING PAN/$PdCl_2$ NANOFIBER – THE INFLUENCE OF THE PREPARATION METHOD

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***Abstract* – Adsorbent and catalytic materials has received attention, especially if obtained as nanofibers. Polyacrylonitrile (PAN) has allowed the obtaining of carbon nanofibers from the electrospinning process followed by a thermal treatment. Pd has the capability of storage/react several compounds, such as hydrogen. Therefore, the aim of this work was obtaining in a single step electrospun nanofibers decorated with Pd. Four different preparation methods were evaluated and, mainly due to the ability of Pd atom to form a complex with dimethylformamide (DMF). FTIRS and XPS analysis indicate that Pd atom remains on fibers, even after sample heating. These fibers are uniform and scanning electron microscopy does not show cluster formation. A preliminary model explaining these data was proposed.**

Keywords: **nanofibers, Pd, H_2 storage, electrospinning**

I. INTRODUCTION

Nowadays, the search for materials that can be applied in the hydrogen storage has received much attention. In order to storage it such materials must be able to adsorb and desorb hydrogen molecules efficiently [1,2,3].
As adsorption depends on surface area, nanofibers are an excellent option and have attracted much attention from scientific community, due their characteristics such as high surface to volume ratio and easiness of producing [4,5]. On nanofibers manufacturing process, electrospinning stands out by means of low-cost setups. Moreover, electrospinning allows obtaining nanofibers from several different polymeric solutions and/or mixtures as long as the adequate solution characteristics, such as viscosity, are settled.
Polyacrylonitrile (PAN) solutions normally presents such features and has been extensively studied in the last decade; furthermore, with PAN is possible to easily obtain carbon nanofibers from an electrospinning process followed by a thermal treatment in inert ambient [4,5].
Several different heavy metal compound can storage hydrogen, one of most efficient is palladium [3]. On the other hand, carbon fibers can be decorated with Pd by immersion in $PdCl_2$ chemical solutions. Some authors have reported to reach high capacities of hydrogen storage with such approach [3], however the weak bond of C-Pd can jeopardize the performance of this material [8].
Therefore, the aim of this work is the development of simple ways for obtaining PAN fibers with Pd ions incorporated. The approach consisted in development of solution where PAN and Pd ion are already mixed in order to favor the production in a single step of nanofibers that present Pd atom in a free form, i. e., adequate for hydrogen adsorption.

II. EXPERIMENTAL

Method
Solution preparation: Considering data present on the literature, i. e., Pd complexation with DMF [6] and the inclusion of this solvent in the PAN macrostructure during solubilization [7], several different preparation methods were tested, as shown on Table 1. Therefore, in Solution 1, the important driving force is the competition between PAN and Pd ion for DMF molecules. On the other hand, Solution 2 only Pd atoms will compete, not only for DMF but also tor PAN molecules. Solution 3 is the opposite, in this case the complexation of Pd atoms is privileged and PAN molecules will compete afterwards. Finally, the Solution 4 corresponds only to the mixing of two well developed samples, which means that weak interactions were expected. The solution 5 was prepared in the conventional way and was used as reference. All the solutions were 6% w/w PAN/DMF and 1% w/w $PdCl_2$/PAN, respectively.

TABLE 1
COMPOSITION OF THE SOLUTIONS

#	Solution	Description
1	(PAN+$PdCl_2$): DMF	PAN and the $PdCl_2$ dry powder are mixed before being stirred with the DMF during 12 h.
2	(PAN+DMF): $PdCl_2$	PAN is dissolved in the DMF and stirred during 12 h. Following, $PdCl_2$ is mixed until total dissolution
3	($PdCl_2$+DMF): PAN	$PdCl_2$ is dissolved in the DMF and stirred during 12 h. Following, PAN is added and the solution is mixed until the total dissolution
4	(PAN+DMF): ($PdCl_2$+DMF)	PAN is dissolved in DMF, $PdCl_2$ is dissolved in the DMF, and both solutions are stirred during 12 h. Following, the two resulting solutions are mixed and stirred until the total dissolution
5	Pure PAN	PAN is stirred with DMF until total dissolution

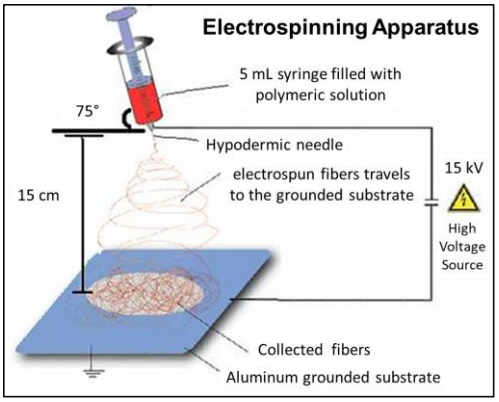


Figure 1: Schematics of the electrospinning apparatus.

Fibers Production: The fibers were electrospun using a conventional apparatus, as shown in Figure 1. The electrospinning process was conducted as follows: a 5 mL syringe with a hypodermic needle (22G1) was filled with the solution and 15 kV was applied to the needle that was kept 15 cm from the grounded base. The electrospinning process was conducted during 20 min.

Fiber characterization: The fibers morphology and diameters were evaluated by optical and scanning electron microscopy (SEM). The chemical bonds and their interaction between the polymer and the $PdCl_2$ were evaluated by Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIRS) and X Ray photoelectron spectroscopy (XPS).

Solution characterization: The viscosity was the solution property used to evaluate the macroscopic interaction between PAN and $PdCl_2$. To measure the absolute viscosity of the studied solutions the Brookfield Viscometer RV-DV II was used. As the volume of the solution was less than the regular spindle can measure, a small sample adapter was used in the measurements.

Materials

Polyacrylonitrile (PAN) and N,N Dimethylformamide (DMF) were purchased from Sigma-Aldrich and, $PdCl_2$, from Synth. To make the fiber characterization easier, it was collected over a (100) silicon substrate.

III. Results

It is known that during the electrospinning process, the fiber diameters are influenced by the solution conductivity, viscosity and by the process parameters [3]. So, it is expected that an increase in the viscosity may result in larger fiber diameter [4,5]. However, as observed in Figure 2, the diameter of the fibers decreases while the viscosity of the precursor solutions increases.

The palladium chloride can form ion complex with dimethylformide [6], indicating that the preparation method of the solution can influence the chemical interaction among DMF, PAN and $PdCl_2$. As described in Table I, the solutions 3 and 4 were prepared by dissolving $PdCl_2$ in DMF before the addition of the polymer as powder or as dissolved in the solvent, respectively. As can be observed in Figure 2, although the respective low solution viscosity these electrospun fibers have higher diameters. It is understood that the complex formation between PAN and $PdCl_2$ decreases the availability of free DMF molecules in the solution and influences the mechanism of polymer dissolution resulting in low viscosity. Otherwise, there is less Pd ions in the solution due to the complex formation and, possibly, during the electrospinning process, occurs less repulsion between the polymer molecules resulting in fiber with higher diameter.

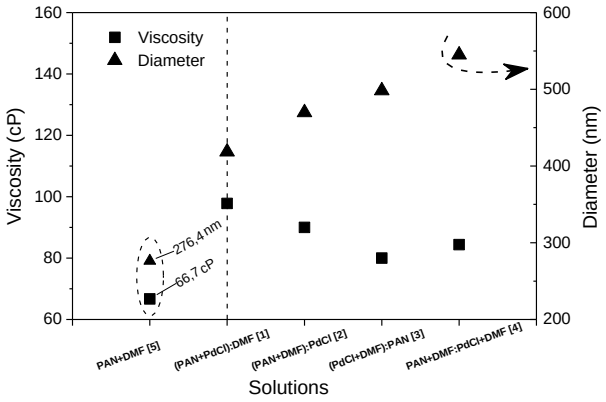


Figure 2: Variations in the viscosity of the studied PAN/$PdCl_2$ solutions and in the diameters of the fibers electrospun from these solutions.

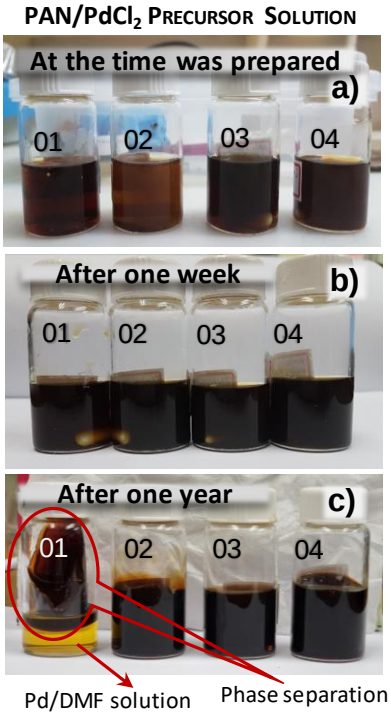


Figure 3: Variation in the solutions color evidencing the Pd complex formation; a) as prepared; b) after one week; c) after one year.

In solution 1, due to the proximity during solubilization, the interaction between PAN molecule and Pd atoms can be favored; therefore the "apparent" molecular weight of the polymer changes and viscosity increases. However, PAN-Pd interaction also corresponds to less complexation and the effective charge on the atom increases; thus repulsion is privileged and the fiber diameter decreases. Solution 2 is an intermediary situation

between solution 1 and 5, Pd atoms probably are not completely complexed when interact with PAN molecules whereas this polymeric structure is already involved by DMF molecules.

PAN/DMF solutions are transparent and light yellow. However, as can be seen in Figure 3, PAN/$PdCl_2$ solutions are dark brown indicating that Pd complexation occurred. Furthermore, solution ageing for over one year shows different behavior for each solution. Whereas for Solutions 3 and 4 a homogeneous dark color liquid material remains, in solution 1 occurs phase separation with the formation of a dark solid material and remained solution with light yellow color that resembles PAN/DMF solutions and Solution 2 presents some solid material dispersed in the liquid. The formation of this solid is an indicative of strong interaction between Pd atom and PAN molecule, which can lead to three-dimensional rigid structures during ageing.

FTIR analysis was used to unravel chemical environment and the respective species interactions. Films were produced by dropping small solution amount on a silicon wafer; thus, no chemical stress due to unexpected driving forces is presumed to be present on these samples. On the other hand, the electrospinning process and the consequent electrostatic fields can impose such different interactions among chemical species.

As expected, [9,10,11], for all fibers and films, FTIR spectra show the main bands of PAN molecule: amine groups (~ 3300 - 3500cm^{-1}), C≡N (~2240 cm^{-1}), C-H (~1450 cm^{-1}) and Figure 4a shows typical results. On fibers, the addition of $PdCl_2$ changes peak maximum and its shape on the 1000 – 1800 cm^{-1} region and details in Figure 4b) point out these features. Moreover, the spectra show different behavior, depending on solution manufacturing methods, to the bands 1658 cm^{-1} and 1608 cm^{-1}. Cipriani et al [11] indicates bands at 1660 cm^{-1} region as C=O species, due to the solvent presence (DMF molecules) and PAN film in the figure shows a single well resolved band on this region. The addition of $PdCl_2$ salt on this environment ([PAN+DMF]/$PdCl_2$) compete with the DMF C=O bond and a 1608-cm^{-1} band is partially revealed. With two different solutions being mixed ([PAN+$PdCl_2$]), both conditions (PAN and the salt involved by DMF molecules) are settled down before the mixture and the FTIR shows two resolved bands. Finally, the mixture of polymer and salt prior to the addition of the solvent favors a competition mechanism and the bands are found, but completed mixed (not resolved). The 1608 cm^{-1} is uncommon on PAN films or fibers.

Nonetheless, Huang et al [9] assigned this band as C=N species, presents in oxidized PAN fibers; this oxidized material can also crosslink with PAN molecule. Badii et al [10] found a similar band (C=N), also due to oxidation/cyclization, that was assigned at 1592 cm^{-1} and Cipriani et al [11] considers the range 1610-1575 cm^{-1} indicative of PAN degradation and formation of C=C and C=N. Since these films were not exposed to thermal treatment or oxidant reactants, a possible explanation to the appearance of this vibration band at 1608 cm^{-1} is the Pd atom connected to the nitrogen (N) in the DMF molecule, but this band is not found in [$Pd(DMF)_2Cl_2$] infrared spectrum [12], or a direct interaction with the nitrile species on PAN molecule, as explained later on the qualitatively model.

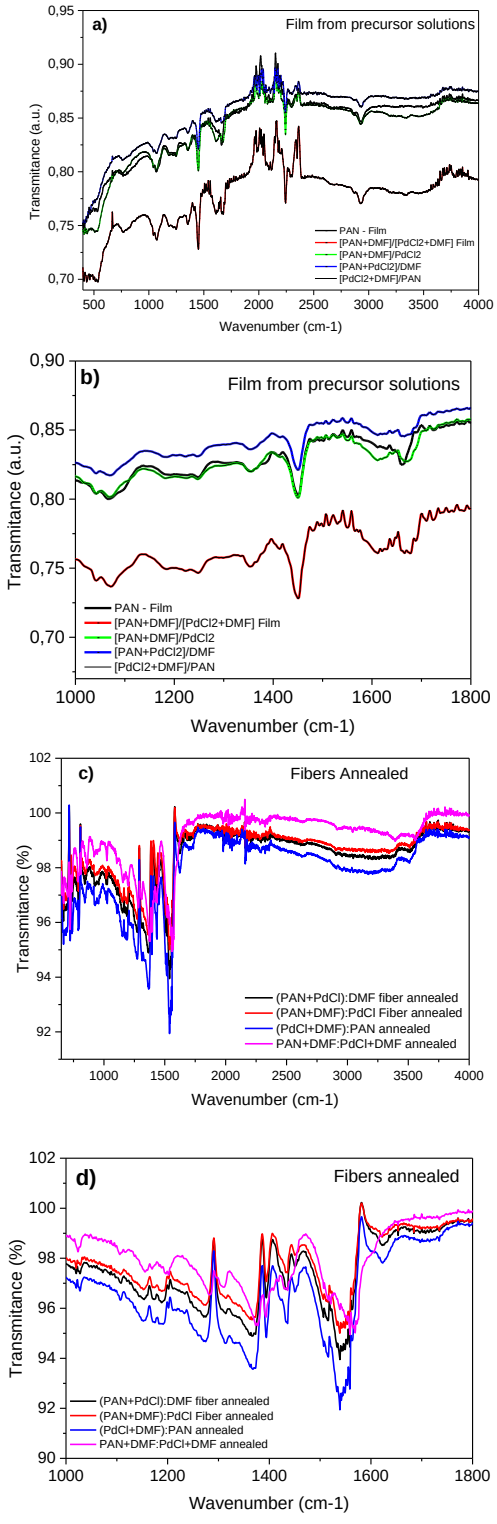


Figure 4: FTIRS analysis: (a) typical spectra for film, fiber and after thermal annealing, and details of (b) fibers and thermal annealing of (c) films and (d) fibers

Regarding [$Pd(DMF)_2Cl_2$] spectrum, a strong band is expected in 1629 cm^{-1} and, in fact, some fibers actually show vibration on this range, especially if Pd was solved by DMF before the addition of PAN molecules.

Thermal annealing (500ºC) of films (Figure 4c) and fibers (Figure 4d) leads to similar behavior, with prominent band on 1550 cm-1 due to cyclization and other CH bands. However, the decrement of 1660 cm^{-1}, assigned as solvent [11], is more evident on fibers, probably due to the high surface/area ratio. For both, films and fibers, the preservation of 1660 cm-1 seems to be linked with Pd complexation by DMF molecules. It is worth noting that Raman analysis did not find graphite.

Since FTIR analysis shows different chemical environment on fibers decorated with Pd, XPS analysis was carried out to evaluate Pd chemical shifts. Figure 5a shows typical results. The horizontal baseline on these spectra indicates that there is no contamination and C, Pd and O peaks are evident. Regarding PAN molecules, C peak, on Figure 5b, points out that there is no significant chemical shift. According to [13], XPS sign of Pd(0) is expected at ~335 eV, which does not occur on these spectra, and $3d_{5/2}$ sign of $PdCl_2$ complex range from 334.8 eV to 336.4 eV but reaches 338 eV for nanoparticles or films. Two different solutions clearly showed peaks on such range and Figure 5C presents such peaks. Furthermore, on these fibers C/Pd atomic weight ratio can achieve up to 0.0097 and 0.0018 for Solutions 2 and 4, respectively, i.e., an expressive amount. Thus, this data allows one to infer that the fibers electrospun from solutions 2 and 4 have freer Pd than the other solutions which probably means that competition for DMF molecules (Solution 1) as well as the complexation of the Pd ion (Solution 3) binds more strongly the Pd ion to the polymer structure.

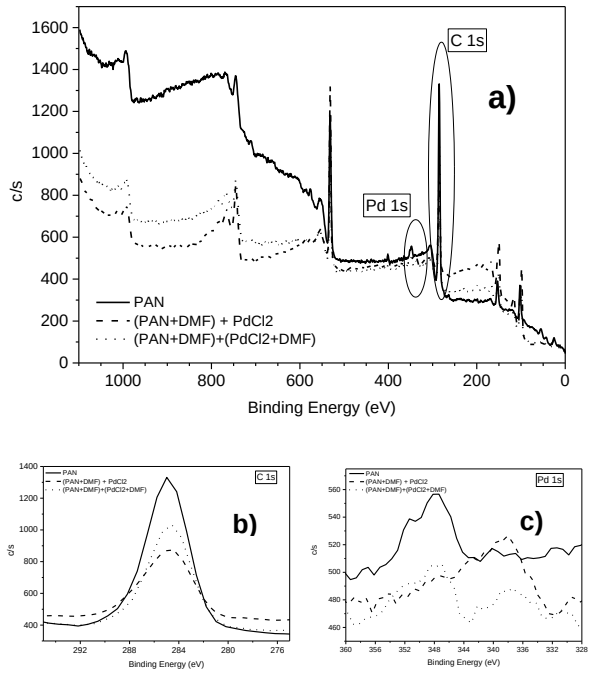


Figure 5: XPS analysis. (a) full spectra and details of (b) C and (c) Pd signals.

On the other hand, besides the variation in the electrospun fiber diameters and in the chemical environment on the films, there is no variation in their morphology that can be observed in the SEM images as shown in Figure 6. That seems to indicate that there is no clusterization of Pd atoms.

A preliminary model representing the chemical interaction between Pd and the solvent is proposed based on the previous discussions. Table 2 shows the most probably interaction of PAN/DMF/Pd for each solution, the main characteristics, fiber diameter, viscosity and chemical bonds.

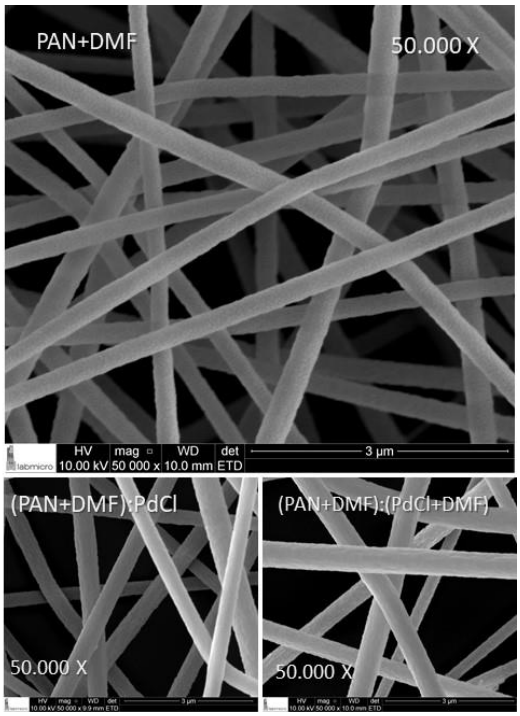


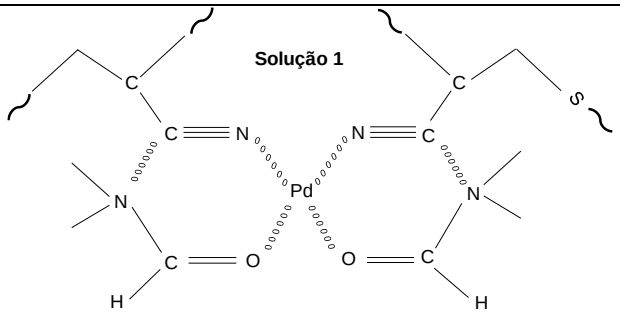
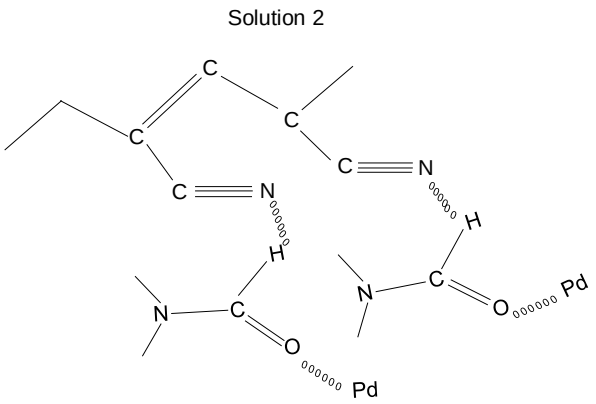
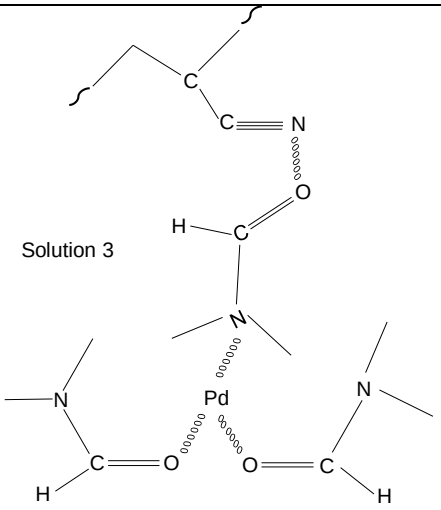
Figure 6: SEM images from the fibers electrospun of the solutions without Pd compared to the fibers electrospun from solutions 2 and 4 with Pd.

IV. CONCLUSIONS

This work presented the preliminary results of the influence on the preparation method of PAN/$PdCl_2$/DMF electrospinning precursor solutions. Due to Pd complexation with DMF, the preparation method influences the interaction between Pd and PAN. Depending on the preparation method the quantity of incorporated Pd on the fiber surface can vary, thus it is expected that the action of Pd as a catalytic or in the hydrogen storage is influenced. It can also be observed that although the solution viscosity decreases the diameters of electrospun fibers is larger than expected.

The FTIRS analysis confirms that Pd complexes with DMF by means of bonds to N; furthermore, thermal treatment does not remove significant bands regarding Pd complex. XPS pointed out Pd(II) incorporation and high C/Pd atomic ratio. Finally, the low-cost setup can be easily operate to produce in a single step nanofibers decorated with Pd. Thus, the results suggest that the fiber electrospun from solutions 2 and 4 are promising to produce fiber decorated with Pd after the thermal treatment.

TABLE 2
PROPOSED ELECTRONIC STRUCTURE AFTER THE CHEMICAL INTERACTIONS FOR EACH SOLUTION, THE MAIN CHARACTERISTICS, FIBER DIAMETER, VISCOSITY AND CHEMICAL ENVIRONMENT.

Solution	Main Characteristics	Visual observation	Fiber diameter	Viscosity	Chemical Environment	Most probably interaction PAN / DMF / Pd
1	Complexation competition	Phase separation	lowest	highest	Two not resolved bonds	
2	PAN/DMF strong interaction	Partial phase separation	medium	medium	Partially reveled bond Freer Pd	
3	Pd/DMF strong interaction	Homogeneous appearance	high	lowest		
4	PAN and Pd/DMF strong interaction	Homogeneous appearance	highest	low	Two reveled bonds, Freer Pd	Similar to solution 2 and solution 3

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