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PII: S0014-3057(19)30923-1

DOI: <https://doi.org/10.1016/j.eurpolymj.2019.07.048>

Reference: EPJ 9173

To appear in: *European Polymer Journal*

Received Date: 7 May 2019

Revised Date: 30 July 2019

Accepted Date: 31 July 2019

Please cite this article as: Quílez-Bermejo, J., Ghisolfi, A., Grau-Marín, D., San-Fabián, E., Morallón, E., Cazorla-Amorós, D., Post-synthetic efficient functionalization of polyaniline with phosphorus-containing groups. Effect of phosphorus on electrochemical properties, *European Polymer Journal* (2019), doi: <https://doi.org/10.1016/j.eurpolymj.2019.07.048>

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Post-synthetic efficient functionalization of polyaniline with phosphorus-containing groups. Effect of phosphorus on electrochemical properties.

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ABSTRACT: P-postmodified polyaniline was obtained by reacting phosphorus trichloride (PCl_3) and chlorodiphenylphosphine (PPh_2Cl) and polyaniline (PANI), under mild conditions. The reaction was found to be very selective, as only the imine groups were involved in the P-functionalization, and efficient as well, affording a P-loading of 3 at.% and 5 at.% for PPh_2Cl and PCl_3 , respectively. All the polymers were characterized by different techniques and the results were endorsed by theoretical calculations. Experimental and Density Functional Theory results proved that the reaction occurs through the imine groups and the phosphorus atoms, generating N-P bonds. The electrochemical properties of the N-P modified materials were evaluated and the catalytic activity towards oxygen reduction reaction was measured. It was found that a high concentration of phenyl groups from PPh_2Cl (about 3 at.%) affected negatively the activity of the catalyst since they prevented the access of the oxygen molecules to the catalytic active sites. However, a lower amount of $-\text{PPh}_2$ groups (1 at.%) or the use of PCl_3 avoided this hindrance and resulted in an improved catalytic activity with respect to pristine PANI.

Keywords

Polyaniline · Phosphorus · Post-modification · Electrochemical properties · modified polyaniline

1. Introduction

Over the past decades, the synthesis of new nanostructured functional materials with useful properties has garnered great attention in the scientific community. In particular, conducting polymers (CPs) have generated great interest from a fundamental and applied research points of view because of their promising electrical, electrochemical, optical and biocompatibility properties[1,2]. Polyaniline (PANI) was discovered in 1977 and, among CP, it is one of the most studied due to its high electrical conductivity, environmental and thermal stability and low-cost synthesis[1–3] that makes PANI a useful material in many different applications like biological sensing[4,5], corrosion protection[6,7], charge storage[8], catalysis[9–12], organic light emitting diodes[12] and as a precursor of N-doped carbon materials[13–15], among others.

One of the most investigated applications of PANI is as catalyst of different reactions, such as synthesis of 2-substituted benzothiazoles[9], 2-substituted benzimidazoles[10,11] and bio-esters transesterification and esterification reactions[12]. Indeed, polyaniline was also used in electrocatalytic reactions such as hexavalent chromium reduction[16] or CO₂ reduction[17].

An interesting feature of most CPs is that their properties can be tailored by derivatization of the pristine polymer or of the parent monomer. In particular, in the case of PANI, the possible modifications may be listed into three groups[1]: (i) homopolymerization of substituted anilines[18,19], (ii) copolymerization of aniline with substituted anilines[20–24] and (iii) functionalization of the final polymer (PANI post-modification)[25,26].

Interestingly, the rational post-modification of PANI is actually one of the most challenging targets of the scientific community and consists in improving the material performance by modifying, through specific chemical reactions, the nature of the pristine polymer and thus its properties[2]. This approach implies a controlled modification of the polymer backbone via chemical reactions on the post-synthesized polymer[2]. In this sense, the most common post-modification of the PANI is the de-doping process of the amine group, aimed to eliminate or replace the counterion resulting from the PANI synthesis, thus triggering different properties[27,28]. It has also been shown that there is a wide range of modifications

of polyaniline by nucleophilic or electrophilic reactions through acid-base chemistry, chemical modification by charge transfer groups, electrochemical modification, photo modification or, even, modification by charge injection[29–32]. All these post-modification of PANI have led to a wide range of applications; for instance, reversible capture of Hg[33] or Li-ion batteries[34].

Another type of post-modifications of polyaniline is the derivatization with different functional groups, such as thiols, amines, boranes, halogens and cyanides[1]. Moreover, some preliminary P-modification polyaniline studies have been carried out. Plesu et. al.[7] evaluated the influence of different organic phosphorus acids during the synthesis of PANI in order to improve its solubility in organic solvents. Furthermore, Eftekhari et. al.[35] used phosphoric acid as an electrolyte in the PANI polymerization. Although the polymerization was not successful, they demonstrated that the phosphoric acid promotes the formation of various phosphorus-containing functional groups on the aniline rings. However, to the best of our knowledge, no selective and efficient phosphorus-based chemical post-modification of PANI has been reported yet.

In this context, the objective of this work is to propose a novel and efficient route for the post-modification of PANI with phosphorus-containing groups, by selective chemical reactions between polyaniline and different phosphorus precursors, under mild conditions. The resulting functionalized materials have been characterized by X-ray photoelectronic spectroscopy (XPS), transmission electronic microscopy (TEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and evaluated as electrocatalysts towards oxygen reduction reaction (ORR) by rotating ring-disk electrode (RRDE). For this purpose, phosphorus trichloride (PCl_3) and chlorodiphenylphosphine (PPh_2Cl) were used as derivatizing agents. Theoretical calculations based on Density Functional Theory (DFT) were also performed with the aim of understanding the functionalization reactions. The combination of experimental and computational results led to a better understanding of the reactivity of PANI, and of the effects of the introduction of phosphorus-based functional groups on its electrochemical properties.

2. Experimental

2.1 Materials and reagents

Aniline was purchased from Sigma Aldrich and was distilled under reduced pressure prior to its use, in order to remove the impurities (e.g. aniline oligomers formed by oxidation during the storage). Phosphorus trichloride and chlorodiphenylphosphine were purchased from Sigma Aldrich. Triethylamine (NEt_3) was purchased from Fluka. Dichloromethane (CH_2Cl_2) was purchased from Panreac. Ammonium persulfate ($(\text{NH}_4)_2(\text{S}_2\text{O}_8)$), ammonium hydroxide (NH_4OH) and potassium hydroxide (KOH) were purchased from Sigma-Aldrich. Sulfuric acid (98%) was purchased from VWR-Chemicals Prolabo. All the solutions were prepared using ultrapure water (18 M Ω .cm from an Elga Labwater Purelab system). The N_2 (99.999%) and O_2 (99.995%) were provided by Air Liquide and were used without any further purification or treatment.

2.2 PANI synthesis

Polyaniline was prepared by chemical polymerization from a solution of 1 M HCl containing 0.067 M of aniline and ammonium persulfate in a stoichiometric ratio. The mixture was kept under stirring (500 rpm) during 3 h at 0 °C. After 3 h of polymerization, doped-polyaniline was treated with 1 M of NH_4OH for 24 h with the aim of obtaining the de-doped polyaniline. The synthesized PANI was washed several times with distilled water and dried at 120 °C overnight.

2.3 PANI modification

Three different post-modification routes have been used. The mildest synthesis of P-modified PANI consisted in the reaction between 1 g of PANI, 1.2 g of PPh_2Cl as derivatizing agent and 5 mL of NEt_3 , in 25 mL of CH_2Cl_2 , at 25 °C, during 24 h in an inert atmosphere.

The second route consisted in the use of the same phosphorus precursor, atmosphere and duration but in stronger conditions: without a base, at 120 °C and solvent free.

Lastly, in order to study the influence of the phosphorus precursor, the last route of PANI post-modification consisted in the use of an excess of PCl_3 that worked as both reactant and solvent at 60 °C during 24 h in an inert atmosphere.

After each functionalization, the materials were washed with isopropanol several times and dried in an oven at 100 °C. In the case of PCl_3 , the development of some gaseous HCl was observed during the washing step. This was due to the reaction of the P-Cl species with the alcohol that produces the corresponding, most stable, P- OC_3H_7 groups (XPS analysis evidences, see discussion below and Scheme 1) with simultaneous formation of HCl.

All post-modifications were carried out three times in order to check the reproducibility of the resultant materials.

Table 1 summarizes the different PANI post-modification routes and their nomenclature.

Table 1. Nomenclature and conditions of each phosphorus postmodification

Precursor	Temperature (°C)	Solvent	Nomenclature
PPh_2Cl	25	CH_2Cl_2	PANI_PPh2Cl_25
PPh_2Cl	120	No	PANI_PPh2Cl_120
PCl_3	60	No	PANI_PCl3

2.4 Physicochemical characterization

The samples were characterized by Transmission Electron Microscopy (TEM) coupled to EDX with JEOL JEM-2010 microscope operating at 200 kV with a spatial resolution of 0.24 nm. PANI and PANI samples after post-modification were subjected to thermogravimetric analysis in air atmosphere conditions using a thermobalance (SDT 2960 instrument, TA) in order to check the influence of the phosphorus functional groups in the gasification of the polyaniline, that is, in the reactivity towards oxygen.

The surface composition and oxidation states of the elements of the prepared materials were studied using XPS in a VG-Microtech Multilab 3000 spectrometer with an Al K α radiation source (1253.6 eV). The deconvolution of the N1s XPS spectra was done by least squares fitting using Gaussian-Lorentzian curves, the full-width at half-maximum (FWHM) was maintained between 1.4 and 1.8 eV, while for P 2p XPS spectra analysis was performed using Gaussian functions with Lorentzian component, considering the two doublet peaks (P 2p_{1/2} and P 2p_{3/2}) separated by 0.84 eV, an area ratio of 0.5 and the same FWHM, in all cases, below 1.9 eV. In all cases, a Shirley line was used for the background determination.

2.5 Electrochemical measurements

The electrochemical characterization of the materials was performed in an Autolab PGSTAT302 (Metrohm, Netherlands) potentiostat. A rotating ring-disk electrode (RRDE, Pine Research Instruments, USA) equipped with a glassy carbon disk (5.61 mm diameter) and an attached platinum ring was used as the working electrode. The carbon disk was modified with the samples using 120 μ L of a 1 mg·mL⁻¹ dispersion (0.02% Nafion[®] in ethanol) of each polymer, obtaining a catalyst loading of 0.5 mg·cm⁻². A catalyst loading of 0.1 mg/cm² was also used for comparison purposes. The electrochemical behaviour was studied by cyclic voltammetry (CV) in 0.1 M H₂SO₄ between 0.0 and 1.0 V vs RHE. These measurements were performed using graphite as a counter electrode and Ag/AgCl electrode as a reference. In this study, all potentials are referred to the reversible hydrogen electrode (RHE) in order to make easy the comparison with ORR tests. The samples were also characterized by electrochemical impedance spectroscopy (EIS). Impedance spectra were measured at 0.5 V vs RHE in the frequency range of 10 mHz to 100 kHz with an amplitude for the voltage signal of 10 mV in 0.1 M H₂SO₄ and 0.1 M KOH solutions using Ag/AgCl electrode as a reference. However, all potentials have been referred to the reversible hydrogen electrode (RHE).

The study of the electrocatalytic activity towards ORR was also performed in the rotating ring-disk electrode. A graphite rod was used as a counter electrode, while a reversible hydrogen electrode immersed in the same electrolyte without oxygen was used as a reference electrode. The electrocatalytic activity

towards ORR was studied by linear sweep voltammetry (LSV) in an O₂ saturated 0.1 M KOH and 0.1 M H₂SO₄ aqueous solutions, in a potential range comprised between 0.0 and 1.0 V (vs RHE), at different rotation rates, from 400 to 2025 rpm and at a scan rate of 5 mV·s⁻¹. The potential of the ring was held constant at 1.5 V (vs. RHE) during all measurements. The number of transferred electrons implied in the reaction was calculated from the hydrogen peroxide oxidation at the Pt ring electrode as follows:

$$n = \frac{4I_D}{I_D + I_R/N}$$

where I_R and I_D are the current measured at the ring and the disk, respectively, and N is the collection efficiency of the ring, which was experimentally determined to be 0.37.

2.6 Computational calculations

Density functional theory (DFT), applying the B3LYP/6-31G(d) method[36–39], through Gaussian 09 software[40] was used in this study. The self-consistent-field (SCF) energies of transitions were determined and are reported in kcal/mol (1 Hartree = 627.5095 kcal/mol).

The reaction energies have been calculated using the differences between the energies of the optimized structures of products and reagents.

$$Energy_{reaction} = \sum_n E(Products) - \sum_m E(Reagents)$$

being *n* and *m* the number of products and reactants, respectively, and *E* is related to the SCF energy of the compounds. The results show the free energies.

3. Results and discussion

3.1 Physicochemical characterization

The post-modification of polyaniline with phosphorus groups was successfully carried out by three different methodologies. Table 2 shows the final weight obtained by the different routes. This final/initial weight ratio is always higher than 100% because of the introduction of new functional groups in the

pristine material. Comparing the same precursor (i.e., PPh₂Cl), when stronger reaction conditions were applied, the obtained sample presented higher weight, what is consistent with a higher functionalization degree.

Table 2. Final weight of sample (%) and atomic percentage obtained by XPS of carbon, nitrogen, oxygen, phosphorus and chlorine

Sample	Final weight / %	C / %	N / %	O / %	P / %	Cl / %
PANI	-	83.1	11.7	3.5	-	1.7
PANI_PPh ₂ Cl_25	105	85.4	9.6	2.9	1.1	1.0
PANI_PPh ₂ Cl_120	131	84.6	6.6	4.0	3.7	1.1
PANI_PCl ₃	124	67.1	7.7	15.2	4.8	5.1

The morphology of the prepared materials was characterized by transmission electron microscopy (TEM). Figure 1 shows the TEM images for each modified-PANI and the pristine PANI. In general, polymer nanostructure is determined by the ratio between the intra- and interchain interactions, what can result in globular, laminar or fibre structures[41,42]. In our case, both PANI and post-modified PANI present laminar arrangement.

Figure 1. TEM images of (a-b) pristine PANI, (c-d) PANI_PPh2Cl_25, (e-f) PANI_PPh2Cl_120 and (g-h) PANI_PCl3 at different magnifications.

Figure 2. N1s spectra of pristine PANI, PANI_PPh2Cl_25, PANI_PPh2Cl_120 and PANI_PC13.

In order to get a better understanding of the nature of the phosphorus-modified PANI and the mechanism through which the modification process occurs, XPS analysis has been performed. Table 2 shows the atomic percentage obtained by XPS and the N1s and P2p spectra of all materials are shown in Figures 2 and 3.

Figure 3. P2p spectra of all phosphorus doped PANI samples

PANI and post-modified PANI present important differences in their elemental composition. The main difference, when PCl_3 is used as a phosphorus precursor, is the lower amount of carbon, what is indicative of a higher functionalization (Table 2). Moreover, the oxygen content increases from 3% in pristine PANI to 15% in PANI_ PCl_3 . This can be explained by the substitution of some chloride atoms in the P-Cl bonds, by isopropanol during the washing, which would lead to the formation of $\text{P-OC}_3\text{H}_7$ groups, together with HCl formation (Scheme 1). This is supported by the gas observed during the washing step. It is also important to highlight the modification level; the higher the temperature used during the functionalization, the higher the phosphorus content obtained using PPh_2Cl as a reagent (Table 2). On the other hand, the maximum phosphorus content is obtained by the modification with PCl_3 , even though the temperature used is lower than in PANI_ PPh_2Cl _120, what points out the relevance of the modification agent.

Figure 2 highlights some differences in the nature of nitrogen species present in the samples, depending on the phosphorus precursor and temperature used during the functionalization. Pristine PANI was also studied for comparison purposes. In this sense, PANI shows two peaks at 398.5 and 399.5 eV, associated with the presence of imines and amines, respectively[43–45]. The N1s spectra of PANI_PPh₂Cl_25 is similar to that of the pristine PANI, probably because of the low amount of phosphorus (1.1%, see Table 2), which did not produce significant changes in the N species of the polyaniline. Only a small peak appears at 399.1 eV, which could be related to N-P species[46,47], and a slight reduction of the imines contribution is produced (from 41 to 33%). On the other hand, when stronger experimental conditions were applied (sample PANI_PPh₂Cl_120), important chemical changes are observed in the N1s spectrum. Indeed, the peak associated with the amines (399.5 eV) is still present in the spectrum; however, the imines peak has completely disappeared, and the new signal associated with N-P is clearly observed in the N1s spectrum at 399.1 eV. This suggests the selective interaction of the imine species with the phosphorus precursor through the formation of N-P bonds. This selectivity towards the imine groups also explains the no need of a base during the functionalization reaction. Furthermore, a new peak appears at higher binding energies (400.6 eV), which could be related with the presence of positively-charged N produced as a consequence of the high temperature used in the modification procedure[48]. Then, the chloride anion, which has been eliminated by the nucleophilic attack between the nitrogen and the phosphorus atom, interacts with these positively-charged N groups. Scheme 2 illustrates this proposed route and Table 2 supports the presence of chlorine atoms in the polymer chain.

In the case of PANI_PCl₃ sample, the peak associated with the imine groups also disappears and the creation of the N-P species is observed at similar binding energies as well. In this case, the N-Cl peak is smaller than using PPh₂Cl as a precursor.

Figure 3 shows the P2p spectra from the XPS analysis of all materials. The first important difference among samples is that the reaction with PCl₃ produces a shift of the P2p spectrum of 1.4 eV to higher binding energies. Considering that both precursors produce X₂P-N type groups (where X = Ph, OC₃H₇),

this shift in the binding energy can be ascribed to the different nature of the phosphorus substituents (X in Scheme 3a).

The P2p spectra of PANI_PPh₂Cl_25 and PANI_PPh₂Cl_120 contain one peak at 132.5 eV, which can be related to Ph₂P-N species[49]. There are no qualitative differences between the two P2p profiles when different temperatures were applied for the modification with this precursor. In fact, the higher temperature of the functionalization with PPh₂Cl only increases the phosphorus loading (see Table 2). PPh₂Cl contains one chloride atom; then, only one nucleophilic substitution may occur, what explains the appearance of a unique peak in the P2p spectra for the materials obtained with this phosphorus precursor.

Scheme 1. Reaction of PANI_PCl₃ with 2-propanol during the washing step

Scheme 2. Proposed reaction between the phosphorus precursor (PCl₃) and pristine PANI.

Scheme 3. (a) Chemical structure of the two possible $X_2\text{-P-N}$ groups in modified PANI and (b) scheme of the cross-linking in PANI_PCl₃.

In the case of PANI_PCl₃, two peaks are observed in the P2p spectrum. The peak at 134.0 eV lies in the typical range of binding energies for P-O compounds[50,51] and can be associated with $(\text{C}_3\text{H}_7\text{O})_2\text{P-N}$ species. A smaller peak at 132.9 eV is also observed. This lower binding energy is characteristic of phosphorus atoms surrounded by a more electropositive environment. This suggests the presence of some inter and/or intrachain cross-linking, in which the phosphorus atom acts as a bridge between two imines moieties through the formation of $\text{N-P}(\text{OC}_3\text{H}_7)\text{-N}$ bonds (Scheme 3b).

XPS for Cl 2p has also been analysed and some differences are observed between the different polymers. Firstly, the presence of two peaks (doublets) at around 197.4 and 200.2 eV for PANI suggests the presence of chloride species and covalently bonded chlorine[52], respectively. These peaks are also observed in the P-modified polyaniline (PANI_PCl₃ and PANI_PPh₂Cl₁₂₀); however, in these modified polymers, the peak associated with covalently bonded chlorine increases in comparison to PANI. These features are in agreement with the scheme of reaction proposed in Scheme 2, where this increase might be related with a Michael addition to carbon atom[53][54]. Interestingly, the peak associated with chloride (red peak in Figure 4) has different binding energies depending on the sample. This points out and supports that the chlorine atoms are in a different chemical environment.

Figure 4. Cl₂p spectra of all phosphorus doped PANI samples

3.2 Computational calculations

In order to better understand the reaction products obtained and to discern whether the previously proposed routes are reasonable, Density Functional Theory (DFT) simulations have been carried out. The energy involved in all reactions previously proposed has been evaluated. For that purpose, B3LYP/6-31G(d) energies of the pristine PANI, phosphorus precursors and possible final products have been calculated, optimizing their structures, testing that all frequencies have positive values. Table 3 shows the free energies of each proposed reaction between the PANI and the phosphorus precursors.

By using PCl₃ as a precursor, the reaction could proceed through two different routes (generating Cl₂-P-N groups, or N-P(Cl)-N bridging bonds, see above). The free energy of the reaction where the phosphorus is bonded through a nitrogen atom has the lowest value, suggesting that the formation of the Cl₂-P-N species is the most probable mechanism. This justifies the higher amount of (C₃H₇O)₂P-N than N-P(OC₃H₇)-N species in the post-modified polyaniline.

Furthermore, during the discussion of the XPS analysis, it was highlighted the importance of the washing of the final material. In this regard, the energy evaluation of the reaction between the isopropanol with the modified PANI was also studied and confirmed a decrease in the total energy after the washing. Therefore, the DFT calculations support the interpretation of the P2p XPS for PANI_PCl₃, where the main peak is associated with the (C₃H₇O)₂-P-N bond, and the minor peak in the same spectrum (132.9 eV) is related to the N-P(OC₃H₇)-N species.

Table 3. B3LYP/6-31G(d) free energies of the possible reactions between polyaniline and PCl₃ or PPh₂Cl

PHOSPHORUS PRECURSOR	REACTION PRODUCT	ΔG° REACTION / kcal·mol ⁻¹	ΔG° WASHING / kcal·mol ⁻¹	ΔG° TOTAL / kcal·mol ⁻¹
PCl ₃	N-P-Cl ₂	23.51	-0.90	22.61
	N ₂ -P-Cl	57.55	-2.17	55.38
PPh ₂ Cl	N-P-Ph ₂	46.79	-	46.79

It is important to highlight the differences in the DFT energies using both phosphorus precursors. The reaction between PANI and PPh₂Cl always has higher energy than with PCl₃ and, therefore, the reaction to form PANI_PCl₃ is most favourable from a thermodynamic point of view. This is coherent with the higher phosphorus content obtained by PANI_PCl₃ and the need of using higher temperatures and high concentration of PPh₂Cl to achieve a significant degree of reaction.

3.3 Thermogravimetric analysis

Thermogravimetric analyses (TGA) were also performed with the aim of evaluating the reactivity of the polymers towards the gasification in air atmosphere. In this sense, all polymers were subjected to a heat treatment of 5°C/min until 900°C in air (100 mL/min).

Figure 5. Thermogravimetric analysis profile of all polymers in air atmosphere.

Figure 5 displays the TGA profiles, where it can be observed that the P-containing samples exhibit lower reactivity and, consequently, higher resistance towards gasification in air. This hindrance towards the oxidation by phosphorus groups has already been studied extensively in P-doped carbon materials and it has been related to the presence of C-O-P and C-P-O species[50,55,56]. However, Figure 5 also shows differences depending on the kind of phosphorus precursor used in such modifications. In fact, PANI_PCl₃ is the material with lowest reactivity and does not achieve the complete burn-off until temperatures near 700 °C, whereas PANI_PPh₂Cl₁₂₀ and PANI_PPh₂Cl₂₅ are completely gasified at 650 °C.

Not only the amount of phosphorus, but also the nature of the phosphorus precursor seems to have an effect on the reactivity of the materials.

3.4 Electrochemical results

Figure 6 shows the cyclic voltammograms of the post-modified PANI samples in 0.1 M H₂SO₄ aqueous solution for two loadings (i.e., 0.1 and 0.5 mg/cm²). There are important differences in the electrochemical behaviour of the samples. Pristine PANI presents different peaks, which are indicative of the redox

process associated with its changes in the oxidation state. The peak corresponding to the leucoemeraldine-emeraldine transition appears at around 0.30 V vs Ag/AgCl[57,58]. On the other hand, the second peak, which is associated with the emeraldine- pernigraniline, is not well defined (0.7 vs Ag/AgCl[59]). This is probably due to the used synthetic process. The peaks are observed for both mass loadings (Figure 6a and b) although they are broader for the highest loading used due to the increased thickness of the layer.

When the mass loading is 0.1 mg/cm², that is for a thin layer of sample, PANI_PCl₃ and PANI_PPh₂Cl₂₅ show voltammograms similar to that of pristine PANI but with lower current, whereas PANI_PPh₂Cl₁₂₀ displays a voltammogram without any significant peaks. This observation could be due to different reasons. The phenyl groups may produce an important steric hindrance, which would prevent the accessibility of the ions, making the redox reaction less probable. Furthermore, the phenyl groups increase the hydrophobicity of the polymer surface, thus, the interaction between the polymer and the electrolyte is less efficient as well. In fact, steric hindrance[60–62] and the hydrophobic character[63] are known to be responsible for poor electrochemical properties. These differences are much more important when a thicker sample layer is used, what emphasizes that the mass transfer within the polymer layer is very much affected by the functionalization.

Although a larger amount of phosphorus has been introduced in PANI_PCl₃ (P ≈ 5 at.%), the sample PANI_PPh₂Cl₁₂₀ (with P ≈ 4 at.%) shows the most important differences with the electrochemical behaviour of the pristine PANI. In this case, the main difference is that hydrophilic and less steric hindrance species (i.e., (C₃H₇O)₂P-N) are present in PANI_PCl₃ sample, what permits a more efficient electrochemical response in the aqueous electrolyte. Therefore, both the amount of phosphorus and the nature of the precursor play an important role in the electrochemical properties of the P-postmodified polyaniline.

Figure 6. Steady-state voltammograms for the different materials obtained by the post-modification of polyaniline with a loading of (a) $0.1 \text{ mg}\cdot\text{cm}^{-2}$ and (b) $0.5 \text{ mg}\cdot\text{cm}^{-2}$. $V = 5 \text{ mV}\cdot\text{s}^{-1}$, $0.1 \text{ M H}_2\text{SO}_4$

Figure 7 shows the Nyquist plots of the three post-modified PANI and the pristine PANI at 0.5 V vs RHE in 0.1 M KOH and $0.1 \text{ M H}_2\text{SO}_4$ solutions, measured for the highest loading of polymer (i.e., $0.5 \text{ mg}/\text{cm}^2$). In alkaline conditions, the plots are very similar for all the samples. All of them exhibit a similar intercept at high frequencies, which is determined by the electrolyte resistance. The slope in the medium-lower frequency region, that determines the Equivalent Distributed Resistance (EDR), are similar. The slope of the low frequency region is not vertical because of a distribution in macroscopic path lengths, for example due to a lack of uniformity in the active layer thickness[64]. Since at these conditions PANI and the modified polymers are not electroactive, the contribution from the charge transfer resistance is not observed.

In the Nyquist plots obtained in acidic electrolyte, the differences among samples are remarkable and reflect the differences observed in electroactivity that were described from the CV (see Figure 6 and discussion). There are important differences in the semicircles/arcs observed for the different materials. In the case of PANI the smallest semicircle is observed, what reflects the faster charge transfer occurring for this material, whereas the largest is found for sample PANI_PPh2Cl_25 in which the effect from the hydrophobic and large phenyl groups is evident. Interestingly, the sample PANI_PPh2Cl_120 with the highest content of phenyl groups do not show any evidence for charge transfer and its profile is similar to that obtained in alkaline conditions.

3.5 Electrocatalytic activity towards oxygen reduction reaction

The electrocatalytic activity towards oxygen reduction reaction (ORR) of all materials was studied in O₂-saturated 0.1 M KOH and 0.1 M H₂SO₄ solutions. Linear sweep voltammetry analysis was performed using RRDE at different rotation rates. The ORR can take place with a 2 electrons path to produce H₂O₂, through a 4 electrons route to produce H₂O or through a 2+2 electrons multi-steps path that results in the production of H₂O. The next equations summarize the reactions through which the ORR may occur.

All materials do not show electrocatalytic activity towards oxygen reduction reaction in 0.1 M H₂SO₄ (not included) between 0.0 and 1.0 V vs RHE; however, they have in alkaline medium. In this sense, Figure 8 compares the electrocatalytic behaviour in 0.1 M KOH solution of PANI and all materials obtained from the post-modification of the polymer. The behaviour of glassy carbon electrode has been added for comparison purposes. LSV curves of PANI_PCl₃ and PANI_PPh₂Cl₂₅ show an improvement in the catalytic activity towards oxygen reduction reaction in comparison with pristine PANI; however, PANI_PPh₂Cl₁₂₀ has a similar behaviour to the original polymer with a performance close to the glassy carbon electrode. The reason that can explain the lower catalytic activity of PANI_PPh₂Cl₁₂₀ could be strongly related to the already mentioned steric hindrance or hydrophobic character of the phenyl groups that impede the redox process. So, the new active sites created by the phosphorus functionalization are probably physically blocked by the high amount of -PPh₂ groups and only when the amount of phosphorus loading is lower (e.g. PANI_PPh₂Cl₂₅) or the phosphorus precursor does not contain such substituents (e.g. PANI_PCl₃) the P- active sites are accessible to the oxygen molecule.

Figure 7. Nyquist plot of all post-modified polyanilines and pristine polyaniline in 0.1 M KOH (left) and 0.1M H_2SO_4 (right).

Figure 8. Linear sweep voltammetry curves and number of transferred electrons for the prepared materials in O_2 saturated 0.1 M KOH at $5 \text{ mV} \cdot \text{s}^{-1}$ and 1600 rpm

These results suggest that the post-modifications, which maintain the redox properties of the pristine PANI, result in the highest activities towards ORR due to the higher catalytic activity promoted by the

N-P species, which have been proposed as efficient active sites towards oxygen reduction reaction in other materials[59].

Figure 8 also includes the number of transferred electrons during the oxygen reduction reaction. Pristine PANI shows a number of electrons close to 3, which means a yield of 50% towards hydrogen peroxide formation and 50 % towards water generation. However, PCl_3 based post-modified polyaniline produces new catalytic species, which favour the reaction through 2 electrons pathway. Despite a different phosphorus precursor is used, PANI_PPh₂Cl_25 also shows high selectivity towards hydrogen peroxide. Regarding PANI_PPh₂Cl_120, although it exhibits the same catalytic activity and number of transferred electrons-profile as pristine PANI, the number of electrons is also lower than PANI. This reflects that the active sites activity does not depend on the type of phosphorus precursor used during the functionalization, but it depends on the nature of the new generated N-P species.

All post-modifications of polyaniline with phosphorus groups make the catalysis of oxygen reduction favoured towards hydrogen peroxide generation. The hydrogen peroxide is a very useful product in the chemical industry. It is an environmentally friendly oxidizing agent that does not generate hazardous residues and, then, its production is also very important[65]. In this sense, the phosphorus post-synthetic modification of polyaniline makes this polymer more active and selective towards hydrogen peroxide formation.

4. Conclusions

Phosphorus functionalized PANI has been prepared by post-synthetic modification strategies involving the direct reaction of PANI and two phosphorus precursors, PCl_3 and PPh_2Cl in different experimental conditions. In this functionalization process, the imine groups in the PANI react selectively with PPh_2Cl precursor to form N- PPh_2 species and with PCl_3 to form terminal moieties N-P(OC_3H_7)₂ and cross-linked, bridging N-P(OC_3H_7)-N groups.

Electrochemical characterization allows us to conclude that the phenyl groups of PPh_2 - species prevent the electrolyte mobility because of their steric hindrance and their hydrophobic character. However, this

does not occur when PCl_3 is used since the reaction with isopropanol during the washing step forms N-P(OC_3H_7) species.

Such steric hindrance and hydrophobicity provided by phenyl groups also affect negatively the oxygen reduction reaction. Therefore, materials which present a higher content of -PPh₂ moieties (4 at.%) displayed poor catalytic activity, almost comparable to pristine PANI and bare glassy carbon. However, if the -PPh₂ concentration is lower (1 at.%) or the phosphorus precursor does not have phenyl groups (such as P(OC_3H_7)₂) the resulting catalytic activity is higher than the pristine PANI due to the presence of N-P species.

Furthermore, irrespective of the phosphorus precursor, the oxygen reduction reaction occurs through a 2 electrons pathway, where hydrogen peroxide is the main product, thus indicating that they are good candidates as catalysts for hydrogen peroxide production, in contrast with pristine polyaniline, which displays a lower activity and selectivity.

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ACKNOWLEDGMENT

(The authors thank MINECO, MICIUNIN and FEDER (RTI2018-095291-B-I00 and MAT2016-76595-R) for the financial support.

DATA AVAILABILITY

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations, but they can be requested to the corresponding author.

REFERENCES

- [1] M. Jaymand, Recent progress in chemical modification of polyaniline Dedicated to Professor Dr.

doi:10.1016/j.progpolymsci.2013.05.015.

- [2] C. Barbero, H.J. Salavagione, D.F. Acevedo, D.E. Grumelli, F. Garay, G.A. Planes, G.M. Morales, M.C. Miras, Novel synthetic methods to produce functionalized conducting polymers I. Polyanilines, *Electrochim. Acta.* 49 (2004) 3671–3686. doi:10.1016/j.electacta.2003.11.035.
- [3] A.A. Syed, M.K. Dinesan, Review: Polyaniline-A novel polymeric material, *Talanta.* 38 (1991) 815–837. doi:10.1016/0039-9140(91)80261-W.
- [4] P. Lin, F. Yan, Organic thin-film transistors for chemical and biological sensing, *Adv. Mater.* 24 (2012) 34–51. doi:10.1002/adma.201103334.
- [5] T. Ahuja, I.A. Mir, D. Kumar, Rajesh, Biomolecular immobilization on conducting polymers for biosensing applications, *Biomaterials.* 28 (2007) 791–805. doi:10.1016/j.biomaterials.2006.09.046.
- [6] W.K. Lu, R.L. Elsenbaumer, B. Wessling, Corrosion Protection of Mild-Steel by Coatings Containing Polyaniline, *Synth. Met.* 71 (1995) 2163–2166. doi:10.1016/0379-6779(94)03204-J.
- [7] N. Plesu, G. Ilia, A. Pascariu, G. Vlase, Preparation, degradation of polyaniline doped with organic phosphorus acids and corrosion essays of polyaniline-acrylic blends, *Synth. Met.* 156 (2006) 230–238. doi:10.1016/j.synthmet.2005.11.006.
- [8] A. Gabe, M.J. Mostazo-López, D. Salinas-Torres, E. Morallón, D. Cazorla-Amorós, Synthesis of conducting polymer/carbon material composites and their application in electrical energy storage, 2017. doi:10.1016/B978-0-08-100789-1.00008-3.
- [9] M. Abdollahi-alibeik, S. Poorirani, Perchloric Acid – Doped Polyaniline as an Efficient and Reusable Catalyst for the Synthesis of 2-Substituted Benzothiazoles, *Phosphorus , Sulfur , Silicon Relat. Elem.* (2009) 37–41.

- [10] M. Abdollahi-Alibeik, M. Moosavifard, FeCl₃-doped polyaniline nanoparticles as reusable heterogeneous catalyst for the synthesis of 2-substituted benzimidazoles, *Synth. Commun.* 40 (2010) 2686–2695. doi:10.1080/00397910903318658.
- [11] M. Abdollahi-Alibeik, M. Moosavifard, S. Poorirani, Synthesis of 2-substituted benzimidazoles in the presence of polyaniline nanoparticles doped with 12-tungstophosphoric acid as reusable heterogeneous catalyst, *Synth. React. Inorganic, Met. Nano-Metal Chem.* 43 (2013) 1365–1371. doi:10.1080/15533174.2012.761233.
- [12] A. Drelinkiewicz, Z. Kalembe-Jaje, E. Lalik, R. Kosydar, Organo-sulfonic acids doped polyaniline - Based solid acid catalysts for the formation of bio-esters in transesterification and esterification reactions, *Fuel*. 116 (2014) 760–771. doi:10.1016/j.fuel.2013.08.079.
- [13] G. Ćirić-Marjanović, I. Pašti, N. Gavrilov, A. Janošević, S. Mentus, Carbonised polyaniline and polypyrrole: towards advanced nitrogen-containing carbon materials, *Chem. Pap.* 67 (2013) 781–813. doi:10.2478/s11696-013-0312-1.
- [14] J. Quílez-Bermejo, E. Morallón, D. Cazorla-Amorós, Oxygen-reduction catalysis of N-doped carbons prepared: Via heat treatment of polyaniline at over 1100 °C, *Chem. Commun.* 54 (2018) 4441–4444. doi:10.1039/c8cc02105h.
- [15] J. Quílez-Bermejo, C. González-Gaitán, E. Morallón, D. Cazorla-Amorós, Effect of carbonization conditions of polyaniline on its catalytic activity towards ORR. Some insights about the nature of the active sites, *Carbon* 119 (2017) 62–71. doi:10.1016/j.carbon.2017.04.015.
- [16] Y. Yang, M.H. Diao, M.M. Gao, X.F. Sun, X.W. Liu, G.H. Zhang, Z. Qi, S.G. Wang, Facile preparation of graphene/polyaniline composite and its application for electrocatalysis hexavalent chromium reduction, *Electrochim. Acta.* 132 (2014) 496–503. doi:10.1016/j.electacta.2014.03.152.
- [17] F. Köleli, T. Röpke, C.H. Hamann, The reduction of CO₂ on polyaniline electrode in a membrane

- [18] H.J. Salavagione, J. Arias, P. Garcés, E. Morallón, C. Barbero, J.L. Vázquez, Spectroelectrochemical study of the oxidation of aminophenols on platinum electrode in acid medium, *J. Electroanal. Chem.* 565 (2004) 375–383. doi:10.1016/j.jelechem.2003.11.005.
- [19] M. Abidi, S. López-Bernabeu, F. Huerta, F. Montilla, S. Besbes-Hentati, E. Morallón, The chemical and electrochemical oxidative polymerization of 2-amino-4-tert-butylphenol, *Electrochim. Acta.* 212 (2016) 958–965. doi:10.1016/j.electacta.2016.07.060.
- [20] S. Dkhili, S. López-Bernabeu, C. Kadir, F. Huerta, F. Montilla, S. Besbes-Hentati, E. Morallon, An Electrochemical Study on the Copolymer Formed from Piperazine and Aniline Monomers, *Mater.* 2018, Vol. 11, Page 1012. 11 (2018) 1012. doi:10.3390/MA11061012.
- [21] S. Dkhili, S. López-Bernabeu, F. Huerta, F. Montilla, S. Besbes-Hentati, E. Morallón, A self-doped polyaniline derivative obtained by electrochemical copolymerization of aminoterephthalic acid and aniline, *Synth. Met.* 245 (2018) 61–66. doi:10.1016/j.synthmet.2018.08.005.
- [22] J. Arias-Pardilla, H.J. Salavagione, C. Barbero, E. Morallón, J.L. Vázquez, Study of the chemical copolymerization of 2-aminoterephthalic acid and aniline. Synthesis and copolymer properties, *Eur. Polym. J.* 42 (2006) 1521–1532. doi:10.1016/j.eurpolymj.2006.02.003.
- [23] C. Sanchís, H.J. Salavagione, J. Arias-Pardilla, E. Morallón, Tuning the electroactivity of conductive polymer at physiological pH, *Electrochim. Acta.* 52 (2007) 2978–2986. doi:10.1016/j.electacta.2006.09.031.
- [24] M. Abidi, S. López-Bernabeu, F. Huerta, F. Montilla, S. Besbes-Hentati, E. Morallón, Spectroelectrochemical study on the copolymerization of o-aminophenol and aminoterephthalic acid, *Eur. Polym. J.* 91 (2017) 386–395. doi:10.1016/j.eurpolymj.2017.04.024.
- [25] D. Yoo, J.J. Lee, C. Park, H.H. Choi, J.H. Kim, N-type organic thermoelectric materials based on polyaniline doped with the aprotic ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate, *RSC*

- [26] Y. Wang, J. Zhang, D. Sheng, C. Sun, Preparation and applications of perfluorinated ion doped polyaniline based solid-phase microextraction fiber, *J. Chromatogr. A*. 1217 (2010) 4523–4528. doi:10.1016/j.chroma.2010.04.075.
- [27] B.H. Kim, D.H. Park, J. Joo, S.G. Yu, S.H. Lee, Synthesis, characteristics, and field emission of doped and de-doped polypyrrole, polyaniline, poly(3,4-ethylenedioxythiophene) nanotubes and nanowires, *Synth. Met.* 150 (2005) 279–284. doi:10.1016/j.synthmet.2005.02.012.
- [28] C. Bian, A. Yu, De-doped polyaniline nanofibres with micropores for high-rate aqueous electrochemical capacitor, *Synth. Met.* 160 (2010) 1579–1583. doi:10.1016/j.synthmet.2010.04.019.
- [29] A. Malinauskas, Self-doped polyanilines, *J. Power Sources*. 126 (2004) 214–220. doi:10.1016/j.jpowsour.2003.08.008.
- [30] G. Venugopal, X. Quan, G.E. Johnson, F.M. Houlihan, E. Chin, O. Nalamasu, Photoinduced Doping and Photolithography of Methyl-Substituted Polyaniline, *Chem. Mater.* 7 (1995) 271–276. doi:10.1021/cm00050a007.
- [31] Y. Qin, Alginate fibers: an overview of the production processes and applications in wound management, *Polym. Int.* 57 (2008) 171–180. doi:10.1002/pi.
- [32] P. Kovacic, J.W. Timberlake, Doping of Polyaniline: Mechanism, Captodative Effect, Biochemical Relationships, and Chronology, *Polym. J.* 20 (1988) 819–822. doi:10.1295/polymj.20.819.
- [33] Y. Kim, Z. Lin, I. Jeon, T. Van Voorhis, T.M. Swager, Polyaniline Nanofiber Electrodes for Reversible Capture and Release of Mercury(II) from Water, *J. Am. Chem. Soc.* 140 (2018) 14413–14420. doi:10.1021/jacs.8b09119.
- [34] D. Wang, X. Wang, X. Yang, R. Yu, L. Ge, H. Shu, Polyaniline modification and performance

enhancement of lithium-rich cathode material based on layered-spinel hybrid structure, *J. Power Sources*. 293 (2015) 89–94. doi:10.1016/j.jpowsour.2015.05.058.

- [35] S. Matsumura, A.R. Hlil, C. Lepiller, J. Gaudet, D. Guay, Z. Shi, S. Holdcroft, A.S. Hay, Ionomers for proton exchange membrane fuel cells with sulfonic acid groups on the end-groups: Novel branched poly(ether-ketone)s, *Am. Chem. Soc. Polym. Prepr. Div. Polym. Chem.* 49 (2008) 511–512. doi:10.1002/pola.
- [36] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B*. 162 (1989) 165–169. doi:10.1016/0009-2614(89)85118-8.
- [37] A.D. Becke, Density-functional exchange approximation with correct asymptotic behaviour, *Phys. Rev. A*. 38 (1988) 3098–3100.
- [38] M.M. Franci, W.J. Pietro, W.J. Hehre, Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements, *J. Chem. Phys.* 77 (1982) 3654.
- [39] P.C. Hariharan, J.A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chim. Acta*. 28 (1973) 213–222.
- [40] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, et. al. Cheeseman, J. R., Gaussian 09, Revision D. 01; Gaussian, Inc., Wallingford CT, (2016).
- [41] T. V. Freitas, E.A. Sousa, G.C. Fuzari, E.P.S. Arlindo, Different morphologies of polyaniline nanostructures synthesized by interfacial polymerization, *Mater. Lett.* 224 (2018) 42–45. doi:10.1016/j.matlet.2018.04.062.
- [42] M. Oyharçabal, T. Olinga, M.P. Foulc, S. Lacomme, E. Gontier, V. Vigneras, Influence of the morphology of polyaniline on the microwave absorption properties of epoxy polyaniline composites, *Compos. Sci. Technol.* 74 (2013) 107–112. doi:10.1016/j.compscitech.2012.10.016.

- [43] E. Raymundo-Piñero, D. Cazorla-Amorós, A. Linares-Solano, J. Find, U. Wild, R. Schlögl, Structural characterization of N-containing activated carbon fibers prepared from a low softening point petroleum pitch and a melamine resin, *Carbon* 40 (2002) 597–608. doi:10.1016/S0008-6223(01)00155-5.
- [44] S. Biniak, G. Szymański, J. Siedlewski, A. Świątkowski, The characterization of activated carbons with oxygen and nitrogen surface groups, *Carbon* 35 (1997) 1799–1810. doi:10.1016/S0008-6223(97)00096-1.
- [45] D. Salinas-Torres, S. Shiraishi, E. Morallón, D. Cazorla-Amorós, Improvement of carbon materials performance by nitrogen functional groups in electrochemical capacitors in organic electrolyte at severe conditions, *Carbon* 82 (2015) 205–213. doi:10.1016/j.carbon.2014.10.064.
- [46] C. Wang, Y. Zhou, L. Sun, P. Wan, X. Zhang, J. Qiu, Sustainable synthesis of phosphorus- and nitrogen-co-doped porous carbons with tunable surface properties for supercapacitors, *J. Power Sources*. 239 (2013) 81–88. doi:10.1016/j.jpowsour.2013.03.126.
- [47] V.G. Bairi, U.B. Nasini, S. Kumar Ramasahayam, S.E. Bourdo, T. Viswanathan, Electrocatalytic and supercapacitor performance of Phosphorous and Nitrogen co-doped Porous Carbons synthesized from Aminated Tannins, *Electrochim. Acta*. 182 (2015) 987–994. doi:10.1016/j.electacta.2015.10.011.
- [48] M.S. Ram, S. Palaniappan, A process for the preparation of polyaniline salt doped with acid and surfactant groups using benzoyl peroxide, *J. Mater. Sci.* 39 (2004) 3069–3077. doi:10.1023/B:JMSC.0000025834.43498.cf.
- [49] J.P. Paraknowitsch, Y. Zhang, B. Wienert, A. Thomas, Nitrogen- and phosphorus-co-doped carbons with tunable enhanced surface areas promoted by the doping additives, *Chem. Commun.* 49 (2013) 1208–1210. doi:10.1039/c2cc37398j.
- [50] X. Wu, L.R. Radovic, Inhibition of catalytic oxidation of carbon/carbon composites by phosphorus,

- [51] F. Quesada-Plata, R. Ruiz-Rosas, E. Morallón, D. Cazorla-Amorós, Activated Carbons Prepared through H₃PO₄-Assisted Hydrothermal Carbonisation from Biomass Wastes: Porous Texture and Electrochemical Performance, *Chempluschem*. 81 (2016) 1349–1359. doi:10.1002/cplu.201600412.
- [52] H.S.O. Chan, S.C. Ng, W.S. Sim, K.L. Tan, B.T.G. Tan, Preparation and Characterization of Electrically Conducting Copolymers of Aniline and Anthranilic Acid: Evidence for Self-Doping by X-ray Photoelectron Spectroscopy, *Macromolecules*. 25 (1992) 6029–6034. doi:10.1021/ma00048a026.
- [53] B.D. Mather, K. Viswanathan, K.M. Miller, T.E. Long, Michael addition reactions in macromolecular design for emerging technologies, *Prog. Polym. Sci.* 31 (2006) 487–531. doi:10.1016/j.progpolymsci.2006.03.001.
- [54] M. Aldissi, S.P. Armes, X-ray Photoelectron Spectroscopy Study of Bulk and Colloidal Polyaniline, *Macromolecules*. 25 (1992) 2963–2968. doi:10.1021/ma00037a027.
- [55] J.M. Rosas, R. Ruiz-Rosas, J. Rodríguez-Mirasol, T. Cordero, Kinetic study of the oxidation resistance of phosphorus-containing activated carbons, *Carbon* 50 (2012) 1523–1537. doi:10.1016/j.carbon.2011.11.030.
- [56] Y.J. Lee, L.R. Radovic, Oxidation inhibition effects of phosphorus and boron in different carbon fabrics, *Carbon* 41 (2003) 1987–1997. doi:10.1016/S0008-6223(03)00199-4.
- [57] C.C. Hu, J.Y. Lin, Effects of the loading and polymerization temperature on the capacitive performance of polyaniline in NaNO₃, *Electrochim. Acta*. 47 (2002) 4055–4067. doi:10.1016/S0013-4686(02)00411-5.
- [58] M.J. Bleda-Martínez, E. Morallón, D. Cazorla-Amorós, Polyaniline/porous carbon electrodes by chemical polymerisation: Effect of carbon surface chemistry, *Electrochim. Acta*. 52 (2007) 4962–

- [59] D. Salinas-Torres, F. Montilla, F. Huerta, E. Morallón, All electrochemical synthesis of polyaniline/silica sol-gel materials, *Electrochim. Acta.* 56 (2011) 3620–3625. doi:10.1016/j.electacta.2010.11.059.
- [60] W. Li, A. Yu, D.C. Higgins, B.G. Llanos, Z. Chen, Biologically Inspired Highly Durable Iron Phthalocyanine Catalysts for Oxygen Reduction Reaction in Polymer Electrolyte Membrane Fuel Cells, *J. Am. Chem. Soc.* 132 (2010) 17056–17058.
- [61] R. Baker, D.P. Wilkinson, J. Zhang, Comparison of two new substitutes iron Phthalocyanines as electrocatalysts for the oxygen reduction and hydrazine oxidation reaction, *ECS Trans.* 16 (2009) 43–61.
- [62] S.I. Yamazaki, M. Yao, N. Fujiwara, Z. Siroma, T. Ioroi, K. Yasuda, CO electro-oxidation by carbon-supported Rh tetraphenylporphyrins that have o-methyl groups on meso-phenyl substituents, *J. Electroanal. Chem.* 668 (2012) 60–65. doi:10.1016/j.jelechem.2012.01.007.
- [63] G.E. Yalovega, V.A. Shmatko, A.O. Funik, M.M. Brzhezinskaya, *Advanced Materials*, 175 (2016) 299–315. doi:10.1007/978-3-319-26324-3.
- [64] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, *Electrochim. Acta.* 45 (2000) 2483–2498. doi:10.1016/S0013-4686(00)00354-6.
- [65] A. Asghar, A.A. Abdul Raman, W.M.A.W. Daud, Recent advances, challenges and prospects of *in situ* production of hydrogen peroxide for textile wastewater treatment in microbial fuel cells, *J. Chem. Technol. Biotechnol.* 89 (2014) 1466–1480. doi:10.1002/jctb.4460.

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Highlights

- Efficient methodology for post-synthetic functionalization of polyaniline with phosphorus-containing compounds
- The electroactivity of modified polyaniline depends on the phosphorus precursor
- DFT results proved that the reaction occurs through the imine groups and the phosphorus atoms.