# Electrochemical Capacitive Properties of Ny/PP/GO Electro-spun Composite Coating on Stainless Steel in Acid Media

César A. García-Pérez, Carmina Menchaca-Campos, Miguel A. García-Sánchez, and Jorge Uruchurtu

*Abstract* — **Composite materials were manufactured to obtain singular properties to be used as in electrochemical driven energy systems. An electrochemical evaluation was performed on electro-spun nylon 6,6 fibers (Ny), with different concentrations of tetra-para-amino-phenyl porphyrin (PP) and graphene oxide (GO) composite coating over stainless steel (SS), immersed in 1M $H_2SO_4$ aggressive sulfuric acid solution. Different film coatings behavior was obtained and compared using electrochemical impedance spectroscopy (EIS). Also, cyclic voltametry (CV) were performed on nylon/PP/GO composite coating system at different scan rates, and over film covered carbon cloth. For the electro-spun composite coating on stainless steel EIS, lower electro-spinning times present higher impedance, hence some corrosion protection. For greater electro-spinning times, larger capacitance values were observed. These were possibly due to thicker coating or mass transport adsorption-diffusion process through the composite film, respectively. For the composite coating, porphyrins, and graphene oxide interaction present ionic conductivity, reducing the impedance and promoting proton formation, property which could be used in charge storage systems.**

*Keywords* — **Capacitance, composite coating, electrochemical evaluation, graphene oxide, porphyrin, nylon 66.**

## I. Introduction

Manufacturing of porous composite and hybrid materials take advantage of characteristic and singular properties of each material component forming them to produce singular new properties from their interactions. Ny/PP/GO composite compound has proven to be useful in energy applications such as: fuel cell bipolar plates, super capacitors plates, etc. [1].

Fuel cell polymer electrolyte membrane (PEM) bipolar plates are graphite made for good corrosion resistance, but durability under mechanical stress is diminished, when compared to metallic plates [2], [3]. These as well, present disadvantages such as electrochemical metal corrosion, producing reduction in contact resistance and sometimes fouling of the catalyst and the ionomer [4]-[6].

Carbon porous materials [7]-[11], transition metal oxides [13]-[17] and conducting polymers [18]-[20] are electrode materials disposable to be used in energy storage. These materials present some disadvantages;therefore, efforts are directed towards the development of nanocomposite or hybrid electrodes.

Graphene oxide is obtained treating graphite with strong oxidizers and is formed of carbon, oxygen and hydrogen being functionalized in some places of the graphite surface where defects are present. When dispersed in basic solutions, monomolecular sheets of graphene oxide, is yielded from the bulk material [21], and similar disordered and irregular packed layer structure is maintained with carboxyl and carbonyl groups placed at the edges. Organic functional groups attached within, in the surface and around the grapheme oxide layers made feasible its covalent union with chemical species.

Synthetic tetra-pyrrole macro-cycle porphyrins present many properties, due to the rich electronic/photonic characteristics [23]. The simple synthesis and purification make them suitable for technological material use. Formed by four pyrrole rings bonded through methane bridges (=CH-), they form a highly conjugated and planar macro-cycle, with four central nitrogen atoms delivering complexation properties. Metallic ions are accommodated in the central molecule space, with an atomic radius of less than 0.20 nm. The larger ions therefore will be accommodated outside of the molecular plane [3], [4], [24].

Most polymeric materials possess high electrical resistivity, plastic deformation and low conductivity and thermal stability rendering limited technological applications. The combination of graphene oxide and polymers show resistive properties, and when including polymer electric donor dopants, the conductivity properties are enhanced. Porphyrin has shown in a reversible way the ability to protonate/ deprotonate. Taking these into consideration, porphyrins and graphene oxide show excellent properties, and when these are incorporated into polymeric matrixes forming a nanocomposite or hybrid material, some shortcomings may be leveled off.

Nylon is a low cost polymer used under different applications, having good mechanical conditions such as: strength, stiffness, hardness and toughness due the attraction of their chains from hydrogen bonds and cross-linking, being a barrier for protection of metal corrosion.

A possibility of solving metallic bipolar plate passive film dissolution and metallic corrosion is coating them with a Ny/PP/GO composite, improving charge transport and energy transfer through the fuel cell [24]-[26]. This nanocomposite overcomes the individual compound

C. A. García-Pérez, Centro de Investigación en Ingeniería y Ciencias Aplicadas-IICBA, Universidad Autónoma del Estado de Morelos, México.
C. Menchaca-Campos, Centro de Investigación en Ingeniería y Ciencias Aplicadas-IICBA, Universidad Autónoma del Estado de Morelos, México.

M. A. García-Sánchez, Departamento de Química, UAM-Iztapalapa, México.
J. Uruchurtu, Centro de Investigación en Ingeniería y Ciencias Aplicadas-IICBA, Universidad Autónoma del Estado de Morelos, México.
(e-mail: juch25@uaem.mx).

limitations combining their beneficial aspects. Ny and GO provide good mechanical behavior improving electrical conductivity and extending useful life [2], [15]. The purpose of the present research is the electrochemical evaluation and performance of Ny/PP/GO electro-spun polymer coating as energy storage capacity as well as electrochemical behavior and corrosion protection of stainless steel plate substrate.

## II. EXPERIMENTAL PROCEDURE

### A. Sample Preparation

Electro-spinning of Ny and its different mixtures with PP and/or GO was prepared at room temperature. The experimental setup (Fig. 1) and parameters are presented in Table I [1].
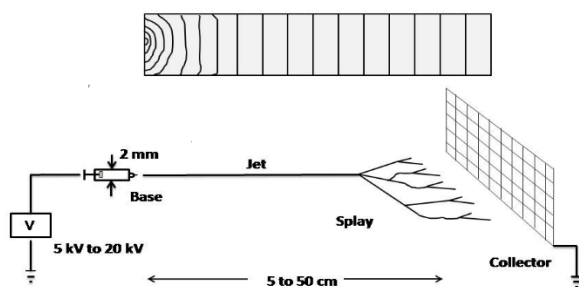


Fig. 1. Electro-spinning experimental set-up.

TABLE I: EXPERIMENTAL PARAMETERS FOR ELECTRO-SPINNING

| Composite | Solvent | Charge (kV) | FlowRate (l/min) | Viscosity (cp) | Collector (cm$^2$) |
|---|---|---|---|---|---|
| Nylon | Formic Acid | 12 | 0.3 | 122.24 | 15 |
| Nylon/GO | Formic Acid | 12 | 0.4 | 102.16 | 12 |
| Nylon/PP | FormicAcid/ Chloroform | 12 | 0.4 | 101.86 | 12 |
| Nylon/PP/ GO | FormicAcid/ Chloroform | 13 | 0.2 | 106.96 | 12 |

For the Ny/PP electro-spun composite coating, porphyrin concentrations were 5 or 100 mg equivalent to 0.1% and 1% by weight of the complete compounds mix. GO concentrations of 25% or 50% were used for the Ny/GO film formation, and for the Ny/PP/GO system the weight percent were 0.1% and 1% porphyrin and 25% GO. Electro-spinning times were five minutes, one or two hours for all cases. Experimental procedure and material characterization were reported, previously [1], [2].

### B. Plate Material

Stainless steel 316 (wt. %: C 0.035, Cr 17.9, Ni 10.3, Mo 2.8, Si 0.3, Mn 1.5, S 0.014, P 0.032, Fe balance). Distance between electro-spinning tip and collectors were 12 or 15 cm. Stainless steel probes were place at the collector screen, in order to be covered with the different electro-spun composite coatings. Afterwards, these were used as metallic plates exposing a 3 cm$^2$ to the sulfuric acid solution (pH 2) for electrochemical evaluation. Previously, before electro-spinning the collector stainless steel plate was grounded with

600 grit using SiC emery paper [13], [14]. Then the stainless steel collector plates were cleaned by de-ionized water, degreased with ethanol and dried in hot air before testing.

### C. Electrochemical Measurement

The different electro-spun composite coatings on stainless steel were evaluated performing electrochemical impedance spectroscopy (EIS) at the open circuit potential, using a Gamry 1000 interface electrochemical instrument (current range 100pA-1A) in the frequency range 10 kHz to 0.01 Hz with ±10 mV amplitude. An Ag/AgCl reference electrode and a graphite rod as counter electrode were used [1], [27], [28]. Similarly, EIS measurements were performed substituting the metallic plate substrate (316 stainless steel) by a conductive carbon cloth. Modification in GO concentration from 25% to 80% and 1% porphyrin were made, to obtain the lowest ionic resistance, because electro-spinning becomes difficult to use at concentrations greater than 50% GO. The best Ny/PP/GO paste composite coating was selected and applied, using 100 mg of PP and 80% w/w of GO.

### D. Cyclic Voltametry

According to the results observed in the EIS, cyclic voltametry was used to determine the charge storage capacitive properties of the Ny/PP/GO compound at different scanning rates: 5, 10, 20, 50, 100, 200 and 300 mV/s. A three electrode arrangement namely: carbon cloth working electrode, Ag/AgCl reference and graphite auxiliary electrodes were used. Previously, the coatings detailed synthesis and characterization were presented in the literature, by the authors [29], [30].

## III. RESULTS AND DISCUSSION

### A. Characterization by EIS

#### 1) Characterization of Ny/GO coating

Fig. 2 presents the EIS Nyquist plot showing the impedance behavior for the SS (blank) sample covered with the electro-spun Ny/GO coatings for different times of electro-spinning, at two different GO concentrations: 25% and 50 %. Capacitive behavior was observed as an almost increasing straight line, associated to passive metals. In the presence of SS covered with an electro-spun Ny/GO coating, the straight line observed is closer to the imaginary impedance axis suggesting even greater capacitive behavior ascribed to a very good protective coating for the 50% GO concentration after 3 and 5 minutes of electro-spinning time.

#### 1) Characterization of Ny/PP coating

Similar behavior was observed (see Fig. 3), for the Ny/PP electro-spun coating at different porphyrin quantity (5mg and 100 mg) and electro-spinning times. For higher PP quantities and especially for higher electro-spinning times which, correspond to an increase in coating thickness, the real and imaginary impedance increased when compared to the former case. The capacitive imaginary impedance for longer electro-spinning times, becomes slightly larger, associated to a greater time constant, commonly associated to a porous conducting surface coating or passive metal films produced by the film or the coating thickness.
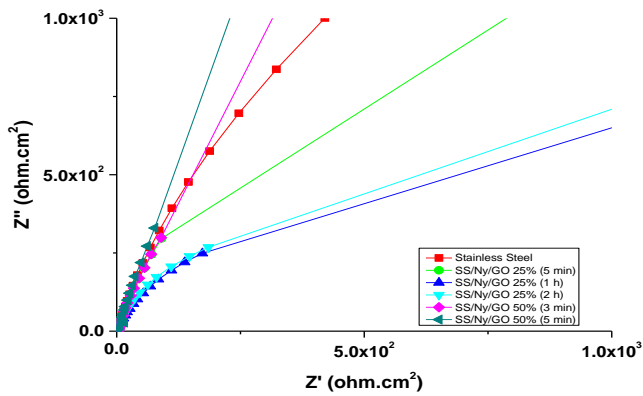
Fig. 2. EIS Nyquist plots electrochemical evaluation for stainless steel and Ny/GO composite coating at 25% and 50% GO concentrations in 1M H$_2$SO$_4$ solution at different electro-spinning times.
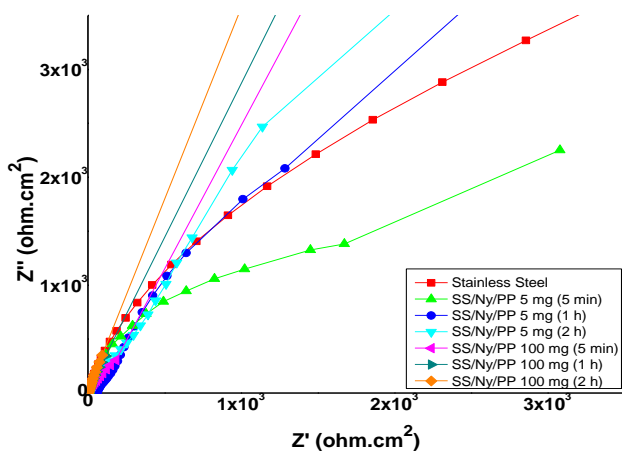


Fig. 3. EIS Nyquist plots electrochemical evaluation for SS electro-spun Ny/PP composite coating with 5 mg and 100 mg of PP in a 1M H$_2$SO$_4$ solution at different electro-spinning times.

### 2) Characterization of Ny/PP/GO coating

From the previous EIS results obtained and presented, a significant capacitive change was not observed with increasing GO or PP concentrations, therefore a decision was made to use 25% GO and 100 mg PP maintaining them constant, and only changing the electro-spinning times from 5 minutes to 1 and 2 hours.

The Nyquist plots obtained and presented in Fig. 4, showed two capacitive depressed semicircles with different impedance values. The semicircle diameters correspond to the electro-spun film coating at higher frequencies and charge transfer resistances at lower frequencies respectively. The semicircle diameters decreased and comparing them to the 5 minutes electro-spun coating sample, the real impedance is lower for longer electro-spinning times.

Also, for these higher electro-spinning time samples, a mass transport low frequencies section at the lowest frequencies is also present and associated to a third time constant. A higher PP content due to increased electro-spinning times and related to a thicker coating layer promotes a real impedance decrease, when the electro-spinning time rose from 5 minutes to 1 and 2 hours. This was due to changes

in the time constants. For these ternary composite coating systems, the coating is less protective for metallic substrate but diffusion-controlled process, for longer electro-spinning times. Detailed SEM analysis of the coatings were performed and presented in the literature [1].
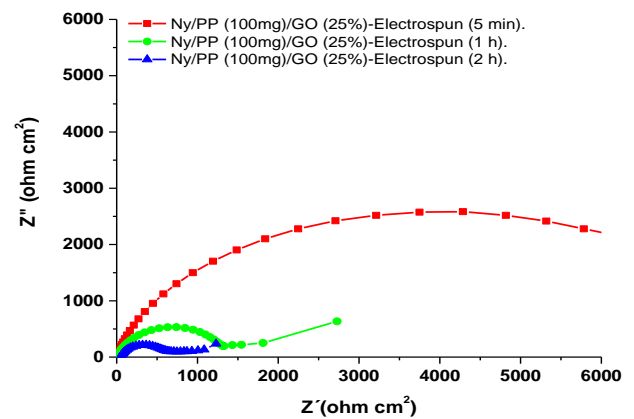


Fig. 4. EIS Nyquist plots electrochemical evaluation, of stainless steel Ny/GO/PP in a 1M H$_2$SO$_4$ solution at different electro-spinning times.

Using equivalent electric circuit, the EIS data fitting was performed using the Z view software, to obtain the electrochemical parameters. This is in agreement and a common practice to the observed phenomena for organic protective coatings [29]-[31]. In the circuit proposed: Rs is the solution resistance, Rct is the charge transfer resistance and R$_{film}$is the protective film resistance, whereas the ideal capacitance C$_{film}$ and C$_{dl}$ values were fitted due to impedance depressed semicircles by CPE constant phase elements as the double layer and film capacitance values and W being the Warburg impedance, respectively. Table II presents the electrochemical impedance spectroscopy (EIS) data, obtained for the Ny/PP/GO system coating at different times of electro-spinning, using the circuit given in Fig. 5.

It is shown in Table II, the electrochemical values obtained from electric circuit data fitting where low resistance values were observed, associated to the porous characteristic of the composite coating electro-spun over the SS surface. For the SS/Ny/PP (100 mg)/GO (25%) the highest charge transfer resistance value was obtained for the 5 minutes coating electro-spun, reflecting the lowest corrosion rate obtained for the different coating systems.
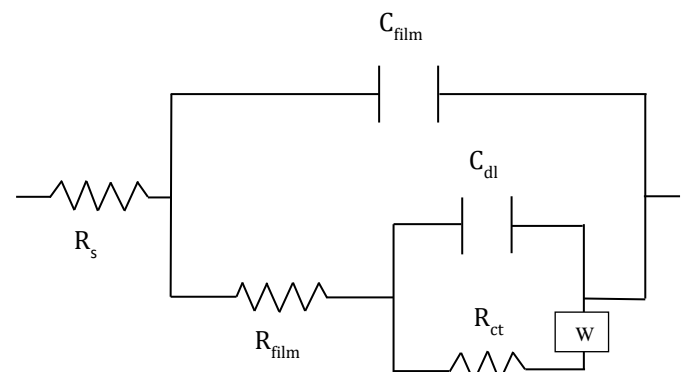


Fig. 5.EIS equivalent electric circuit data fitting for coating systems.

TABLE II: EIS EXPERIMENTAL ELECTRIC CIRCUIT DATA FITTING OF THE NY/PP/GO SYSTEMS IN H₂SO₄SOLUTION AT DIFFERENT TIMES OF ELECTRO-SPINNING

| Samples | $R_s$ (Ω) | $R_{film}$ (Ω.cm²) | $CPE_{film}$ (F/cm²) | $R_{ct}$ (Ω.cm²) | $C_{PEdl}$ (F/cm²) | Rw (Ω.cm²) | Cw (F/cm²) |
|---|---|---|---|---|---|---|---|
| Blank (SS) | 2.7 | -- | --- | 9141 | 3.4E-04 | 2.3E4 | 9.9E-4 |
| Ny/PP100 mg/ GO25% (5 min) | 1.9 | 104 | 7.4E-06 | 8030 | 6.6E-04 | 1188 | 1.42E-2 |
| Ny/PP100 mg/ GO25% (1 h) | 3.9 | 1220 | 1.6E-05 | 1015 | 3.9E-03 | 625 | 2.7E-2 |
| Ny/PP100 mg/ GO25% (2 h) | 49.9 | 547 | 1.4E-04 | 654 | 7.4E-03 | 179 | 9.3E-2 |

Nylon (Ny), Graphene Oxide (GO), Porphyrin (PP). Stainless Steel (SS).

It can be observed in the Nyquist plot (Fig. 4), and data fitting in Table II that the impedance in the SS/Ny/PP systems changes for different electro-spinning times, causing that longer electro-spinning times induce higher capacitance values as a function of time (see Table II). The data fitting shows the presence of different time constants (RC) for all cases, where the electro-spun composite coating was used. The first is due to the coating impedance, with low resistance values, and the second corresponds to the charge transfer process and the effect of the double layer capacitance.

Capacitance values observed suggests a loaded storage capacity for the different systems coating, as seen in Table II. The capacitance for all the electro-spun composite coating system presents high values, therefore great charge storage, appropriate for different applications.

### B. Specific Capacitance

#### 1) Carbon Cloth Electrode Impedance

The Nyquist impedance plot for the Ny/PP/GO deposited electrode on a carbon cloth substrate to obtain the coating capacitance is presented in Fig.6. A clear capacitive behavior was obtained and observed, with a change in the impedance as compared to the carbon cloth blank sample, due to its film and double layer resistances and associated capacitances, and from the mass transport diffusion process at the lowest frequencies. This was confirmed from electrochemical voltamograms at different scanning rates, presented in Fig. 7.

Fig. 7 presents the specific capacitance as a function of the potential scan rate: the specific capacitance of the electrodes can be calculated according to the following equation (1) from CV curves:

$$C = I / mV \qquad (1)$$

where I is the current, m is the mass of reactive material, and V is the potential scan rate. The specific capacitance of the Ny/PP/GO electro-spun composite coating was obtained through the current as a function of potential originated by the electron transfer reaction, occurring on the electrode surface.

By comparison, in the electro-spun Ny/GO compound coatings the GO concentration and the electro-spinning times affect the changes in the coating behavior response, as reported for the organic coatings [1], [28]. These will be reflected in a better metallic corrosion protection. Regarding the Ny/PP electro-spun coating system, concentration, and electro-spinning times, for low PP content and longer times the impedance increases while at higher contents the capacitance increases. Therefore, a compromise may be proposed depending upon the application as the change results is more pronounced in the overall impedance behavior.
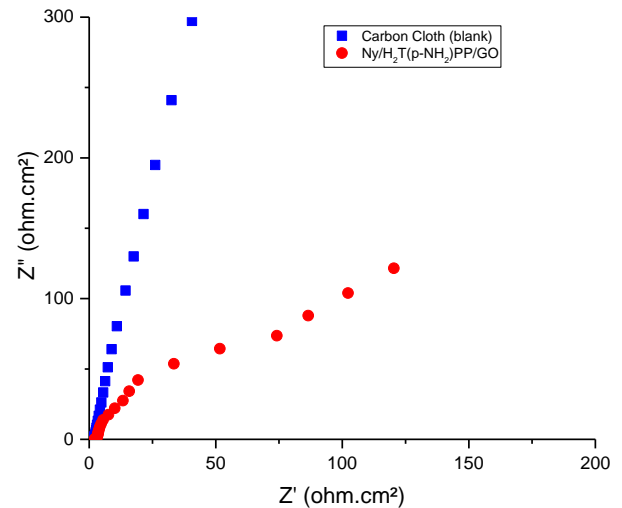


Fig. 6. Electrochemical impedance of the Ny/PP(100mg)/GO(80%) composite deposited on carbon cloth.
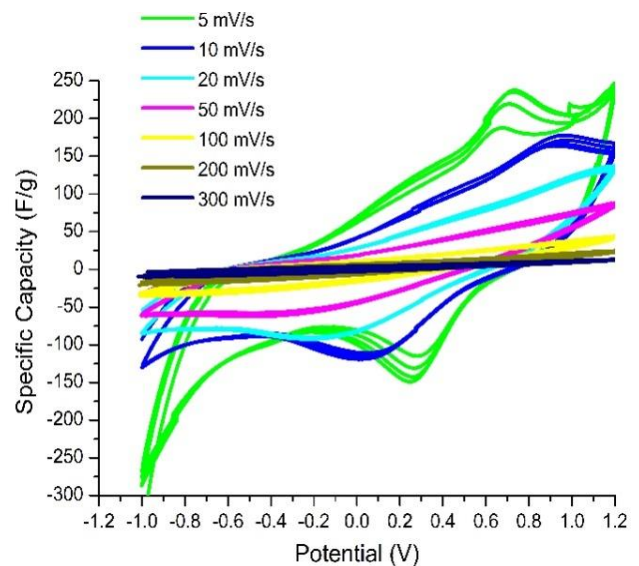


Fig. 7. Cyclic voltametry of nylon/PP (100mg)/GO (80%) compound at different scan rates.

For the ternary electro-spun composite coating formed, overall complex electrochemical reactions may take place in the metal coating interface, promoting modified barrier effects [1], [36]. This may be due to the adsorption and diffusion of species through the coating network. This is because of the Ny/GO physical coating barrier and the electrical properties of the PP and GO combinations, regulating the hydrogen ions within the film making it difficult to reach the metallic substrate [36], [37]. This is possible due to the intricate formed porous electro-spun coating layer of fibers as barrier and reflected in the capacitance values, presented in Table II. Also, the change of

the impedance compared to the SS blank sample as seen in the EIS Nyquist plots indicates great improvement in ionic conductivity of the system, reinforcing the theoretical explanation [38], [ 39].

The voltametric results obtained and presented in Figure 7 revealed a slow reaction process that is reflected in the specific capacitance properties of the electro-spun coating. The voltametric scan rate demonstrates an effect in the shape of the curve formed. At higher rates the voltamogram becomes flat while at lower rates it tends to widen forming a more rectangular shape related to more capacitive behavior presenting two peaks belonging to the anodic and cathodic reactions taking place at those potentials, and an increase in the specific capacitance [40], [41]. The schematic representation of the passage of protons through stainless steel Ny/PP/GO electro-spun composite coating mechanism is graphically presented in Fig. 8.
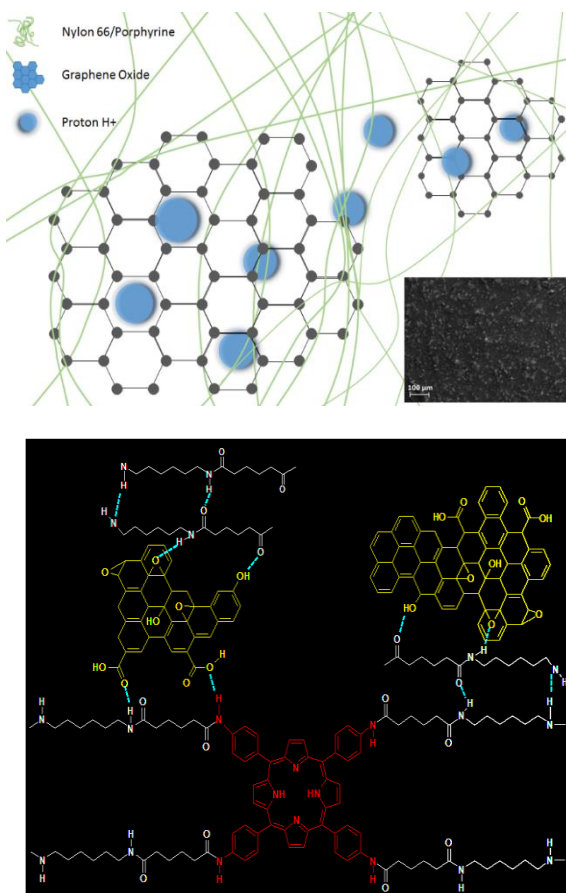


Fig. 8. Schematic representation of the passage of protons through stainless steel Ny/PP/GO electrospun composite coating and chemical structure of Ny/H$_2$T(*p-NH$_2$*)PP/GO and dipole-dipole interactions and hydrogen bridge between species.

## IV. Conclusions

Electro-spun Ny/PP and Ny/GO composite coatings present some protective corrosion properties for stainless steel in the acid solution. The proton mass transport was considered the overall controlling reaction taking place through the binary electro-spun coating compounds determined by EIS technique.

The ternary electro-spun Ny/PP/GO composite coating changed the charge transfer resistance, with the increase of proton formation and by mixing two species, its transport and porphyrins acting as receptor-promoter of hydrogen ions

while graphene oxide allows the passage of these protons.

The electro-spun Ny/PP/GO coating systems are adequate corrosion protection coating. The electro-spun composite coating presents good ionic conductivity and capacitive properties, making it attractive for technological applications such as: coated electrodes in bipolar plates, PEM fuel cell type membranes, super-capacitors, etc.

Future research will include the evaluation of the protective coating ageing, the overall evaluation of the films as storage device or super-capacitor. Consider the effect of the position of the amino group in the porphyrin macromolecules and the specific surface, to correlate these parameters with the efficiency as an energy system.

## References

[1] C. García-Pérez, C. Menchaca-Campos, M. A. García-Sánchez, E. Pereyra-Laguna, O. Rodríguez-Pérez and J. Uruchurtu-Chavarín. "Nylon/Porphyrin/Graphene oxide fiber ternary composite, synthesis and characterization. *Open J. of Comp. Mats*.,2017;7:146-165.

[2] C. Menchaca-Campos, C. García-Pérez, I. Castañeda, M. A. García-Sánchez, R. Guardián and J. Uruchurtu. Nylon/Graphene oxide electrospun composite coating. *J. of Polymer Sci.*,2013;2013:1-9.

[3] T. de J. Licona-Sánchez, G. A. Álvarez-Romo, L. H. Mendoza-Huizar, C. A. Galán-Vidal, M. Palomar-Pardavé, M. Romero-Romo, H. Herrera-Hernández, J. M. Juárez-Garcíaand J. Uruchurtu. Nucleation and growth kinetics of electrodeposited sulfate-doped polypyrrole: determination of the diffusion coefficient of SO$_4^{2-}$ in the polymeric membrane. *J. Phys. Chem. B*, 2010;114:9737-9743.

[4] Y. R. Lee, S. C. Kim, H. Lee, H. M. Jeong, A. V. Raghu, K. R. Reddy and B. K. Kim. Graphite oxides as effective fire retardants of epoxy resin. *Macromol. Research*, 2011;19:66–71.

[5] K. R. Reddy, B. C. Sin, K. S. Ryu, J. Noh and Y. Lee. In situ self-organization of carbon black–polyaniline composites from nanospheres to nanorods: Synthesis, morphology, structure and electrical conductivity. *Synthetic Metals*,2009;159:1934-1939.

[6] V. Mehta and J. S. Cooper. Review and analysis of PEM fuel cell design and manufacturing. *J. Power Sources*, 2003;144:32–53.

[7] V. Ruiz, Blanco, C. Raymundo-Pinero, E. Khomenko, V. Beguin and F.R. Santamaria. Effects of thermal treatment of activated carbon on the electrochemical behaviour in supercapacitors. *Electrochim. Acta*, 2007;52:4969-4973.

[8] K. W. Nam, W. S. Yoon and K. B. Kim. X-ray absorption spectroscopy studies of nickel oxide thin film electrodes for supercapacitors, *Electrochim. Acta*, 2002;47:3201-3209.

[9] T. Kudo, Y. Ikeda, T. Watanabe, M. Hibino, M. Miyayama, H. Abe and K. Kajita. Amorphous V$_2$O$_5$/carbon composites as electrochemical supercapacitor electrodes. *Solid State Ionics*, 2002;152-153:833-841.

[10] Y. U. Jeong and A. Manthiram. Nanocrystalline Manganese oxides for electrochemical capacitors with neutral electrolytes. *J. Electrochem. Soc.*, 2002;149:A1419-A1422.

[11] R. N. Reddy and R. G. Reddy. Sol–gel MnO$_2$ as an electrode material for electrochemical capacitors. *J. Power Sources*, 2003;124:330-337.

[12] H. Wang, and J. A. Turner. Ferritic stainless steels as bipolar plate material for polymer electrolyte membrane fuel cells. *J. Power Sources*, 2004;128:193–200.

[13] K. R. Reddy, H. M. Jeong, Y. Lee and A. V. Raghu. Synthesis of MWCNTs-core/thiophene polymer-sheath composite nanocables by a cationic surfactant-assisted chemical oxidative polymerization and their structural properties. *J. Polymer Sci. Polymer Chem. Part A*, 2010;48:1477-1484.

[14] M. U. Khan, K. R. Reddy, T. Snguanwongchai, E. Haque and V. G. Gomes. Polymer brush synthesis on surface modified carbon nanotubes via in situ emulsion polymerization. *Colloid and Polymer Sci.*, 2016;294:1599–1610.

[15] F. Gnädinger, P. Middendorf and B. Fox. Interfacial shear strength studies of experimental carbon fibres, novel thermosetting

polyurethane and epoxy matrices and bespoke sizing agents. *Composites Sci. and Tech*., 2016;133:104-110.

[16] M. Hassan, K. R. Reddy, E. Haque, A. I. Minett and V. G. Gomes.High-yield aqueous phase exfoliation of graphene for facile nanocomposite synthesis via emulsion polymerization. J. *Colloid and Interface Sci*., 2013;410:43-51.

[17] S. J. Han, H. Lee, H. M. Jeong, B. K. Kim, A. V. Raghu and K. R.Reddy. Graphene modified lipophilically by stearic acid and its composite with low density polyethylene. *J. Macromol. Sci. Part B: Phys*., 2014;53:1193-1204.

[18] O. Barbieri, M. Hahn, A. Herzog and R. Kotz. Capacitance limits of high surface area activated carbons for double layer capacitors. *Carbon*, 2005;43:1303-1310.

[19] H. Wang, M. Yoshio, A. K. Thapa and H. Nakamura. From symmetric AC/AC to asymmetric AC/graphite, a progress in electrochemical capacitors. *J. Power Sources*, 2007;169:375-380.

[20] Z. J. Zhang, X.Y. Chen, B.N. Wang and C.W. Shi. Hydrothermal synthesis and self-assembly of magnetite ($Fe_3O_4$) nanoparticles with the magnetic and electrochemical properties. *J. Cryst. Growth*,2008;310:5453–5457.

[21] Y. R. Lin and H. Teng. A novel method for carbon modification with minute polyaniline deposition to enhance the capacitance of porous carbon electrodes. *Carbon*, 2003;41:2865-2871.

[22] R. Borup and N. Vanderborgh. Design and testing criteria for bipolar plate materials for PEM fuel cell applications.*Mat. Res. Soc. MRS. Proc*.,1995;393:151–155.

[23] A. S. Woodman, E. B. Anderson, K. D. Jayne and M.C. Kimble. Development of corrosion-resistant coatings for fuel cell bipolar plates. *Am. Electroplater and Surf. Finishers Soc., AESF Proc*., 1999;6:21-24.

[24] M.A. García-Sánchez, F. Rojas-González, E.C. Menchaca-Campos, S.R. Tello-Solís, R. I., Y. Quiroz-Segoviano, L.A. Diaz-Alejo, E. Salas-Bañales and E. Campero. A. crossed and linked histories of tetrapyrrolic macrocycles and their use for engineering pores within Sol-Gel matrices. *Molecules*, 2013;18:588-653.

[25] V. V. N. Obreja. On the performance of supercapacitors with electrodes based on carbon nanotubes and carbon activated material: A review. *Physica* E, 2008;40:2596-2605.

[26] F. C. Wu, R. L. Tseng, C. C. Hu and C. C Wang. Physical and electrochemical characterization of activated carbons prepared from firewoods for supercapacitors. J. Power Sources, 2004;138:351-359.

[27] M. J. L. Oestergaard, A. Visgaard and E. Maahn.AC impedance measurements on coatings for desulphurisation plants. *Surf. Coat. Int.J*, 1993;76:29-39.

[28] H. Xiao and F. Mansfeld. Evaluation of coating degradation with electrochemical impedance spectroscopy and electrochemical noise analysis. *J. Electrochem. Soc*., 1994;141:2332-2337.

[29] J. N. Murray and H. P. Hack. Testing Organic Architectural Coatings in ASTM Synthetic Seawater Immersion Conditions Using EIS. *Corrosion*, 1992;48:671-685.

[30] C. Menchaca-Campos, E. Pereyra-Laguna, C. García-Pérez, M. F. Dominguez, M. A. García-Sánchez and J. Uruchurtu. Synthesis and Characterization of Reduced Graphene Oxide/Polyaniline/Au Nanoparticles. In *Hybrid Material for Energy Applications*, Chapter 6, Graphene Oxide - Applications and Opportunities, G. S. Kamble, Ed. London: IntechOpen, 2018, pp.75-92.

[31] S. Hu, M. Lozada-Hidalgo, F. C. Wang, A. Mishchenko, F. Schedin, R. R. Nair, E. W. Hill, D. W. Boukhvalov, M. I. Katsnelson, R. A. W. Dryfe, I. V. Grigorieva, H. A.Wu and A. K. Geim. Proton transport through one atom thick crystals. *Nature*, 2014;516:227-230.

[32] L. A. Díaz-Alejo, E. C. Menchaca-Campos, J. Uruchurtu-Chavarín, R. Sosa-Fonseca and M. A. García-Sánchez. Effects of the addition of ortho- and para-$NH_2$ substituted tetraphenyl porphyrins on the structure of nylon 66. *Int. J. of Polymer Science*, 2013:1-14.

[33] G.Qu, J. Cheng, X. Li, D. Yuan, P. Chen, X. Chen, B. Wang and H. Peng. Supercapacitors: A fiber supercapacitor with high energy density based on hollow graphene/conducting polymer fiber electrode. *Adv. Mater*., 2016;28:3646-3652.

[34] J. Zhang, L. B. Kong, B. Wang, Y. C. Luo and L. Kang. In-situ electrochemical polymerization of multi-walled carbon nanotube/polyaniline composite films for electrochemical supercapacitors. *Synth. Met.*, 2009;159:260-266.

[35] B. N. Popov, M. A. Alwohaibiand R. E. White. Using electrochemical impedance spectroscopy as a tool for organic coating solute saturation monitoring. *J. Electrochem. Soc*., 1993;140:947-951.

[36] S. H. Choi, D. H. Kim, A. V. Raghu, K. R. Reddy, H. Lee and K. S. Yoon, "Properties of graphene/waterborne polyurethane nanocomposites cast from colloidal dispersion mixtures. *J. Macromol. Sci. Part B: Phys*.,2012;51:197-207.

[37] K. Kierzek, E. Frackowiak, G. Lota, G. Gryglewicz and J. Machnikowski. Electrochemical capacitors based on highly porous carbons prepared by KOH activation. *J. Electrochim. Acta*, 2004;49: 515-523.

[38] M. Cakici, K. R. Reddy and F. Alonso-Marroquin. Advanced electrochemical energy storage supercapacitors based on the flexible carbon fiber fabric-coated with uniform coral-like $MnO_2$ structured electrodes. *Chemical Eng. J*., 2017;309:151-158.

[39] M. Hassan, E. Haque, K. R. Reddy, A. I. Minett, J. Chen and V. G. Gomes. Edge enriched graphene quantum dots for enhanced photo-luminescence and supercapacitance. *Nanoscale*,2014;6:11988-11994.

[40] G. Wang, L. Zhang and J. Zhang. A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev*., 2012;41:797-828.

[41] D. I. Njoku, M. Cui, H. Xiao, B. Shang and Y. Li. Understanding the anticorrosive protective mechanisms of modified epoxy coatings with improved barrier, active and self healing functionalities: EIS and spectroscopic techniques. *Scientific Reports*, 2017;7;15597:1-15.