Mechanism of Nanocomposite Formation in the Layer-by-Layer Single-Step Electropolymerization of $\pi$-Conjugated Azopolymers and Reduced Graphene Oxide: An Electrochemical Impedance Spectroscopy Study

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**ABSTRACT:** This work presents a study of the formation mechanism of electrochemically deposited alternating layers of azopolymer and graphene oxide, as well as a systematic study of the physicochemical characteristics of the resulting nanocomposite films by electrochemical impedance spectroscopy. The nanocomposite films were constructed by cyclic electropolymerization, which allowed for the assembly of thin films with alternating azopolymers and reduced graphene oxide (rGO) layers in one step. Morphological characterizations were performed by atomic force microscopy and scanning electron microscopy and verified that the electrodeposition of the poly(azo-BBY) polymeric film occurred during the anodic sweep, and the deposition of graphene oxide sheets took place during the cathodic sweep. By analyzing the electrochemical impedance spectra using equivalent circuit models, variations in the resistance and capacitance values of the system were monitored as a function of the amount of electrodeposited material on the fluorine doped tin oxide electrode. In addition, the interfacial phenomena that occurred during the electroreduction of the rGO sheets were monitored with the same method.

**INTRODUCTION**

The scaling down of new devices has led to the development of thin films consisting of diverse functional materials for diverse applications, ranging from electronic devices to the medical field.1–3 Among the strategies for the construction of thin films, the use of electrochemical techniques for the formation of electrosynthesized (or electropolymerized) nanomaterials is promising because of the great control over the system under construction, which allows the design of nanometric structures with morphologies and physicochemical properties.4–5 Thus, a deep knowledge in the area of electropolymerization is of particular importance for the development and architecture of new functional nanomaterials.

Composite nanomaterials (nanocomposites) are materials that are produced from two or more materials to obtain advantages of the desired properties and characteristics of each of its constituents.6–7 Among the many materials used for the formation of nanocomposites, the use of graphene and its derivatives has received special attention in research because of their excellent physicochemical properties.8–10 The development of graphene-based composite materials includes the use of inorganic materials, organic crystals, metal organic frameworks, biomaterials and polymers.11 These composite materials are intensively exploited in batteries,12 supercapacitors,13 fuel cells,3 photovoltaic devices14 and sensory platforms.15 In particular, the development of graphene–polymer-based composites demonstrates great potential in various applica-
ations, such as electrocatalysis, drug delivery, biosensors and biomedical materials.

Materials containing azobenzene compounds are of great interest to the scientific community, and they are used to develop new functional materials because of their photochromic properties. The photochromic behavior results from the generation of stable cis–trans isomers based on the azo group (−N=N−) with the incidence of a light source. This phenomenon, called photoisomerization, was first studied and published by Hartley in 1937. The fast and easy interconversion property between two stable isomeric forms makes azobenzene compounds attractive materials for the development of molecular switches, which are used in molecular machine development. Its use also extends to the construction of polymer chains, composing the azopolymer class and further expanding its possibilities for technological applications. Azopolymers can be defined as macromolecules that are made of a large number of small units containing the azo group (N=N) connected by covalent bonds. As azobenzene derivatives, azopolymers are colored because of their ability to absorb visible light from the electromagnetic spectrum. With the proper design, changing the length of the polymer chain by adding electron-donor or electron-acceptor groups allows for a full range of spectral colors to be obtained with azopolymers. The great interest regarding azopolymers lies at the intersection of the advantages presented by conductive polymers (PCs) and azobenzene compounds because azopolymers containing π-conjugated chains are the only conductive polymers capable of photoresponse properties. Thus, several studies have focused on the application of azopolymers in photo-anisotropic systems, photoinduced mass transport, and photosensitive liquid crystal elastomers, among others.

In the present work, we describe the development of a new functional nanomaterial through electropolymerization. The physicochemical properties of the nanocomposite, formed by electrochemical layer-by-layer assembly with alternating layers of reduced graphene oxide (rGO) and Bismarck brown Y π-conjugated azopolymer, was investigated mainly by electrochemical impedance spectroscopy (EIS) using equivalent circuit models.

**RESULTS AND DISCUSSION**

**Layer-by-Layer Electropolymerization of Nanocomposite Azopolymer–Graphene Oxide Thin Films.** Figure 1 shows the cyclic voltammogram for the electropolymerization of the layer-by-layer electrochemical poly(azo-Bismarck brown Y)-rGO film. An increase in current magnitude values was observed with an increasing number of cycles. This behavior is typical and indicative of an increase in the number of electroactive materials on the fluorine doped tin oxide (FTO) electrode surface. The redox pair process \( E_{pa} = +0.60 \text{ V} \) and \( E_{pc} = -0.05 \text{ V} \) vs saturated calomel electrode (SCE) was related to the oxidation and reduction equilibrium of azopolymeric groups involving \( 2e^- \) and \( 2H^+ \) in acidic medium.

\[
\begin{align*}
\text{Hydrazine} & \quad (\text{0.05 V vs. SCE}) \\
\text{Azo} & \quad (\text{+0.60 V vs. SCE})
\end{align*}
\]

The electroformation of azo dye-based polymeric films is widely discussed in the literature. These studies focus on azobenzene electrochemistry, where an upper limit potential of +0.80 V generates radical cations of the amino groups, which react with each other, forming a nitrogen–nitrogen bond (hydrazine), which is subsequently oxidized, producing \( 2H^+ \) and giving rise to an azo bond. Therefore, the formation of the azopolymeric film during anodic sweep begins after the potential of +0.80 V vs SCE is reached, and the terminal amino groups of the monomers are oxidized to a radical cation (BBY*) in acidic medium (step 1—Scheme 1). At this stage, the formed radicals react with each other (head-to-head coupling) to form a nitrogen–nitrogen covalent bond (hydrazine) (step 2). The formed dimer may be again oxidized because of the presence of the amino terminal groups on both sides of the Bismark brown Y molecule, thus recoupling with other monomers and/or dimers (step 3), allowing the polymer chain to propagate over the surface of the FTO conductive substrate. The present work proposes that the formation of the poly(azo-Bismarck brown Y)-rGO nanocomposite film occurs by an electrochemical layer-by-layer mechanism, which generates a structure composed of poly(azo-BBY) polymeric film and rGO alternate layers. The material layer will be deposited depending on the direction of the applied potential sweep, the formation of a polymeric film from the oxidation of the Bismark brown Y monomer occurs during the anodic sweep, and the electrodeposition of graphene sheets on the poly (azo-BBY) film takes place during the cathodic sweep, as schematically illustrated in Scheme 2.

Reversing the sweep to the cathode direction results in the electrodeposition of the graphene oxide sheets. Therefore, electrodeposition occurs when the graphene oxide sheets, upon contact with the azopolymer layer, undergo a partial reduction of their oxygenated groups, making them insoluble in aqueous media and generating a partially rGO sheet layer on top of the poly(azo-BBY) thin film, which was generated during the anodic sweep.
For the present work, the minimum potential of \( -0.30 \) V versus SCE was chosen because it is sufficient to trigger hydrogen evolution (HER) (starting at approximately \( -0.2 \) V vs SCE) needed to rGO sheets. It is important to highlight...
that this value is much lower in comparison to the other values found in the literature for the electrodeposition of oxide from graphene oxide sheets. The values used in the literature studies are close to $-1.0 \text{ V (vs ECS)}$.\textsuperscript{35,39,40} Thus, the presence of the poly(azo-BBY) film causes a catalytic effect on the generation of hydrogen, facilitating the electroreduction and electrodeposition of the graphene oxide sheets.

After 20 potential cycles, a thin film of poly(azo-BBY)-rGO with electrochemically deposited alternating layers was obtained and verified by scanning electron microscopy.

Figure 2. SEM cross section image of poly(azo-BBY)-rGO film under FTO recorded at 150kX magnification (A) SEM images of the electrodes of (B) poly(azo-BBY)\textsubscript{(cathodic)} and (C) poly(azo-BBY)\textsubscript{(anodic)} recorded at 100 kX magnification. AFM surface electrode images of (D) poly(azo-BBY)\textsubscript{(cathodic)} and (E) poly(azo-BBY)\textsubscript{(anodic)}. The SEM images were artificially colored. The original images can be found in the Supporting Information (Figure S1).
(SEM), as shown in Figure 2. Figure 2A shows a cross-sectional image of the electrode covered with the nanocomposite film. It was possible to identify the interface of the FTO of the FTO electrode and the poly(azo-BBY)-rGO thin film on the FTO layer. Figure 2A shows the magnification of the region, which is highlighted in yellow in Figure 2A. It was possible to verify the presence of two distinct material regions corresponding to the polymer and graphene oxide, as indicated by the arrows.

A mechanism of the electroformation of the nanocomposite film by electrochemical layer-by-layer was proposed based on studies of the formation of nanocomposite films using mixed graphene oxide monomer and suspension solution. Morphological measurements were conducted to suggest the alternating electropolymerization of the poly(azo-BBY) and rGO layers. A second film was manufactured by applying 19.5 potential cycles, and the electropolymerization process was stopped during the anodic sweep ($E_{\text{stop}} = +1.0 \, \text{V vs SCE}$) to obtain poly(azo-BBY) as the outermost material (last layer). Afterward, SEM images were recorded (Figure 2B,C), verifying the changes in the morphology of the films. For simplicity, the films were called poly(azo-BBY)-rGO (cathodic) (Figure 2B) and poly(azo-BBY)-rGO (anodic) (Figure 2C). The film of poly(azo-BBY)-rGO showed a higher apparent surface roughness and larger amount of small agglomerates compared to poly(azo-BBY)-rGO (cathodic) which resembled a surface with a graphene “blanket”. This morphology aligns with the work of Teixeira and collaborators who reported cluster formation in poly(azo-BBY) films on FTO surfaces, which is a characteristic feature indicating the presence of the poly(azo-BBY) film as the outermost layer.  

The surface of the poly(azo-BBY)-rGO (cathodic) film showed lower apparent roughness and greater uniformity because of the coverage of the poly(azo-BBY) film with a thin layer of rGO. These characteristics resembled those of literature studies that reported on the coating of graphene sheets. In addition, atomic force microscopy (AFM) images were taken for both films described above (Figure 2D,E). Based on the AFM images of poly(azo-BBY)-rGO (cathodic) (Figure 2D) and poly(azo-BBY)-rGO (anodic) (Figure 2E) films, mean particle size values of 75.2 and 57.1 nm, respectively, were calculated. This result supports the hypothesis of the outermost layer, which covers the electrode surface, being responsible for the morphological differences in the films.

**UV–Vis Characterization of Poly(azo-Bismarck Y) and Poly(azo-Bismarck Y)-rGO.** Figure 3 shows the UV–vis absorption spectrum of the poly(azo-BBY)-rGO electrochemically produced layer-by-layer film and the spectrum of the poly(azo-BBY) film for comparative analysis. Both films show two characteristic azobenzene absorption peaks, which are located at 345 and 422 nm in the poly(azo-BBY) film spectrum and at 405 and 462 nm in the poly(azo-BBY)-rGO nanocomposite film spectrum; the peaks are assigned to π−π* transitions of the trans and cis forms, respectively. For the poly(azo-BBY)-rGO nanocomposite film, redshifts were verified for both isomeric forms, and the displacement values were $\Delta \lambda_{\text{trans}} = 60 \, \text{nm}$ and $\Delta \lambda_{\text{cis}} = 40 \, \text{nm}$. In addition, the nanocomposite film has three absorption peaks in addition to the aforementioned characteristic peaks of cis–trans isomeric forms compared to the poly(azo-BBY)-containing film because of the presence of graphene oxide in the polymer matrix. The first peak is located at 304 nm with a shoulder at approximately 340 nm, which is characteristic of the π−π* transition of rGO. The second and third peaks at 544 and 620 nm were attributed to the polaronic state of the nanocomposite, generated by the presence of rGO. The existence of an absorption peak attributed to the polaronic state of the nanocomposite film (544–620 nm) is indicative of the increased number of distortions in the polymer chain, which results in an increase in the electron conductivity performance of the poly(azo-BBY)-rGO nanocomposite film compared to the poly(azo-BBY) film, as verified in a previous study conducted by our research group. By employing Tauc’s relationship, it was possible to calculate the band gap ($E_{\text{gap}}$) of the allowed direct transitions of the polymeric film and the nanocomposite film.
Electrochemical Impedance Spectroscopy Study: Influence of the Cycle Number on the Interfacial Properties. The influence of the number of potential cycles applied in the construction of polymeric thin films is an important factor for the electrochemically generated film performance. The number of potential cycles applied during electropolymerization controls the amount of material deposited and influences physicochemical and morphological aspects.62,63

The growth of the poly(azo-BBBY)-rGO nanocomposite thin film was evaluated by electrochemical impedance spectra analysis. Equivalent circuit models were used to study changes in the interfacial properties of films formed with different numbers of cycles applied during electropolymerization. The film’s characteristics and properties were investigated in 0.50 mol L⁻¹ KCl (pH = 2.0) upon applying potentials of −0.30 and +0.30 V versus SCE; because of these potentials, it was possible to evaluate the nanocomposite film in its reduced (hydrazine—lower conductivity) and oxidized (azo—higher conductivity) forms.28,34,58

The complex plane spectra obtained for poly(azo-BBY)-rGO films constructed with different applied cycle numbers are shown in Figure 4. For the analysis of the Nyquist spectra, equivalent circuit models were used for fitting the spectra through the mathematical adjustments shown in Figure 4C,D. The equivalent circuit model for the applied potential regime films of −0.30 V versus SCE (Figure 4C) showed the resistance of the electrolyte solution ($R_\text{E}$ = 25 Ω cm²) in series with two parallels, each of which contains a phase constant element (CPE) and charge transfer resistance. For high-mid frequencies, the parallel is composed of $R_\text{ct}$, which is associated with the solution/film interface in parallel to a CPEfilm associated with the capacity of the double electric layer. The second parallel for low-mid frequencies has an $R_\text{ct}$ for the interface between the layers of rGO/poly(azo-BBY) and a CPEfilm associated with charge loading because of the synergistic effect of the conductive polymeric film and the rGO layers. For the spectra obtained at an applied potential of +0.30 V (vs SCE), the equivalent circuit model changed. As shown in Figure 4D, the model displays only the charge transfer resistance ($R_\text{ct}$) associated with the film resistance and the solution/rGO interface in parallel with the CPEfilm element and in series with the element CPEfilm. The absence of the second charge transfer resistance of the rGO/poly(azo-BBY) interface may be related to the formation of a large π-conjugated network, which is built because, at this respective potential, azopolymer is in its oxidized π-conjugated (higher conductivity) state, resulting in effective interaction with rGO layer orbitals.64,65

Investigation of the Cathodic Applied Potential. Figure 5 shows the concentration of electroactive species values ($\Gamma$), calculated from the charge/current ratio obtained by the voltammograms measured for each of the films.36–68 Figure 5 also shows the charge transfer resistance values ($R_\text{ct}$) obtained at −0.30 V (vs SCE) as a function of the cycle number used in the electropolymerization of the nanocomposite film. Figure 5A shows an increase in $\Gamma$ with an increasing number of cycles, reaching stability after the 20th cycle. After 20 applied potential cycles, the polymer chain continues to grow; however, the excess material does not contribute to the increase in the conductivity of the film.

Evaluating the $R_\text{ct}$ values (Figure 5B) related to the azopolymer/rGO interface, a decrease of $R_\text{ct}$ was observed until the 20th potential cycle followed by a subsequent increase of $R_\text{ct}$. Two phenomena need to be considered to understand the behavior of $R_\text{ct}$: (i) the increase in the concentration of electroactive species results in an increase in the resistance of interface rGO/poly(azo-BBBY) because of the less conductive

![Figure 4](https://dx.doi.org/10.1021/acsomega.0c03391)

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form of the polymer by the applied cathodic potential; (ii) the increase in the amount of rGO sheets in the polymeric matrix tends to decrease the resistance of the interface (Scheme 3). Thus, until the 20th cycle, the resistance values of the rGO/poly(azo-BBY) interface has a greater influence on the rGO species than the increased concentration of electroactive species.

As verified by UV−vis measurements, the presence of graphene oxide in the polymeric matrix of the poly(azo-BBY) causes a decrease in the energy of the polymer band gap and increases the distortions of the polymeric chain, resulting in the increase of polarons and bipolar in the film.46,69,70 As a result, there was an increase in the electronic conduction capacity of the nanocomposite film until the 20th cycle. However, after the 20th cycle, the concentration of electroactive species reaches a constant value. Therefore, after the 20th cycle, there was an increase in the amount of nonelectroactive species electrodeposited on the electrode, which does not interact with graphene sheets. However, this deposition also contributed to the increase in the thickness of the nanocomposite film, resulting in a gradual increase in the resistance.

The charge transfer resistance related to the solution/rGO (Rct) interface (Figure 5C) increased with increasing number of cycles, reaching stability in the 20th cycle. Because of the nature of interfacial resistance, the increase in the number of nonelectroactive materials after the 20th cycle did not affect the interfacial phenomena of charge transfer. Any significant changes in the film surface structure after the 20th potential cycle will be verified when evaluating the values of αdl and αfilm.71 The values of the CPE and their respective values of α as a function of the cycle number employed in the electropolymerization are shown in Figure 6. The CPE values for the double electric layer (CPEdl) (Figure 6A) decrease between cycles 5 and 10. This decrease can be attributed to the distortion of the structure due to inhomogeneous nanocomposite coating of the electrode surface, which is likely caused by nanocomposite film nucleation during these cycles.24 This hypothesis can be supported by verifying the values of αdl. The value of α represents the degree of the ideal distance of a capacity element in an electrochemical

Scheme 3. Schematic Representation of the rGO/Poly(azo-BBY) Interface and Its Resistance Behavior
Several studies indicate the possibility of using this parameter as a way to qualitatively estimate the imperfection or roughness of the electrode surface because $\alpha$ is influenced by the arrangement of the electric double layer. Therefore, the decrease of $\alpha_{dl}$ between cycles 5 and 10 might be caused by the nucleation phase (Scheme 4). After the nucleation phase, $\alpha_{dl}$ stabilized, indicating that the electrode is completely covered after the 20th cycle and that the following deposited film layers did not generate significant changes in the homogeneity of the film. Between the 10th cycle and the 20th cycle, an increase in the CPE$_{dl}$ value was observed, with a maximum value of 61 $\mu$F cm$^{-2}$ (Figure 6A). This behavior was related to the increase in electroactive species on the electrode surface, demonstrating a

**Scheme 4. Schematic Representation of Double Layer Capacity Behavior**

- Inner Helmholtz plane (IHP) and Outer Helmholtz plane (OHP).

Figure 6. Capacity values (CPE$_{dl}$ and CPE$_{film}$) (A,C) and their respective values of $\alpha$ ($\alpha_{dl}$ e $\alpha_{film}$) (B,D) obtained by mathematical adjustments of the equivalent circuit model of Figure 4C as a function of the number of potential cycles applied during the electropolymerization step. Applied potential $-0.30$ V vs SCE.
correlation between the CPE$_{dl}$ value and the nanocomposite film.

After the 20th cycle, a decrease of the CPE$_{dl}$ values was observed. Because the values of electroactive species did not change significantly, a dependence on CPE$_{dl}$ values was verified not only as a function of the number of electroactive species but also on factors such as porosity and film thickness. For films with applied cycle numbers greater than 20, an equivalent value of active species was found, but there was an increase in the $R_s$ value of the film, indicating an increase in the amount of nonelectroactive material in the poly(azo-BBY)-rGO. This increase in material likely increased the thickness of the nanocomposite film, resulting in fewer interactions of the active sites with the electrical double layer, thus substantially lowering the CPE$_{dl}$ value.

The nanocomposite film exhibits charge loading behavior through the redox equilibrium between the H$^+$ ions and the polymerazo groups as well as the remaining oxygenated groups of the rGO. Figure 6C shows the plot of the film’s capacity (CPE$_{film}$) as a function of the number of cycles applied during the electropolymerization. CPE$_{film}$ behaved similarly to CPE$_{dl}$. It also depended on the concentration of electroactive species in the nanocomposite film. The behavior of CPE$_{film}$ can be classified into two cycle regions: the first one ranges from the 5th to the 20th cycle and shows an increase in charge capacity because of the increase in active species concentration of poly(azo-BBY)-rGO film over the electrode surface; the second one ranges from the 20th to the 40th cycle and demonstrates the limited diffusion of H$^+$ ions into the inner layers of the nanocomposite film and the resulting decrease in charge capacity because of the increase in the amount of nonelectroactive material deposited after the 20th cycle. The $\alpha_{film}$ values of the CPE$_{film}$ element are significantly lower than the $\alpha_{dl}$ values ($\alpha_{film} < 0.9$ and $\alpha_{dl} > 0.91$), demonstrating a lower structural organization inside the film.

Investigation on Anodic Applied Potential. It is known that the poly(azo-BBY) film shows higher electronic conductivity in the anodic potential regime because of electronic delocalization through the polymeric backbone $\pi$-conjugated. In addition, a strong interaction of the $\pi-\pi$ orbitals between the polymer and the rGO increases the electronic conductivity of the nanocomposite. Thus, the behavior of the poly(azo-BBY)-rGO film was also investigated at an anodic potential of +0.30 V (vs SCE). The single $R_{ct}$ shown in the anodic potential regime, decreased with the increase in the number of applied cycles (Figure 7).

$R_n$ reached its minimum value during the 20th cycle ($455 \Omega \text{cm}^2$). That behavior was similar to the resistance of the rGO/poly(azo-BBY) interface at $-0.30$ V versus SCE, with a similar hypothesis. Until the 20th cycle, an increase in the conductivity of the film was observed as a function of the increase in the amount of active species. Afterward, a decrease in the resistance was observed because of the increase in the nonelectroactive species concentration.

The double layer capacitance values (CPE$_{dl}$) for an applied potential of $+0.30$ V versus SCE were similar to the values obtained for a potential of $-0.30$ V versus SCE, demonstrating that the double layer capacitance resembles both potentials and is related to the concentration of active species of the nanocomposite polymeric film. For an applied potential of $+0.30$ V versus SCE (Figure 8), no significant film capacitance values were verified (CPE$_{film}$), with the maximum value reaching approximately $50 \mu F \text{ cm}^{-2}$, which was 10 times smaller than the calculated value for CPE$_{film}$ under $-0.30$ V versus SCE applied ($500 \mu F \text{ cm}^{-2}$).

In contrast to other conductive polymeric films, such as PANI-based polymers, which exhibit charge loading in anodic potentials, the nanocomposite poly(azo-BBY)-rGO film exhibits charge loading behavior only under negative potentials. This phenomenon is indicative of the charge loading mechanism of the poly(azo-BBY)-rGO nanocomposite film through protons that are present in solution. In some instances, the $\alpha_{film}$ values were close to 0.5, indicating a change in the equivalent circuit model configuration where the CPE element is replaced by the Warburg element. At an applied potential of $+0.30$ V versus SCE, the polymer charge balance is performed by $Cl^-$ anions, which exhibit a lower diffusion coefficient than $H^+$. In addition, the larger hydrated ionic radius results in greater resistance to access the inner parts of the film through the nanocomposite pores.

Time Reduction on Graphene Oxide Layers. It is well known that graphene oxide is partially reduced during the electrodeposition process, thus requiring a subsequent chemical or electrochemical approach to reduce the remaining oxidized species. For poly(BBBY)-rGO, this step was also important, and the increase in the electrochemical performance can be easily realized by cyclic voltammetry (Figure S1). However, literature studies do not address the importance of this reduction of graphene oxide sheets and only report the reduction step in the Experimental Section of the manuscript. Thus, in this work, EIS measurements were conducted to verify the influence of the electrochemical reduction process of graphene oxide sheets in the poly(azo-BBY)-rGO film.

To verify the behavior of the interfaces, spectra were obtained every 10 min, while a negative potential of $-0.30$ V versus SCE was applied to the electrode covered with the nanocomposite film (Figure S2). The equivalent circuit model for the Nyquist spectra analysis was the same as the model presented previously in the potential studies of $-0.30$ V versus ECS. The results obtained from the mathematical adjustments of the equivalent electrical circuit are shown in Figure 9. Additionally, electroreduction was monitored in real time by the chrono-impedance technique (Figure S3).
Both load transfer resistances, $R_{ct}$ and $R_{ct}^*$, stabilized after approximately 50 min. The charge transfer resistance $R_{ct}$ decreased with increasing reduction time and simultaneously increasing $R_{ct}^*$. This result corroborates the hypothesis that graphene oxide layers embedded within nanocomposite films can be reduced by applying a negative potential of $-0.30$ V (vs ECS) because of an increased conductivity compared to the nonreduced or partially reduced form.\(^8^6,^8^7\) $R_{ct}^*$ increased with increasing time of an applied potential of $-0.30$ V versus SCE. The increase of $R_{ct}^*$ may be related to two phenomena: (i) a reduced number of active azo sites inside the film (lower conductive capacity), which reduces the electronic communication in the poly(azo-BBY) film and increases the film resistance; (ii) an increased repulsion between the poly(azo-BBY) and rGO layers due to the presence of rGO layers.\(^6^5,^8^2\)

In terms of capacitance values, $C_{PE_{dl}}$ increased similarly to $R_{dl}$ because both are directly linked to the number of active species in the film. The capacitance of the film ($C_{PE_{film}}$) followed a trend of increasing load, carrying capacity for as long as 30 min, which was followed by a decrease and stabilization after 50 min, demonstrating a dependence on the load carrying capacity and the amount of oxygenated groups in the graphene oxide layers.\(^8^8\) This behavior was verified in a study conducted by Liu and Xue, in which an increase in the loading capacity of graphene oxide was observed and related to the ratio of oxygenated and reduced groups.\(^8^8\) The decrease in capacitance values is also indicative of the effective electrode reduction of graphene oxide, because reduced graphene has lower capacitance values compared to graphene oxide.\(^4^3\)

**CONCLUSIONS**

The electropolymerization technique was used to construct a thin nanocomposite film with alternating layers of poly(azo-BBY) and rGO. It was verified by UV–vis spectroscopy that the presence of graphene oxide in the polymeric structure allows to reduce the band gap energy ($E_{gap}$) between the valence band and the conduction band due to interchain space filling. Through EIS and the use of equivalent circuit models, the growth of the electrochemical layer-by-layer film could be monitored to verify the interface values as a function of the amount of electrodeposited material on the FTO electrode. It was also found that the film has high charge loading values only at negative potentials, unlike other conductive polymers, as well as significant changes in electron transfer resistance values between the reduced and oxidized forms of the film. Finally, the changes in nanocomposite film behavior were obtained as a function of graphene oxide reduction time in the nanocomposite film. The results are important for and promising for the development of intelligent materials based on azo compounds, which can be used for applications such as molecular switches because of the possibility to modulate their resistance values.

**EXPERIMENTAL SECTION**

All electrochemical measurements were performed in a conventional electrochemical cell with a SCE as the reference electrode, platinum wire as the counter electrode and a FTO electrode as the working electrode (1.0 cm²). The electropolymerization process was performed with μ-Autolab type III potentiostat/galvanostat (Eco Chemie) interfaced NOVA 2.0.
The EIS measurements were conducted in a 0.5 mol L\(^{-1}\) KCl (pH 2.0) solution, and potentials of \(-0.30\) and \(+0.30\) V versus SCE were applied at a scan rate of 10 mV s\(^{-1}\) in deaerated aqueous solution (0.1 mol L\(^{-1}\) HCl) containing 10 mmol L\(^{-1}\) of BBY (4,4\'-bis(m-phenylenebisazo)bis-m-phenylenediamine−BBY) and 1.00 mg mL\(^{-1}\) of graphene oxide (Sigma-Aldrich). After coating, the platform was cleaned abundantly with deionized water and exposed to a potential of \(-0.30\) V vs SCE. The impedance measurements were performed with an applied potential of \(-0.30\) V and \(+0.30\) V vs SCE.

Figure 9. Charge transfer resistance (\(R_\alpha\) and \(R_\alpha^*\)) (A) and capacitance values (CPE\(_{dl}\) and CPE\(_{film}\)) (B) and their respective values of \(\alpha\) (\(\alpha_{dl}\) e \(\alpha_{film}\)) (C) obtained by the mathematical adjustments of the equivalent circuit model of Figure 4C as a function of the time applied for electroreduction of graphene oxide present in nanocomposite film at an applied potential of \(-0.30\) V vs SCE.

software. The impedance measurements were performed with Palsens3 interfaced PSTrace 5.6 software. The reagents used were of high purity of \(\geq 98\%\) (Sigma-Aldrich).

The layer-by-layer film was prepared as described by Olean-Oliveira and Teixeira.\(^{58}\) At the FTO surface, potential cycles between \(-0.30\) to \(+1.00\) V (vs SCE) were applied at a scan rate of 10 mV s\(^{-1}\) in deaerated aqueous solution (0.1 mol L\(^{-1}\) HCl) containing 10 mmol L\(^{-1}\) of BBY (4,4\'-bis(m-phenylenebisazo)bis-m-phenylenediamine−BBY) and 1.00 mg mL\(^{-1}\) of graphene oxide (Sigma-Aldrich). After coating, the platform was cleaned abundantly with deionized water and exposed to a potential of \(-0.30\) V (vs SCE) in 0.50 mol L\(^{-1}\) KCl solution. For MEV and AFM comparative measurements, a single poly(azo-BBY)-rGO containing 10 mmol L\(^{-1}\) was abundantly with deionized water and exposed to a potential of 0.30 mV (vs SCE) were applied, as well as a sine wave of 10 mV in a frequency range of 50 kHz to 0.1 Hz with 10 step/dec. All spectra were recorded at 25 °C and under a N\(_2\) atmosphere. The analysis of the complex plane impedance spectra was performed by ZPlot 2.4 software.

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