International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 09 Issue 10 ǁ 2021 ǁ PP. 67-74

Optimization of the chronoamperometry deposition time to get impermeable films from resorcinol solutions

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Abstract

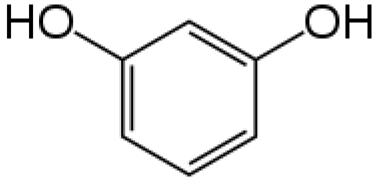
The electrodeposition of films from redox active molecules is of major interest in surface science to afford specific properties to the coated material, for instance protection against corrosion. In this framework, the electrodeposition of derivatives of phenols has been investigated mainly through potential sweep experiments like cyclic voltammetry or differential pulse voltammetry. The deposition under constant potential conditions, namely by chronoamperometry, may offer advantages as the speed of deposition and the use of cheaper instrumentation.However this deposition method has been poorly investigated. Herein, it is shown than 30 s of chronomaperomtry in the presence of a resorcinol (1,3-benzenediol)at optimal potential conditions, allows for the deposition of an insulating and impermeable film to a redox probe like potassium hexacyanoferrate.

Keywords: *Resorcinol, chronoamperometry, film deposition, electrochemical impedance spectroscopy.*

Date of Submission: 20-09-2021 Date of acceptance: 05-10-2021

I. INTRODUCTION

The electrodeposition of coatings from solutions containing molecules like aniline [1], pyrrole [2,3], mixtures of both monomers [4], catecholamines [5-7] or polyphenols [8-10] has mostly been investigated through cyclic voltammetry or differential pulse voltammetry, techniques allowing to investigate the mechanism of the electron transfer and of the chemical reactions following the oxidation-reduction processes. For industrial applications of such coatings, the electrodeposition by means of chronoamperometry, ie by applying a constant potential difference between the working electrode and the reference electrode allows to get coatings in a smaller amount of time and does not require a sophisticated equipment. Based on a previous investigation and on literature data [9], the electrodeposition of films from resorcinol (1,3-benzene diol, scheme 1) yields to coatings impermeable to a redox probe like potassium hexacyanoferrate. In our previous investigation the properties of the coatings obtained by cyclic voltammery (CV) and chronoamperometry were compared but without optimizing the deposition time by chronoamperometry. The question addressed in the present investigation is the following: what is the minimum time required to get an insulating and impermeable film from resorcinol solutions in chronoamperometry experiments performed at the potential corresponding to the oxidation peak potential recorded during CV, namely +0.75 V vs the Ag/AgCl reference electrode ?



Scheme 1: Structure of resorcinol.

II. MATERIALS AND METHODS

2.1. Chemicals and materials

All the used chemicals, anhydrous sodium acetate, resorcinol, and potassium hexacyanoferrate trihydrate were purchased from Sigma Aldrich and used without further purification. All aqueous solutions were freshly prepared before each experiment and were made from distilled and deionized water (Milli Q-Direct 8 system, Millipore). The pH of the sodium acetate buffer was adjusted to 5.0 by titration with concentrated HCl. The pH was checked with a calibrated (at pH = 10.0, 7.0 and 4.0) glass electrode connected to a pH meter

(Hannah Hi221). All the chronoamperometry experiments were performed with resorcinoldissolved at a constant concentration of 1 mg.mL^{-1} corresponding to a constant molar concentration of 9.1 x 10^{-3} mol.L^{-1}.

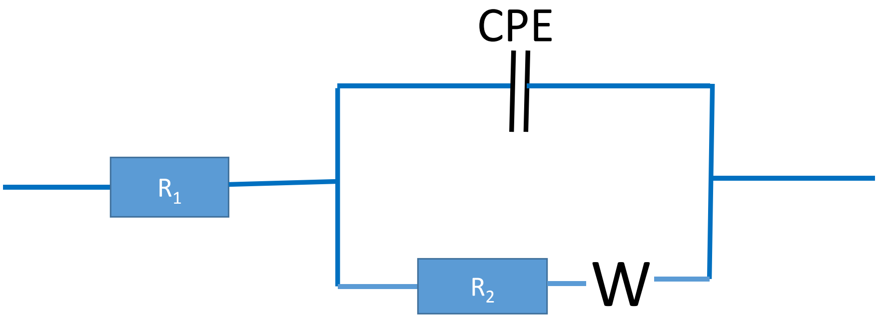
The chronoamperometry experiments and the electrochemical impedance spectra were performed in a three electrode configuration using an amorphous carbon working electrode (ref. CHI104, CHInstruments, Austin, Texas), an Ag/AgCl reference electrode (ref. CHI111) and a platinum wire (ref. CHI115) as the auxiliary electrode. These electrodes were immersed in the desired solutions and the potentials were controlled, as well as the resulting currents measured with a CHI 604B electrochemical set up (CHInstruments, Austin, Texas). Before performing chronoamperometry, the amorphous carbon working electrode was polished with a SiC coated cloth and then with two alumina slurries (1 and 0.1 µm in diameter, Escil, Villeurbanne, France). Finally, the electrodes were rinsed with ethanol, distilled water and sonicated two times (two minutes) in a bath of distilled water. The quality of this polishing and cleaning steps was verified by cyclic voltammetry (CV) in a 1 mM hexacyanoferrate solution at a potential sweep rate of 100 mV.s^{-1} between -1.0 and +1.0 V vs Ag/AgCl. The polishing-cleaning process was satisfactory when the potential difference between the oxidation and reduction peak was lower than 80 mV, the theoretical value for a reversible one electron process being 59 mV at 298 K [11].

2.2. Electrochemical measurements

The chronoamperometric deposition of coatings from resorcinol containing solutions (1mg.mL^{-1} in the presence of 50 mM sodium acetate buffer) was performed at a constant potential of +0.75V vs Ag/AgCl and for durations between 20 and 1000s. The choice of a deposition potential of +0.75V vs Ag/AgCl corresponds to the maximum of the oxidation current recorded during CV scans in the presence of resorcinol solutions at the same pH value as shown in a previous investigation [12]. After each deposition experiment, the electrode was rinsed with sodium acetate buffer and a CV cycle was performed in the presence of this buffer at a potential sweep rate of 100 mV.s^{-1}. These experiments were performed to check for the occurrence of film deposition. To this aim, the obtained CVs were compared to the capacitive curve, obtained in the same conditions, on the polished electrode. If the area under such a curve, namely the total accumulated charge, increases compared to the capacitive CV scan performed in the same conditions but on the polished electrode, this is an indication of effective film deposition. But the conformal character of this film cannot be inferred from such an experiment.

To that aim, the working electrode was immersed again in the 1mM $K_4Fe(CN)_6$ solution and the potential scanned at 100 mV.s^{-1}(between -1.0 and +1.0 V vs Ag/AgCl) to check for the decrease of the faradic current with respect to the freshly polished electrode. In particular a strong reduction of this current shows that the deposited film becomes progressively impermeable to the redox probe. It is totally impermeable when the CV in the presence of the external redox probe becomes undistinguishable from the CV performed on the coating but in the absence of the redox probe.

The electrochemical impedance spectrum of the coating was then measured in the presence of the $K_4Fe(CN)_6$ solution at a constant potential corresponding to the oxidation peak current of the redox probe on the polished and uncoated electrode. A sinusoidal wave of 5 mV in amplitude and with a frequency changing from 10^{5} to 10^{-2} Hz (12 frequency values per decade) was superimposed on the constant applied potential. The obtained impedance spectra were the fitted with a frequency dependent function corresponding to a Randless equivalent circuit (Scheme 2). The fits were performed with the EIS analyser software freely available on the Internet.



Scheme 2: Representation of the Randless equivalent circuit used to fit the electrochemical impedance spectra of the resorcinol based films. R_1 and R_2 correspond to the resistance of the electrolyte solution and to the resistance to the electron transfer across the deposited film respectively. *CPE* is a constant phase element whereas *W*, the Warburg element, represents the resistance of the film to mass transport to the electrode.

III. RESULTS AND DISCUSSION

The current corresponding to the oxidation of resorcinol in conditions of chronoamperometry at a contant potential of +0.75V vs Ag/AgCl is plotted in Figure 1 as a function of the duration of the experiment. In all performed experiments, the current rapidly decreases, overlap after 1s of chronoamperometry, and tend to vanishingly small currents (lower than 10^{-2} µA) at long times. This last finding exemplifies a reduced access of the solubilized resorcinol to the electrode surface where the oxidation process and hence the electron transfer occurs. This small efficiency of electron transfer, already perceptible after 1s of chronoamperometry, reflects the deposition of an insulating film on the electrode surface. The formation of coatings from resorcinol by deposition under potential sweep conditions (CV) is well known from the literature [9].

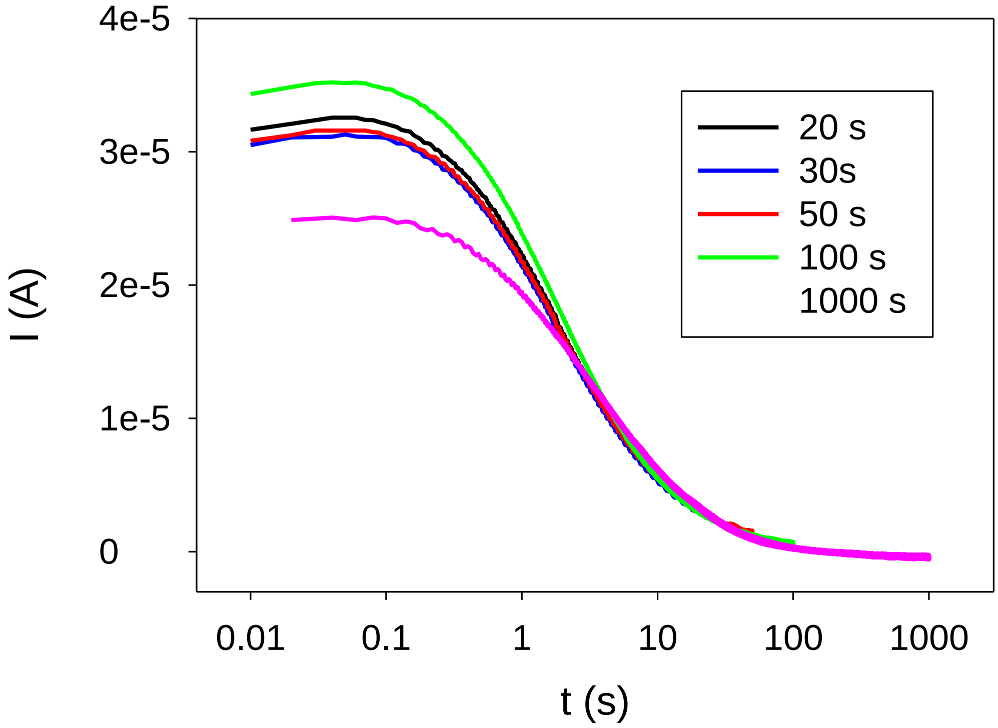


Figure1: Oxidation current of resorcinol (1 mg.mL^{-1}) in chronoamperometyry conditions at +0.75 V vs Ag/AgCl for different durations (as indicated in the inset).

Immediately after the chronoamperometry experiment, the resorcinol containing solution was discarded, the working electrode was rinsed with sodium acetate buffer and a CV cycle was performed at a sweep rate of 100 mV.s^{-1} (Figure 2). Whatever the duration of the chronoamperometry, from 20 to 1000s, the area under the CV curve (performed in the absence of an added redox probe) is significantly larger than the area under the corresponding curve acquired on the polished electrode. This means that the electrode-solution interface has accumulated more charges, has an increased capacitance, and shows that a film has been deposited. In addition the CV curves acquired after chronoamperometry in the presence of dissolved resorcinol show the presence of two well defined oxidation peaks at about +0.4 and +0.75V vs Ag/AgCl. This shows that the obtained deposit is electroactive and contains moieties able to undergo further oxidation. At least one of these two oxidations is irreversible because the CV displays only one broad and small reduction wave centered at around 0V vs Ag/AgCl. This may well explain the surprising reduction in the oxidation current, and hence also in the whole area under the CV curves acquired as a function of increasing deposition time by chronoamperometry. One would have expected a progressive increase in the area under these curves after prolonged electrodeposition when the amount of deposited material increases. The contrary is observed (arrow in Figure 2) and it is assumed that under application of a constant potential of +0.75V vs Ag/AgCl as in the chronomaperometry experiment, the film not only forms but part of the deposited molecules immediately undergo an irreversible oxidation process and cannot be detected anymore by CV after the end of the chronoamperometry step. Indeed, after a constant deposition time, when several successive CVs are performed at a sweep rate of 100 mV.s^{-1} in the presence of sodium acetate buffer only, the intensity of the oxidation wave (between +0.2 and +1.0 V) progressively decreases. This has also been observed when the deposition of the resorcinol based film is itself performed by CV [12].

In addition, the reduction current of oxygen dissolved in water (the experiments were performed in solutions that were not degassed) is shifted to more negative potentials when the electrode is covered with a resorcinol based coating in comparison to the reduction peak current measured on the polished but uncoated electrode. This shows that the coating hinders the electron transfer from the electrode to the dissolved oxygen.

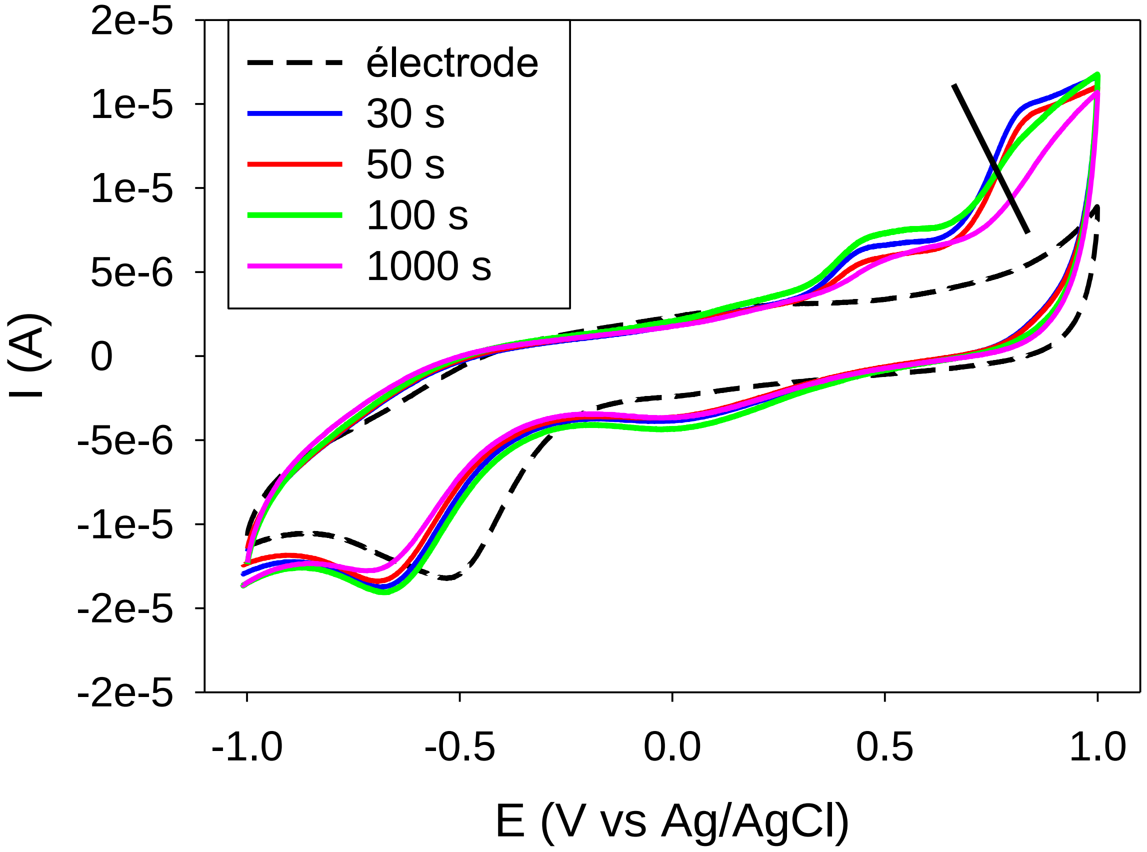


Figure 2: CV curves of the resorcinol based deposits (after a duration indicated in the inset) as obtained under a potential sweep rate of 100 mV.s^{-1} in the absence of an external redox probe. The arrow indicates the evolution of these CV curves when the duration of the electrodeposition under chronoamperomery conditions at +0.75 V vs Ag/AgCl increases.

The hindrance of the diffusion of solutes to the electrode to undergo a redox process there has also been investigated for dissolved potassium hexacyanoferrate (Figure 3). After 20 s of chronomaperometry, the oxidation of hexacyanoferrate is only slightly reduced with respect to the oxidation current measured on the polished electrode. In addition, the oxidation and the reduction peak of the redox probe are shifted anodically and cathodically by about 50 mV respectively. This indicates that hexacyanoferrate anions have still access to the electrode but the presence of an already present resorcinol based coating makes the oxidation and reduction more difficult, ie requires more energy (the potential scale is also an energy scale). However, when the duration of the chronoameromerty in the presence of resorcinol is increased from 20 to 30s, the oxidation current of hexacyanoferrate measured in the subsequent CV experiments is decreased dramatically and is equal to the oxidation current measured in the absence of the added redox probe (curves shown in Figure 2). The same absence of oxidation and reduction current attributed to hexacyanoferrate was found when the duration of the chronoamperometry was increased from 30 to 1000s. This means that no electrons can be exchanged anymore between the dissolved anions and the electrode. This may either be due to the very low electrical conductivity of the resorcinol based film and/or to the absence of pores large enough to allow for hexacyanoferrate anions to reach the electrode. The important point is a major change undergone in the electrochemical properties of the resorcinol based films when the deposition time is increased from 20 to 30s (Figure 3). The assumption is made that the film is made from islands of resorcinol based material that undergo a sudden coalescence between 20 and 30 s of application of 0.75V vs Ag/AgCl to yield a conformal and homogeneous film. This transition from island deposition to an homogeneous film will be investigated in future studies using *in situ* Atomic Force Microscopy in an electrochemical cell.

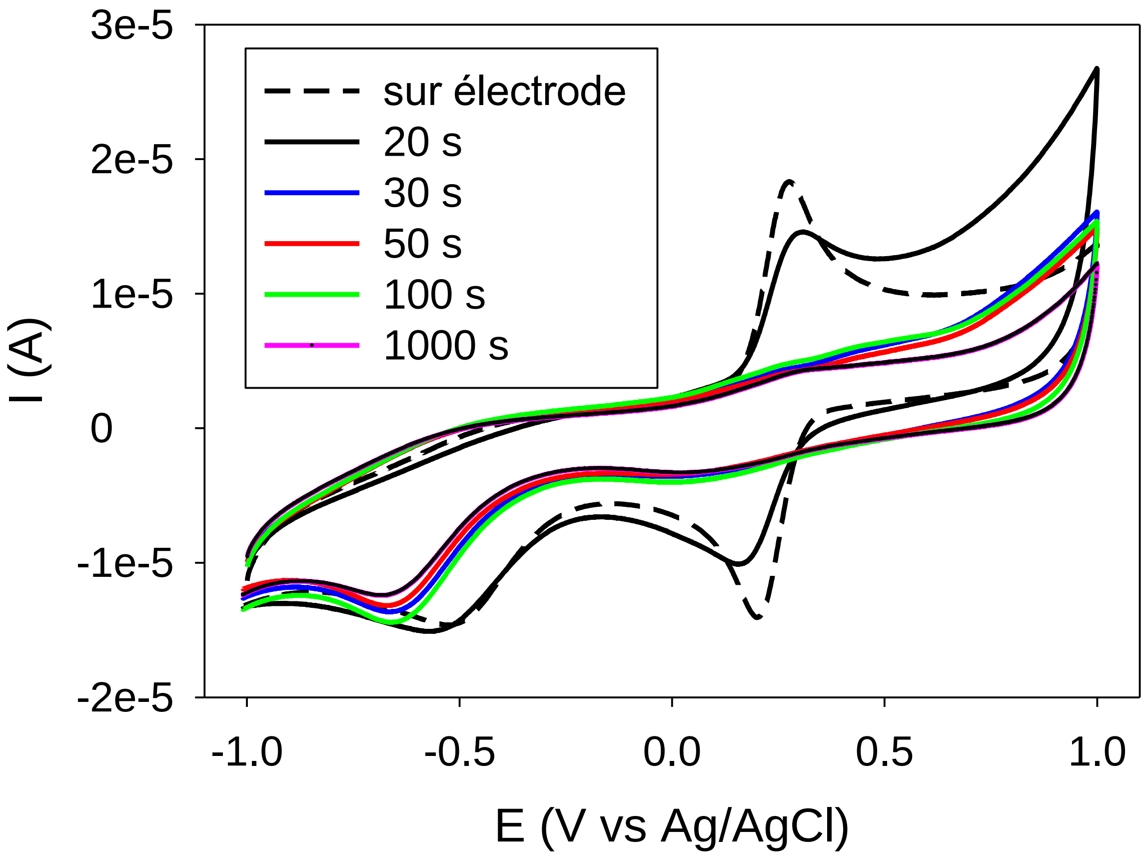


Figure 3: CV curves of the resorcinol based deposits (after a duration indicated in the inset) as obtained under a potential sweep rate of 100 mV.s^{-1} in the presence of 1mM $K_4Fe(CN)_6$ added as an external redox probe.

Electrochemical impedance spectra of the obtained coatings (produced from chronoamperometry durations between 20 and 1000 s) were acquired in the presence of potassium hexacyanoferrate in the frequency range between 10^5 and 10^{-2} Hz (Figure 4A). In agreement with the transition expected from islands to an homogeneous coating, anticipated on the basis of the strong reduction in the oxidation-reduction current of hexacyanoferrate anions (Figure 3), the real and imaginary parts of the electrochemical impedance undergo a strong increase when the deposition time is increased from 20 to 30s. However, for longer deposition times, the real and imaginary parts of the impedance continue to increase but in a less marked manner. All the electrochemical impedance spectra, represented here in the form of Nyquist plots, could be fitted with a model describing the electrochemical behavior of a Randless equivalent circuit (Scheme 2). The good quality of the fits is exemplified in Figure 4B for the impedance spectrum acquired on the film produced after 20s of chronoamperometry in the presence of the resorcinol solution.

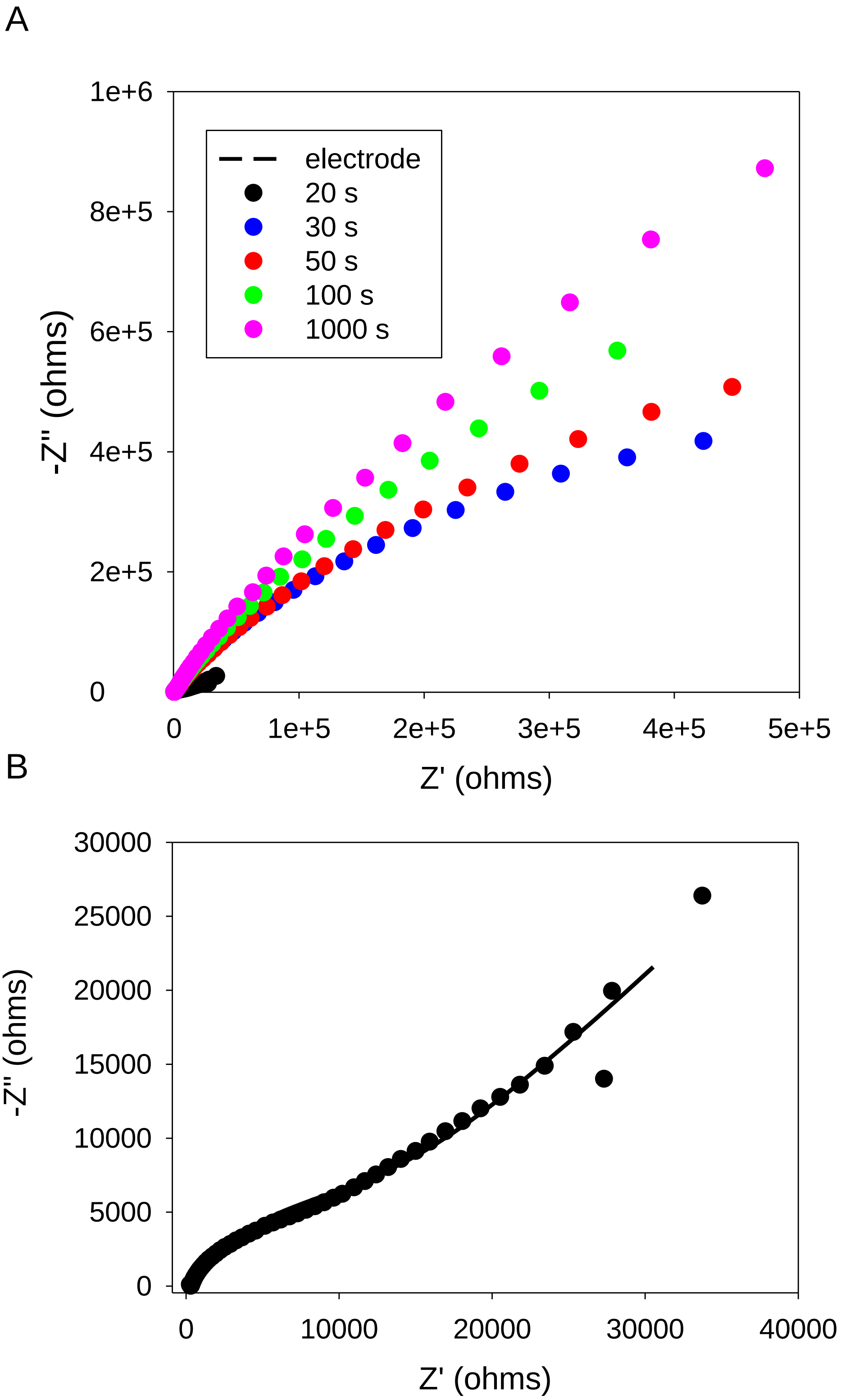


Figure 4:A: Electrochemical impedance spectra of resorcinol based films obtained after Δt seconds (see inset) of chronoamperometry at +0.75 V vs Ag-AgCl. The impedance spectra wereacquired in the presence of 1mM $K_4Fe(CN)_6$.

B: Fit (full black line) of the electrochemical impedance spectrum of the resorcinol based film obtained after 20 s of chronoamperometry using the model corresponding to the Randless equivalent circuit (Scheme 2).

The model corresponding to the Randless equivalent circuit (Scheme 2) implies the use of 5 fitting parameters. The values calculated for R_1, the resistance of the electrolyte solution was stable, 270±25 Ω.cm²from one experiment to the other (as expected) and independent from the time of the deposition process performed by chronoamperometry. The values of the two fitting parameters corresponding to the constant phase element (*CPE* in Scheme 2), namely the specific capacity and the *n* parameter (reflecting the deviation from the behavior of an ideal capacitor) do not show a systematic variation with the deposition time and are close to 10^{-5} F.cm^{-2} and 0.80 respectively (data not shown). More interesting are the variation of the values of the R_2 and *W* parameters, reflecting the resistance to the electron transfer across the film and the resistance attributed to the diffusion of the redox probe through the film respectively, with the duration of the deposition process. R_2 increases by almost two orders of magnitude when the duration of the chronoamperometry increases from 20 to 30s but stays almost unaffected for films obtained after longer deposition times (Figure 5). The Warburg impedance however increases progressively when the deposition time is increased reflecting a lower probability of the redox probe to come in direct contact with the electrode surface by a diffusion process through the coating.

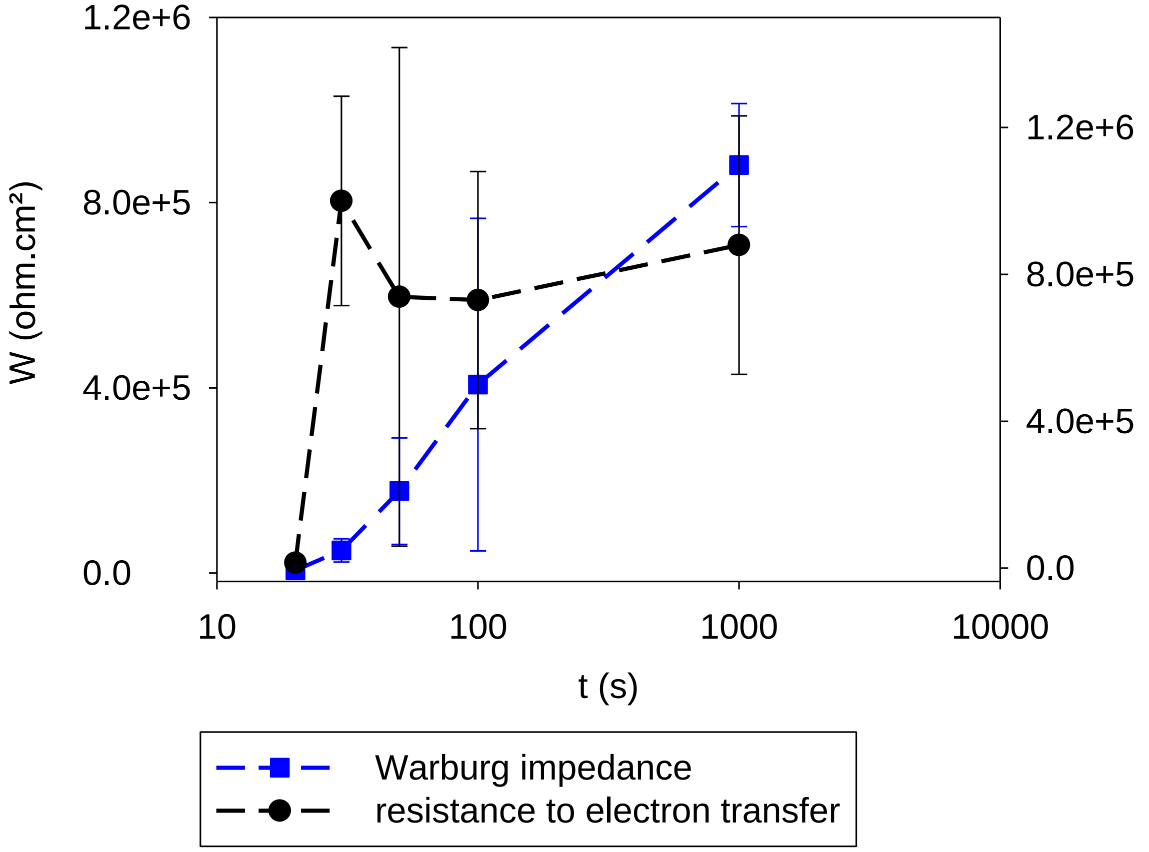


Figure 5: Evolution of the resistance to the electron transfer (black circles and black dashed line) and of the Warburg impedance (blue squares and blue dashed lines) as obtained bit fitting a model corresponding to the Randless equivalent circuit to the impedance spectra of the resorcinol based films as a function of the deposition time (chronoamperometry at +0.75 V vs Ag/AgCl). The error bars correspond to one standard deviation on the fitted values as given by the EIS analyser software.

IV. CONCLUSIONS

Chronomaperometry performed for resorcinol containing solutions at the amorphous carbon-solution interface and at a potential corresponding to the oxidation peak current measured by CV, namely +0.75 V vs Ag/AgCl, allows for the deposition of insulting and homogeneous films. An abrupt transition from a film permeable to hexacyanoferrate anions to an impermeable film occurs for a deposition time between 20s and 30s. This may well reflect a transition from an island like morphology to a conformal and homogeneous film. The morphology of the resorcinol based films as a function of the deposition time by chronoamperometry will be investigated in a future investigation. The electrochemical impedance spectroscopy experiments are in agreement with the CV experiments performed in the presence of potassium hexacyanoferrate, namely that a highly insulating and impermeable coating is formed after only 30s of chronoamperometry at +0.75V vs Ag/AgCl. Such an efficient deposition process from inexpensive and commonly available molecules may allow interesting applications for the protection against corrosion if such coatings remain adherent to the surface of the tested metals.

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