

## Full Paper

# Characterization of Carbon Film Electrodes for Electroanalysis by Electrochemical Impedance

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## Abstract

The interfacial behavior of electrodes fabricated from carbon film resistors of 2 and 20  $\Omega$  in supporting electrolyte solutions of varying pH used in electroanalytical experiments has been characterized by electrochemical impedance spectroscopy with complementary cyclic voltammetric experiments. Equivalent circuits are proposed to fit the experimental data and the influence of electrode pretreatment has also been investigated.

**Keywords:** Electrochemical impedance, Carbon film electrodes, Potential window, Cyclic voltammetry

## 1. Introduction

Carbon is a widely used material for electrodes and electrode substrates [1]. Of the different forms of carbon, that most used is glassy carbon due to its low permeability to gases, low porosity, hardness, good electrical conductivity, inertness and good positive potential range. However, the development of new solid carbon-based electrode materials with wider potential windows is important in order to extend the range of accessible applied potentials; they should also give a fast response and require a minimum of pretreatment. For example, glassy carbon doped with heteroatoms such as nitrogen, silicon and fluorine can improve the potential window [2]. Moreover, an increase of potential window in both positive and negative directions has been observed with boron-doped diamond electrodes [3–7], and with nitrogen-incorporated tetrahedral amorphous carbon electrodes [8].

Carbon film electrodes also show promise and represent another alternative. They have been fabricated by pyrolysis of organic precursors [9] and of methane [10]. The use of magnetron sputtering in the presence of nitrogen has been shown to lead to nitrogen doped diamond-like carbon film electrodes: characterization has been carried out and electroanalytical applications illustrated [11–13]. Sputtered amorphous carbon films have also been characterized electrochemically [14].

The electrodes developed by us and described in [10] are made from carbon film electrical resistors, which are fabricated from ceramic cylinders by pyrolytic deposition of carbon from an organic compound, usually methane. These electrodes have been developed and characterized by cyclic voltammetry with standard redox couples and their application in stripping voltammetry has been demonstrated [10, 15].

Further electrochemical characterization of these electrodes is desirable, in particular in electrolytes which are commonly used in electroanalysis. This enables the choice of the best conditions for electroanalytical experiments to be carried out. This approach, using electrochemical impedance spectroscopy (EIS), was already successfully employed at glassy carbon, mercury thin film and polymer-coated electrodes in different electrolytes [16, 17]. EIS has been widely used to study interfacial processes, in order to obtain information not only about the structure and changes that may occur at the electrode-electrolyte interface, but also about reaction mechanisms and electrode kinetics [18].

In this work, electrodes were made from 2  $\Omega$  and 20  $\Omega$  carbon film resistors and after initial characterization of the potential window by cyclic voltammetry (CV) were examined by electrochemical impedance spectroscopy (EIS) before and after pretreatment conditioning by potential cycling in perchloric acid. Deductions are made concerning the interfacial region in different electrolytes and the influence of applied potential and of the carbon surface structures. This can be important when it is required to identify in what potential regions the electrode surface is electroactive and how electrode pretreatment can influence the electrode processes which are being studied.

## 2. Experimental

### 2.1. Preparation of the Working Electrode

The carbon film resistors (2 and 20  $\Omega$  nominal resistance) are fabricated from ceramic cylinders of length 0.4 cm and external diameter 0.15 cm by pyrolytic deposition of carbon in a furnace at 1100 °C from methane in a nitrogen atmosphere within a slowly rotating quartz bottle, as

described in more detail in [10], and were provided by Prof. H.-D. Liess. The typical thickness of the carbon films was 15  $\mu\text{m}$  for 2  $\Omega$  resistances and 5  $\mu\text{m}$  for 20  $\Omega$  resistances. Each resistance has two tight-fitting metal caps linked to wires as external contact. To make the electrodes one of these metal caps was removed and the other was protected by normal epoxy resin, the contacting wire being sheathed in plastic. The exposed electrode geometric area was ca. 0.20  $\text{cm}^2$ .

Electrochemical pretreatment consisted of cycling the electrode 3 times in 0.1 M perchloric acid solution between potential limits defined by a maximum current of  $\pm 1$  mA at a scan rate of 100  $\text{mV s}^{-1}$  starting at 0.0 V (vs. SCE) in the positive direction [10, 15].

## 2.2. Instrumentation

Cyclic voltammetry experiments were done using a BAS CV-50W analyzer (Bioanalytical Systems, USA) with CV-50W 2.1 software.

Computer-controlled impedance measurements were carried out using a Solartron 1250 Frequency Response Analyzer coupled to a Solartron 1286 Electrochemical Interface (Solartron Analytical, UK), with ZPlot 2.4 software. A sinusoidal voltage perturbation of rms amplitude 10 mV was applied, scanning from 65 kHz to 0.1 Hz with 10 measurement points per frequency decade. Fitting to equivalent circuits was carried out with ZView 2.4 software.

Measurements were made in a glass cell containing a platinum foil auxiliary electrode and a saturated calomel electrode (SCE) as reference.

## 2.3. Reagents and Solutions

All solutions were made from analytical grade reagents and Milli-Q ultrapure water (resistivity  $\geq 18$   $\text{M}\Omega\text{ cm}$ ). Solutions used as supporting electrolytes were 0.1 M  $\text{CH}_3\text{COOH}/\text{NaCH}_2\text{COO}$  buffer (pH 4.4), 0.1 M  $\text{NaClO}_4$  (pH 5.4) and 0.2 M  $\text{H}_3\text{BO}_3$  in 0.1 M KCl pH 7.2 (adjusting with 1 M NaOH).

Experiments were carried out at  $24 \pm 1$   $^\circ\text{C}$ , usually without the removal of oxygen. When required, in impedance experiments, nitrogen was bubbled through the solutions for 10 min prior to recording of spectra.

## 3. Results and Discussion

Before characterization by EIS, it was necessary to examine the electrochemical behavior of the carbon film electrodes by cyclic voltammetry before and after surface pretreatment in the various electrolytes. This information is used to ascertain the potential window and which potentials should be used for the impedance measurements.

### 3.1. Cyclic Voltammetry Experiments

Cyclic voltammetry was used to investigate the potential window of the electrodes in different electrolytes. The best criterion for wide applicability, and usually good performance, of electrodes is a wide usable potential window with low background currents. Thus, potential scans were carried out between limits defined by a maximum current of  $\pm 1$  mA, before and after electrode pretreatment. This pretreatment consisted of cycling three times in 0.1 M perchloric acid solution and was previously found to considerably improve the width of the potential window [10].

Figure 1 shows cyclic voltammograms obtained in different electrolytes for electrodes made from 2  $\Omega$  resistors, and Figure 2 the corresponding voltammograms for electrodes made from 20  $\Omega$  resistors. Figure 1 shows that in acetate buffer there is an increase in potential window at the

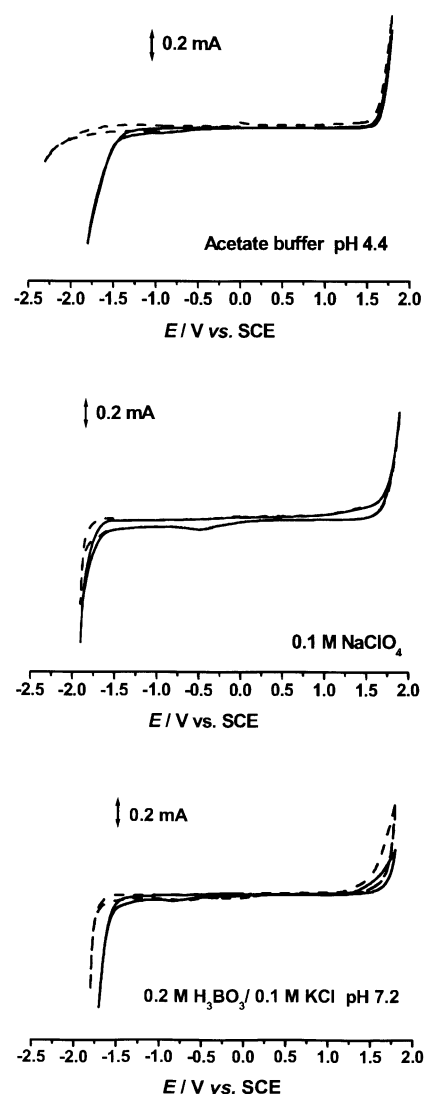


Fig. 1. Cyclic voltammograms obtained with 2  $\Omega$  carbon film electrodes in different electrolytes (—) without pretreatment and (---) after pretreatment. Electrode area 0.2  $\text{cm}^2$ . First cycle, scan rate 100  $\text{mV s}^{-1}$ .

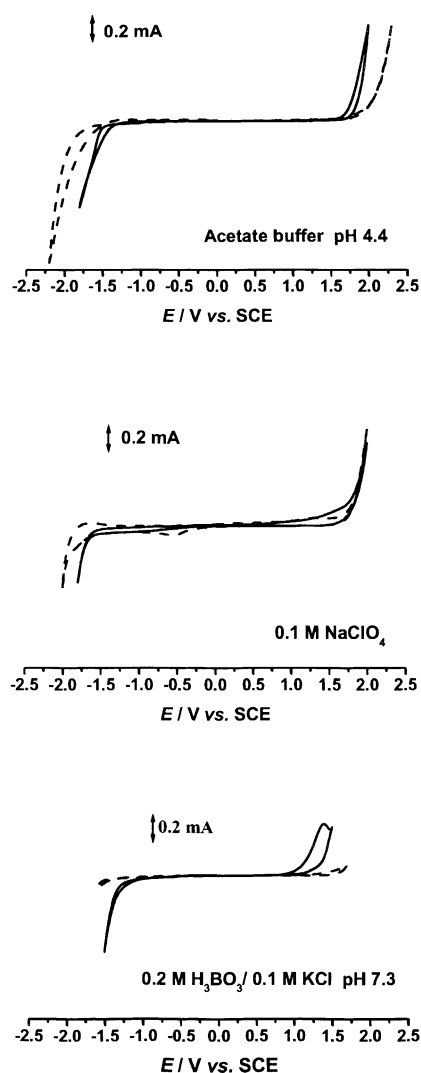


Fig. 2. Cyclic voltammograms obtained with  $20\ \Omega$  carbon film electrodes in different electrolytes (—) without pretreatment and (---) after pretreatment. Electrode area  $0.2\ \text{cm}^2$ . First cycle, scan rate  $100\ \text{mV s}^{-1}$ .

negative limit after electrode pretreatment, but there is no change for the other two electrolytes. For the electrodes from  $20\ \Omega$  resistors (Figure 2) an increase of the potential window, after electrode pretreatment, occurs for all the electrolytes. Further, in  $\text{NaClO}_4$  and acetate buffer, electrodes from  $20\ \Omega$  resistors have a larger potential window than those from  $2\ \Omega$  resistors. Repetition of these experiments with different carbon film electrodes demonstrated very good reproducibility in the CVs after pretreatment, better than without it, and no alterations with time occurred. Carbon film electrodes following pretreatment have a potential window at least as large, and usually larger than, glassy carbon after the same electrochemical pretreatment described here, particularly regarding the negative limit. Additionally, the cathodic peak due to reduction of dissolved oxygen, which is small before pretreatment, becomes even less.

Some resistors were reassembled after use and their dc electrical resistance measured. For both types of resistor the resistance increased by around 20% after pretreatment, suggesting that some of the surface had been etched away, during which the number of surface functional groups could be reduced, in this way diminishing background currents and widening the potential window.

### 3.2. Impedance Measurements

From the cyclic voltammetry experiments and the accessible potential window, it was decided to carry out electrochemical impedance experiments in the three different electrolytes ( $0.1\ \text{M CH}_3\text{COOH/NaCH}_3\text{COO}$  buffer pH 4.22,  $0.1\ \text{M NaClO}_4$  and  $0.2\ \text{M H}_3\text{BO}_3/0.1\ \text{M KCl}$  pH 7.21) at values of applied potential of  $-1.5$ ,  $-1.0$ ,  $-0.5$ ,  $0.5$ ,  $1.0$  and  $1.5\ \text{V}$  (vs. SCE). These values of potential were chosen to cover the whole potential window – the range of potentials used in stripping voltammetry and in the study of oxidation reactions. Experiments were performed before and after electrode pretreatment by potential cycling in perchloric acid. Additionally, spectra to be presented in the figures and tables were recorded in the presence of dissolved oxygen, although complementary experiments were done in the absence of oxygen and will be briefly discussed. This was the approach taken in a previous investigation of electrolyte effects using electrochemical impedance at glassy carbon electrodes [17], in order to use experimental conditions closest to those used in electroanalytical experiments such as square wave anodic stripping voltammetry [10].

#### 3.2.1. Carbon Film Electrodes – $2\ \Omega$ Resistors

Figure 3 shows some typical impedance spectra for carbon film electrodes of  $2\ \Omega$  obtained in acetate buffer over the whole potential range tested. These were obtained in the presence of dissolved oxygen. In general, electrode pretreatment led to smaller values of the impedance in the negative potential region and at very positive potentials. The same trends are seen in borate buffer, whereas in sodium perchlorate solution (pH ca. 5.5) there is a reduction in the values at all applied potentials. The general shape in the complex plane plots is that found at amorphous carbon films [14] and at glassy carbon electrodes [19]. The largest values of impedance are found in acetate buffer, which is in agreement with what was previously observed with glassy carbon and with Nafion-coated glassy carbon electrodes [17]. Unlike the others, the sodium perchlorate solution is not buffered and its pH (initially 5.4) can vary near the electrode surface, particularly after hydrogen or oxygen evolution takes place at the more extreme potentials tested.

Fitting the spectra was attempted with several equivalent circuits. It was found to be difficult to find one single relatively simple circuit which could be used to adjust most of the data at different potentials and in the three electrolyte solutions, before and after electrode pretreatment. It was therefore decided to adjust the “high” frequency feature of

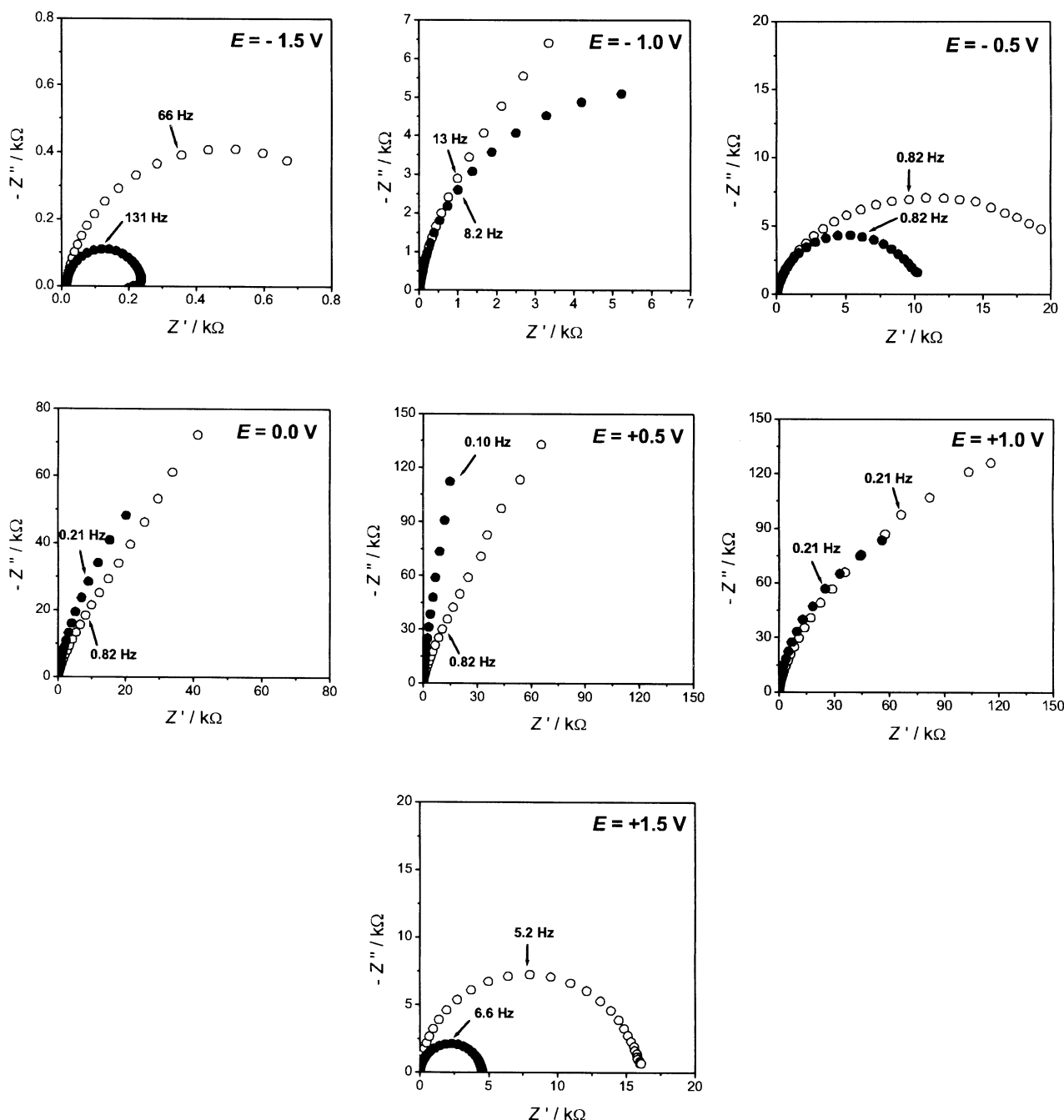


Fig. 3. Complex plane impedance plots for 2  $\Omega$  carbon film electrodes in pH 4.5 acetate buffer: (○) without pretreatment and (●) with pretreatment.

the spectra, this usually corresponding to a minimum frequency value of around 1 Hz. The circuit is shown in Figure 4 and consists of the cell resistance,  $R_{\Omega}$ , and a constant phase element,  $CPE_1$ , in parallel with a charge transfer resistance,  $R_1$ . The CPE is assumed to be a non-ideal capacitance with roughness factor  $\alpha$ , where  $\alpha$  is equal to 1 for a perfectly smooth surface and 0.5 for a porous electrode. The same circuit was used in [14] for amorphous carbon films. The results obtained from the fitting are shown in Table 1.

The cell resistance varied a little according to the electrolyte. In acetate buffer it was  $14.1 \pm 0.2 \Omega$  ( $N=16$ ) and

$13.8 \pm 0.4 \Omega$  ( $N=17$ ) before and after electrode pretreatment, respectively. In  $\text{NaClO}_4$  it was  $11.6 \pm 0.5 \Omega$  ( $N=17$ ) and  $12.0 \pm 0.5 \Omega$  ( $N=17$ ) before and after electrode pretreatment and in  $\text{H}_3\text{BO}_3/\text{KCl}$  the values were  $8.6 \pm 0.3 \Omega$  ( $N=13$ ) and  $7.2 \pm 0.2 \Omega$  ( $N=13$ ). The differences in these values mainly reflect the different ionic strengths of the solutions.

The capacitance values are lowest in acetate buffer, increasing slightly after electrode pretreatment, whereas they decrease in  $\text{NaClO}_4$  and  $\text{H}_3\text{BO}_3/\text{KCl}$  electrolytes. The lowest capacitance values were observed in acetate buffer;

Table 1. Data obtained from analysis of the impedance spectra for 2  $\Omega$  carbon film electrodes (PT: pretreatment).

	$E$ (V vs. SCE)	$C_1$ ( $\mu\text{F}$ )		$\alpha_1$		$R_1$ ( $\text{k}\Omega$ )	
		Without PT	With PT	Without PT	With PT	Without PT	With PT
0.1 M acetate buffer pH 4.5	-1.5	6.3	8.1	0.91	0.95	0.9	0.2
	-1.0	5.7	8.1	0.91	0.94	16.5	10.7
	-0.5	10.2	15.9	0.87	0.93	14.3	9.1
	0.0	10.6	25.2	0.86	0.91	85.7	172
	0.5	6.3	12.9	0.90	0.95	169	2090
	1.0	4.3	11.4	0.91	0.94	143	161
	1.5	2.3	6.0	0.95	0.97	14.7	4.1
0.1 M $\text{NaClO}_4$ pH 5.4	-1.5	36.1	29.4	0.93	0.94	0.2	0.1
	-1.0	92.2	50.2	0.85	0.90	7.6	2.5
	-0.5	137	78.1	0.80	0.85	8.5	2.8
	0.0	65.1	39.2	0.88	0.90	410	28.1
	0.5	25.9	17.2	0.94	0.96	859	26.6
	1.0	20.5	13.2	0.94	0.96	128	25.2
	1.5	16.5	13.3	0.94	0.96	1.5	0.6
0.2 M $\text{H}_3\text{BO}_3$ / 0.1 M KCl pH 7.2	-1.5	48.6	18.8	0.88	0.94	0.1	0.1
	-1.0	26.5	15.9	0.91	0.94	7.7	9.0
	-0.5	63.6	37.6	0.89	0.93	3.5	3.3
	0.0	70.4	35.8	0.84	0.92	183	120
	0.5	32.4	18.4	0.89	0.96	281	590
	1.0	24.0	15.8	0.90	0.95	41.0	81.0
	1.5	15.2	12.1	0.93	0.95	0.4	0.3

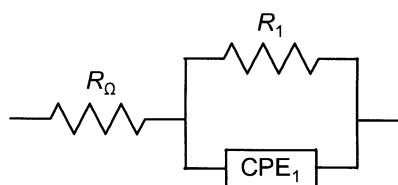


Fig. 4. Equivalent circuit used for fitting the impedance spectra at carbon film electrodes.

this may be related to its lower ionic strength, and a less compact double layer.

There is no significant difference in the roughness factor,  $\alpha$ , in the three electrolytes;  $\alpha$  values increase slightly after electrode pretreatment, which means that this probably leads to a slightly smoother electrode surface, as would be expected after some etching of the surface (see previous subsection). The values of around 0.9 can be compared with those of between 0.7 and 0.8 at glassy carbon electrodes in  $\text{KNO}_3/\text{HNO}_3$  and acetate buffer electrolytes [12].

The lowest  $R_1$  values at the more extreme potentials of  $-1.5$  V and  $+1.5$  V are related with the fact that hydrogen and oxygen evolution, respectively, are commencing at these potentials and so some electrode reaction occurs, also demonstrated by the semi-circular form of the spectra. This is in agreement with the cyclic voltammograms in Figure 1. There are also small peaks at  $+1.0$  V, not visible in Figure 1 owing to the current scale, which are attributed to oxide formation, and between  $-0.5$  V and  $-1.0$  V, due to reduction of oxide and dissolved oxygen. The latter leads to smaller impedance values than those obtained at the other potentials, whereas oxide formation has no effect since

it has already occurred before the spectrum is recorded. The voltammograms suggest that between 0.0 V and  $+1.0$  V there is no electron transfer process, and therefore higher values of  $R_1$  are obtained. In general, the  $R_1$  values decrease after electrode pretreatment (easier electron transfer), except in acetate buffer at intermediate potentials. This fact shows the importance of the effect of chemical groups of the surface and in the interfacial region on the charge transfer rate.

Removal of oxygen has an influence at negative potentials, corresponding to potentials where oxygen is reduced. The shape of the complex plane spectra is the same, so that they can be analyzed by the same equivalent circuit. Capacitances increase slightly, by about 20%, and values of  $R_1$  increase by a factor of 2 to 3 (data not shown). This is similar behavior as observed at glassy carbon electrodes [17].

### 3.2.2. Carbon Film Electrodes – 20 $\Omega$ Resistors

Figure 5 shows some impedance spectra for carbon film electrodes of 20  $\Omega$  obtained in acetate buffer electrolyte. As for the 2  $\Omega$  electrodes, pretreatment led to smaller values of the impedance in the negative potential region and at very positive potentials. The same trends are seen in borate buffer, whereas in sodium perchlorate solution (pH ca. 5.5) there is a decrease in the values at all applied potentials. After removal of dissolved oxygen, the spectra before pretreatment at potentials less than 0.0 V were very irreproducible, reflecting the rather unstable nature of the surface processes and possible localized heterogeneities in surface composition and structure. Indeed, this is reflected

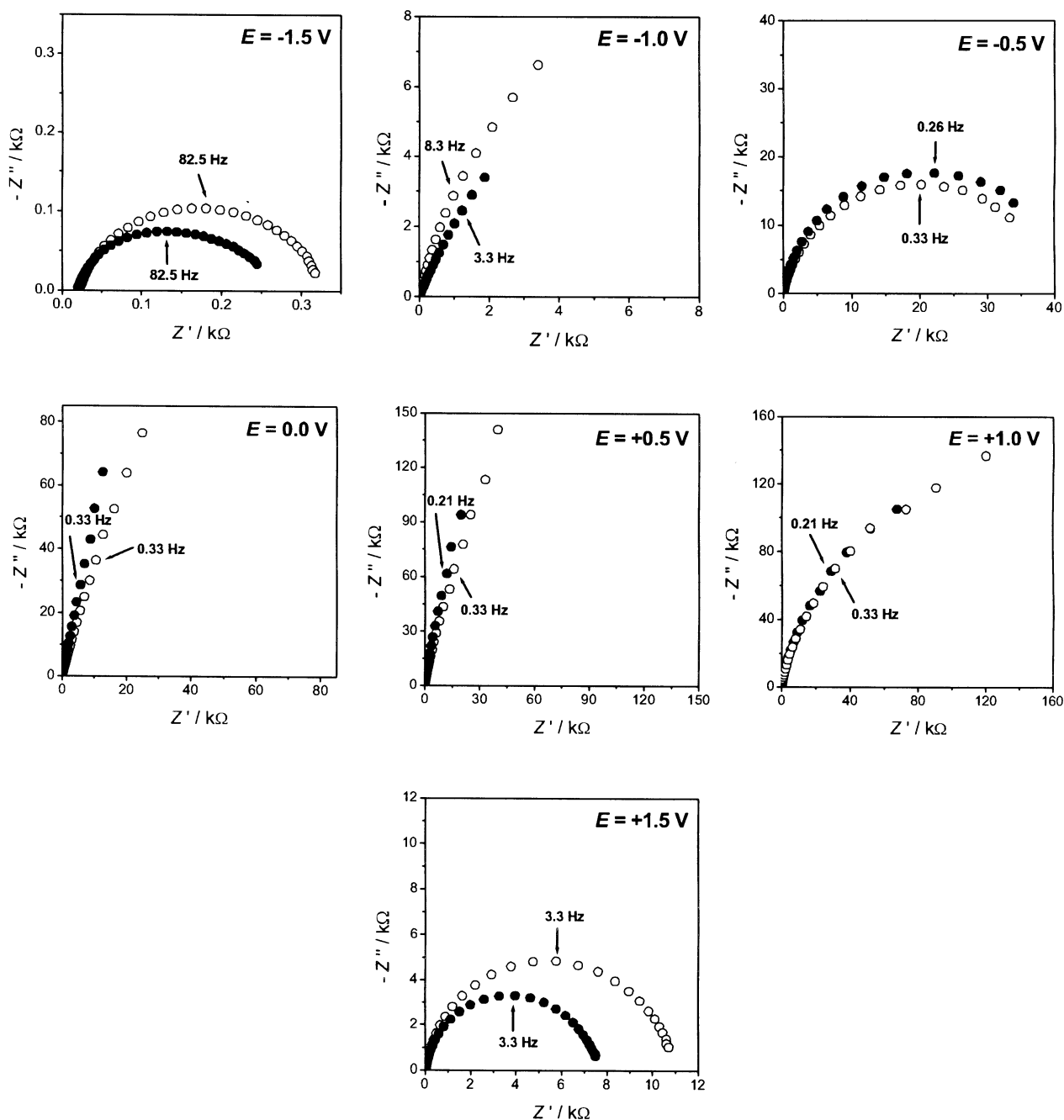


Fig. 5. Complex plane impedance plots for 20  $\Omega$  carbon film electrodes in pH 4.5 acetate buffer: (○) without pretreatment and (●) with pretreatment.

in the generally smaller values of the roughness exponent  $\alpha$ , see below. Following pretreatment, the impedance values obtained were similar to those in the presence of oxygen except in perchlorate solution, where they were higher. This may reflect the lack of control of pH near the electrode surface.

The same equivalent circuit was used for fitting the spectra, and was successful for all cases except, after pretreatment, at 0.0 V and 0.5 V applied potential. The values of  $R_1$  obtained were so large that effectively the resistance does not exist, showing that in these experimental

conditions there is essentially capacitive behavior and the surface is electrochemically inert. Table 2 summarizes the values for the various circuit parameters.

Regarding the cell resistance,  $R_\Omega$ , values found were  $23.2 \pm 0.6 \Omega$  ( $N=20$ ) and  $20.2 \pm 0.7 \Omega$  ( $N=18$ ) in acetate buffer before and after pretreatment, respectively,  $13.8 \pm 1.4 \Omega$  ( $N=17$ ) and  $13.6 \pm 0.7 \Omega$  ( $N=16$ ) in  $\text{NaClO}_4$  solution and  $10.3 \pm 0.6 \Omega$  ( $N=16$ ) and  $10.5 \pm 0.4 \Omega$  ( $N=14$ ) in borate buffer. In  $\text{NaClO}_4$  and  $\text{H}_3\text{BO}_3/\text{KCl}$  electrolytes there was no significant change in  $R_\Omega$  after electrode pretreatment, but in acetate buffer there was a small decrease.

Table 2. Data obtained from analysis of the impedance spectra for 20  $\Omega$  carbon film electrodes (PT = pretreatment).

	$E$ (V vs. SCE)	$C_1$ ( $\mu\text{F}$ )		$\alpha_1$		$R_1$ ( $\text{k}\Omega$ )	
		Without PT	With PT	Without PT	With PT	Without PT	With PT
0.1 M acetate buffer pH 4.5	-1.5	26.7	28.2	0.76	0.79	0.3	0.2
	-1.0	11.7	14.2	0.85	0.88	23.5	53.2
	-0.5	13.8	16.1	0.86	0.88	37.6	40.2
	0.0	14.4	18.8	0.84	0.87	1850	-
	0.5	8.4	12.9	0.87	0.89	1374	-
	1.0	6.5	10.2	0.88	0.89	360	481
0.1 M NaClO <sub>4</sub> pH 5.4	-1.5	35.0	93.3	0.84	0.80	0.1	0.2
	-1.0	44.6	108	0.83	0.84	3.5	3.9
	-0.5	47.8	165	0.81	0.77	7.4	7.5
	0.0	83.8	111	0.79	0.78	4.9	-
	0.5	46.0	47.4	0.82	0.87	175	-
	1.0	14.8	21.2	0.89	0.89	94.1	79.3
0.2 M H <sub>3</sub> BO <sub>3</sub> / 0.1 M KCl pH 7.2	-1.5	31.8	49.8	0.75	0.73	0.1	0.1
	-1.0	20.5	31.4	0.78	0.78	12.5	25.9
	-0.5	15.5	30.4	0.81	0.81	17.7	22.3
	0.0	12.5	23.2	0.82	0.81	872	-
	0.5	10.8	14.1	0.82	0.85	251	-
	1.0	24.4	11.4	0.76	0.86	27.2	218
	1.5	7.9	12.6	0.82	0.84	1.3	1.6

The capacitance values for all electrolytes again increase after electrode pretreatment. The lowest capacitance values were observed in acetate buffer, before and after electrode pretreatment. This fact was also observed with carbon film electrodes of 2  $\Omega$ .

With respect to the roughness factor,  $\alpha$ , the behavior observed with 20  $\Omega$  electrodes is different from that with 2  $\Omega$  electrodes. In general the  $\alpha$  values are smaller than those obtained with 2  $\Omega$  electrodes for all electrolytes at around 0.85 in acetate buffer and perchlorate electrolytes, and slightly lower at around 0.8 in borate buffer. There is no significant change in  $\alpha$  values on pretreatment, but there is a bigger variation in values than observed with 2  $\Omega$  electrodes. This suggests that 20  $\Omega$  electrodes are less reproducible and have rougher surfaces than 2  $\Omega$  electrodes, in agreement with observations from cyclic voltammetry.

With respect to the  $R_1$  values we obtained similar trends as with 2  $\Omega$  electrodes; at potentials -1.5 V and +1.5 V the lowest values can be due to the H<sup>+</sup> (aq.) reduction and to water oxidation, respectively, and at potentials -0.5 V and -1.0 V the small values of  $R_1$  can be attributed to the reduction of oxygen. Nevertheless, here there is a potential region between 0 and 0.5 V which is purely capacitive with no surface reactions occurring after electrode pretreatment.

#### 4. Conclusions

This paper has investigated the properties of carbon film electrodes made from electrical resistors in three different electrolytes which are commonly used in electroanalysis and includes the influence of electrode pretreatment. The shape

of the impedance spectra and the magnitude of the impedance can be significantly influenced by the pretreatment, and the structure of the interfacial region is shown to depend on the pretreatment as well as on the contacting electrolyte. The reactivity of the electrode surface is altered as a consequence.

Electrochemical impedance can be used to determine quantitative parameters as well as providing a fingerprint of the interfacial region. These conclusions are important for the use of these electrodes in electroanalytical experiments where it is necessary to identify in what potential regions the electrode surface is electroactive and how conditioning the surface can influence the electrode processes which are being studied.

#### 5. Acknowledgement

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#### 6. References

- [1] R. L. McCreery, *Electroanalytical Chemistry*, Vol. 17 (Ed: A. J. Bard), Marcel Dekker, New York **1991**.
- [2] N. L. Pocard, D. C. Almeyer, R. L. McCreery, T. X. Neenan, M. R. Callstrom, *J. Mater. Chem.* **1992**, 2, 771.
- [3] R. Ramesham, *Sens. Actuators B* **1998**, 50, 131.
- [4] M. C. Granger, M. Witek, J. Xu, J. Wang, M. Hupert, A. Hanks, M. D. Koppang, J. E. Butler, G. Lucazeau, M. Mermoux, J. W. Stojek, G. M. Swain, *Anal. Chem.* **2000**, 73, 3793.

- [5] J. Xu, M. C. Granger, Q. Chen, J. W. Stojek, T. E. Lister, G. M. Swain, *Anal. Chem.* **1997**, *69*, 591A.
- [6] J. W. Stojek, M. C. Granger, G. M. Swain, *Anal. Chem.* **1996**, *68*, 2031.
- [7] M. C. Granger, J. Xu, J. W. Stojek, G. M. Swain, *Anal. Chim. Acta* **1999**, *397*, 145.
- [8] K. Yoo, B. Miller, R. Kalish, X. Shi, *Electrochem. Solid State Lett.* **1999**, *2*, 233.
- [9] A. Rojo, A. Rosenstratten, D. Anjo, *Anal. Chem.* **1986**, *58*, 2988.
- [10] C. M. A. Brett, L. Angnes, H. D. Liess, *Electroanalysis* **2001**, *13*, 765.
- [11] A. Zeng, E. Liu, S. N. Tan, S. Zhang, J. Gao, *Electroanalysis* **2002**, *14*, 1110.
- [12] A. Zeng, E. Liu, S. N. Tan, S. Zhang, J. Gao, *Electroanalysis* **2002**, *14*, 1294.
- [13] A. Zeng, E. Liu, S. N. Tan, S. Zhang, S. N. Tan, P. Hing, I. F. Annergren, J. Gao, *Thin Solid Films* **2003**, *426*, 258.
- [14] Yu. Pleskov, Yu. E. Evstefeeva, M. D. Krotova, V. V. Elkin, A. M. Baranov, A. P. Dement'ev, *Diamond Rel. Mater.* **1999**, *8*, 64.
- [15] O. M. S. Filipe, C. M. A. Brett, *Talanta* **2003**, *61*, 643.
- [16] C. M. A. Brett, D. A. Fungaro, *Talanta* **2000**, *50*, 1223.
- [17] C. M. A. Brett, V. A. Alves, D. A. Fungaro, *Electroanalysis* **2001**, *13*, 212.
- [18] C. M. A. Brett, A. M. Oliveira Brett, *Electrochemistry, Principles, Methods and Applications*, Oxford University Press, Oxford, **1993**, ch. 11.
- [19] P. Heiduschka, A. W. Munz, W. Göpel, *Electrochim. Acta* **1994**, *39*, 2207.



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