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Electrochemical double-layer capacitance of graphite electrodes: preliminary results

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N. Scromeda and T.J. Katsube

Abstract: Spectral-induced-polarization (spectral-IP) characteristics of 12 pairs of graphite electrodes (diameters of 5.74 and 3.77 cm), used in the two-electrode system for taking electrical measurements of rock and soil samples, have been measured to determine their electrochemical double-layer capacitances. This is a repetition of previous measurements of similar types. The purpose was to determine if specific capacitance values can be assigned to graphite electrodes so that their effect can be subtracted from the two-electrode measurements for increased accuracy.

Electrode characteristics, represented by capacitance over electrode surface area (C_E/A) and frequency-dependence coefficient (α_E), are $1.61 \pm 0.5 \times 10^{-4}$ to $2.94 \pm 0.93 \times 10^{-4}$ F/cm² and 0.23 ± 0.02 to 0.23 ± 0.07 , respectively, for the pairs of electrodes with different diameters. These variations are too large to assign single values to each diameter of electrode. Nevertheless, the repeatability of individual electrode sets with previous measurements is extremely good with almost no errors, so values can be assigned with confidence to each specific set of electrodes.

Résumé : Afin de connaître la capacité électrique de la double couche électrochimique de 12 paires d'électrodes de graphite (à diamètre de 5,74 cm ou de 3,77 cm) utilisées pour prendre des mesures électriques sur des échantillons de roche et de sol au moyen d'un système à deux électrodes, on a déterminé leurs caractéristiques par polarisation provoquée spectrale. Des mesures semblables avaient déjà été effectuées; la présente caractérisation avait plus précisément pour objet de déterminer si on pouvait attribuer des valeurs de capacité spécifique aux électrodes de graphite, afin de soustraire leur effet des mesures à deux électrodes et ainsi d'accroître l'exactitude de ces mesures.

Les caractéristiques des électrodes sont ici représentées par la capacité par unité de surface (C_E/A) et par un coefficient de dépendance en fréquence (α_E), qui s'échelonnent respectivement de $1,61 \pm 0,5 \times 10^{-4}$ à $2,94 \pm 0,93 \times 10^{-4}$ F/cm² et de $0,23 \pm 0,02$ à $0,23 \pm 0,07$. Ces variations sont trop importantes pour que des valeurs distinctes puissent être attribuées aux électrodes de graphite selon leur diamètre. Toutefois, la reproductibilité des résultats obtenus pour un jeu particulier d'électrodes est très bonne, et presque dépourvue d'erreur, de sorte que des valeurs peuvent être attribuées avec confiance à chaque jeu donné d'électrodes.

INTRODUCTION

Spectral-induced-polarization (spectral-IP) characteristics of 12 pairs of graphite electrodes, of two different diameters (5.47 and 3.77 cm), have been measured in order to determine the permittivity or capacitance characteristics of their electrochemical double layers. This is a repetition of similar measurements (Katsube and Scromeda-Perez, 2003) previously performed on graphite electrodes with several different diameters. The purpose is to provide a basic database on the repeatability of these permittivity or capacitance values for the graphite electrodes. These data are necessary in determining the effect of graphite electrodes on measurements of soil or rock samples with a two-electrode sample-holder system, if the electrode plates are in direct contact with the sample. Spectral-IP data previously reported often include this effect, which should be eliminated from future measurements to improve their measurement accuracy. If the repeatability of the permittivity or capacitance determinations for the graphite electrodes is good, permittivity or capacitance values can be assigned to individual graphite electrodes or to each set of electrodes for elimination of their effect, without making these measurements each time a sample is measured. This paper describes and documents the results of this repeatability test.

As previously indicated (Katsube and Scromeda-Perez, 2003), a four-electrode system is often used for laboratory electrical measurements of rock or soil samples. This electrode arrangement, however, causes complications for measurements at varied frequencies or confining pressures, and makes it difficult to study the effect of different rock-forming components. For such cases, a two-electrode sample-holder system is favoured. This system, however, introduces unwanted electrode effects under certain conditions, such as for low-resistivity samples. Often, a certain frequency can be chosen to avoid the electrode effects, but usually only for single frequency measurements. High-resistivity samples often do not cause a problem of this nature. Therefore, for two-electrode sample-holder systems to cover wide ranges of frequency, confining pressure, and sample resistivity, it is necessary to subtract the electrode-capacitance effect. The theory to determine the electrode double-layer permittivity or capacitance values has previously been reported (Katsube and Scromeda-Perez, 2003).

METHOD OF INVESTIGATION

Preparation for test

Six pairs of graphite electrodes with a diameter of 5.74 cm and six pairs with a diameter of 3.77 cm were saturated in de-ionized water (18.3 M Ω •cm). Sheets of filter paper cut to the same diameter as the graphite electrodes were soaked in separate beakers in a 0.01 N NaCl solution (resistivity 7.71 Ω •m) prior to the measurements. One sheet of those filter papers was

placed between the graphite electrodes (Fig. 1a) to separate the two electrode plates and to determine their electrochemical double-layer capacitance values.

Sample holder and measuring system

The sample holder and measuring system used to obtain the data have been frequently described elsewhere (e.g. Katsube, 1975; Gauvreau and Katsube, 1975; Katsube and Walsh, 1987; Katsube and Salisbury, 1991; Katsube and Scromeda-Perez, 2003). The sample holder is a two-electrode system with stainless-steel electrodes but with graphite plates placed between those electrodes and separated by filter paper, as shown in Figure 1a. The equivalent circuit of this system is shown in Figure 1b. The C_E represents the electrode capacitance, which, in this case, is that of the two facing surfaces of the graphite plates, since they are in direct contact with the filter paper. The stray and leakage capacitances of the sample-holder system are eliminated at the time of measurement by methods previously described (Katsube and Collett, 1973; Gauvreau and Katsube, 1975).

The electronic measuring system used in this study, the Solartron Analytical SI-1260 Impedance/Gain-Phase Analyzer, is displayed in Figure 2. The constant-current source (0.1 mA) of the generator is connected to the electrode specimen through 500 Ω resistors on either side of the sample holder. Although this system is able to take measurements in a four-electrode mode, it has been used as a two-electrode system in this study.

Analytical procedure

The complex impedance (Z^*), which is used to determine the spectral-IP characteristics, is expressed by (Katsube and Scromeda-Perez, 2003)

$$Z^* = Z' + jZ'', \quad (1)$$

where Z' and Z'' are the real and imaginary impedances, respectively, and j is $\sqrt{-1}$. The imaginary impedance can be expressed by (Katsube and Scromeda-Perez, 2003)

$$Z'' = 1/(C_E \omega^a) \quad (2)$$

$$\omega = 2\pi f \quad (3)$$

$$a = 1 - \alpha_E, \quad (4)$$

where C_E and α_E are the graphite-electrode electrochemical double-layer capacitance and its frequency coefficient, respectively, and ω and f are the angular frequency and frequency, respectively. Examples of the Z'' - f relationship for the graphite electrodes are shown in Figures 3 and 4. The C_E and α_E values of the graphite plates are determined by matching a linear logarithmic curve to the Z'' - f curve (Equation 2) at the lower frequency end, as shown in Figures 3 and 4. The theory and further details of the method used to determine C_E and α_E from the Z'' - f curve are described elsewhere (Katsube and Scromeda-Perez, 2003).

EXPERIMENTAL RESULTS

Results of the spectral-IP measurements, represented in terms of complex impedance amplitude (Z^+ ; Katsube and Scromeda-Perez, 2003), real impedance (Z'), and imaginary impedance (Z''), for the 12 pairs of graphite electrodes are listed in Tables 1 to 4 for the frequency range 1 to 106 Hz. Measurements were made 24 hours after NaCl solution saturation of the filter paper, to ensure that they represent

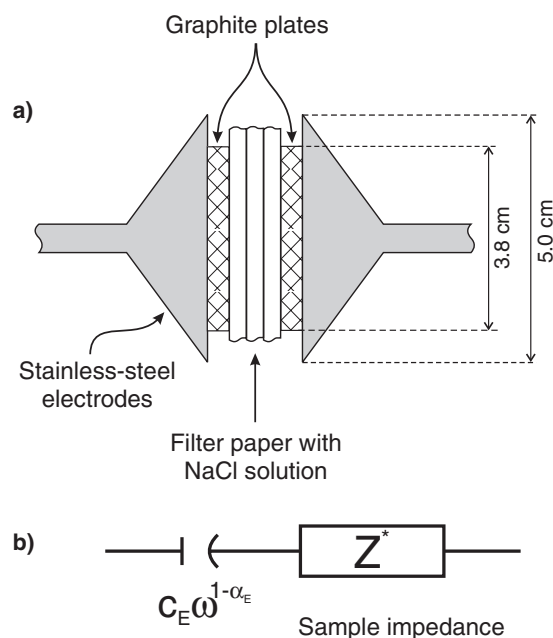


Figure 1. a) Two-electrode sample-holder system used in this study, and b) equivalent circuit of this system (Katsube, 2001). Abbreviation: C_E , electrode capacitance (graphite plate).

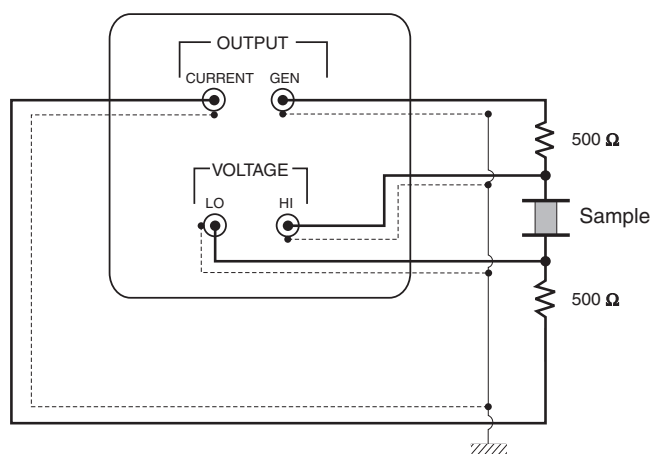


Figure 2. Electronic measuring system (Solartron Analytical 1260 Impedance/Gain-Phase Analyzer) and sample-measuring circuit used in this study.

impedance values that are stable with time (Katsube and Salisbury, 1991). Under this state, it is expected that the NaCl solution would have chemically equilibrated with all the filter paper. Capacitance per cm^2 (C_E/A) and frequency-coefficient (α_E) values for the graphite electrode pairs are listed in Table 5, where A is the area of the graphite-electrode plates. The mean (μ) and standard deviation (σ) calculated for these parameters (C_E/A and α_E) for each set of the 12 pairs of electrodes are also listed in Table 5.

The C_E/A values for the electrodes of 5.74 cm diameter are in the range 1.06×10^{-4} to 2.23×10^{-4} F/cm^2 , with a μ of 1.61×10^{-4} F/cm^2 and a σ of 0.496×10^{-4} F/cm^2 . The α_E values for the same set of electrodes are in the range 0.181 to 0.360, with a μ of 0.225 and a σ of 0.069. The 3.77 cm diameter electrodes have C_E/A values in the range 1.56×10^{-4} to

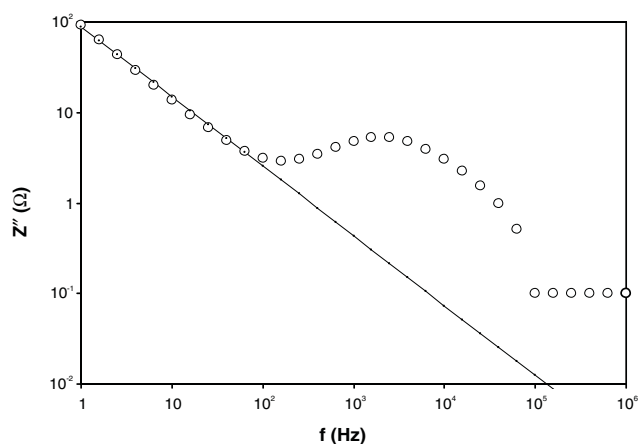


Figure 3. Example of a Z'' - f curve expressed by Equation 2 using the derived values of α_E and C_E for graphite-electrode pair 1a, where $C_E/A = 1.06 \times 10^{-4}$ F/cm^2 and $\alpha_E = 0.230$. Minor adjustments were made to these derived values in order to obtain a visual best fit with the linear section of the Z'' - f curve.

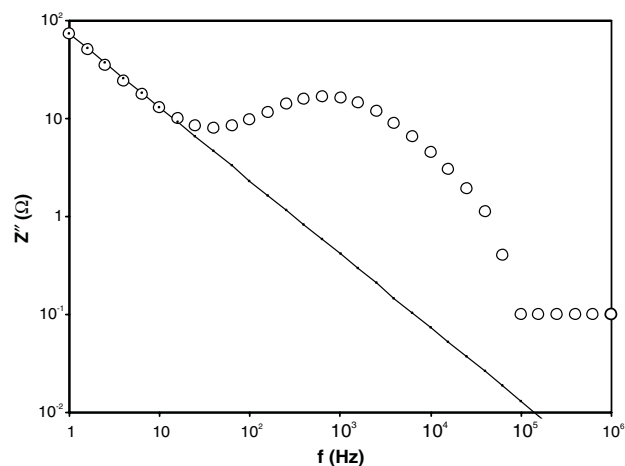


Figure 4. Example of a Z'' - f curve expressed by Equation 2 using the derived values of α_E and C_E for graphite-electrode pair 2b, where $C_E/A = 3.11 \times 10^{-4}$ F/cm^2 and $\alpha_E = 0.251$. Minor adjustments were made to these derived values in order to obtain a visual best fit with the linear section of the Z'' - f curve.

Table 1. Values of Z' , Z'' and Z^* over a frequency range of 1 to 106 Hz for graphite-electrode pairs 1a, 1b, and 1c, measured with one layer of filter paper saturated in 0.01 N NaCl.

Frequency (Hz)	Electrode pair 1a $C_E/A = 1.063 \times 10^{-4} \text{ F/cm}^2$ $\alpha_E = 0.230$ $r_D = 5.74 \text{ cm}$			Electrode pair 1b $C_E/A = 1.253 \times 10^{-4} \text{ F/cm}^2$ $\alpha_E = 0.184$ $r_D = 5.74 \text{ cm}$			Electrode pair 1c $C_E/A = 1.597 \times 10^{-4}$ $\alpha_E = 0.181$ $r_D = 5.74 \text{ cm}$		
	Z^* (Ω)	Z' (Ω)	Z'' (Ω)	Z^* (Ω)	Z' (Ω)	Z'' (Ω)	Z^* (Ω)	Z' (Ω)	Z'' (Ω)
	1	103	43.0	93.8	83.2	46.6	68.9	69.3	43.8
1.6	72.8	35.3	63.6	62.9	43.0	45.9	54.2	40.7	35.8
2.5	52.6	30.0	43.2	50.6	40.2	30.8	45.5	38.6	24.1
4.0	39.5	26.4	29.4	43.4	38.0	20.9	41.1	37.7	16.3
6.3	31.3	24.1	20.1	39.5	36.7	14.5	37.9	36.2	11.3
10	26.3	22.4	13.8	37.5	36.0	10.5	36.5	35.6	8.15
16	23.2	21.2	9.54	35.8	34.9	8.14	35.7	35.1	6.29
25	21.4	20.3	6.74	34.6	33.8	6.97	35.0	34.6	5.37
40	20.2	19.6	4.91	33.4	32.7	6.72	34.4	34.0	5.24
63	19.5	19.2	3.78	32.3	31.4	7.26	33.8	33.3	5.82
10^2	18.9	18.7	3.15	30.7	29.6	8.29	32.6	31.9	6.91
1.6×10^2	18.5	18.2	2.92	28.4	26.8	9.32	31.0	29.8	8.38
2.5×10^2	18.0	17.7	3.03	25.4	23.4	9.91	28.8	27.0	10.1
4.0×10^2	17.4	17.1	3.45	22.1	19.8	9.80	25.9	23.3	11.3
6.3×10^2	16.7	16.2	4.15	18.9	16.6	8.93	22.2	19.0	11.6
10^3	15.5	14.8	4.86	16.1	14.0	7.81	18.4	14.7	11.0
1.6×10^3	14.0	12.9	5.33	13.7	11.9	6.70	14.5	11.0	9.45
2.5×10^3	12.1	10.9	5.30	11.6	10.1	5.69	11.2	8.31	7.45
4.0×10^3	10.2	8.99	4.77	9.74	8.56	4.65	8.57	6.57	5.50
6.3×10^3	8.47	7.50	3.94	8.23	7.40	3.61	6.77	5.53	3.91
10^4	7.15	6.47	3.05	7.13	6.61	2.67	5.63	4.94	2.71
1.6×10^4	6.20	5.78	2.24	6.38	6.09	1.88	4.92	4.56	1.84
2.5×10^4	5.55	5.33	1.56	5.91	5.78	1.25	4.50	4.35	1.18
4.0×10^4	5.16	5.07	0.98	5.65	5.60	0.73	4.29	4.23	0.67
6.3×10^4	4.96	4.93	0.52	5.52	5.51	0.33	4.21	4.20	0.28
10^5	4.49	3.10	3.25	5.00	3.81	3.25	3.91	2.53	2.98
1.6×10^5	4.49	3.11	3.24	4.98	3.80	3.22	3.92	2.52	3.00
2.5×10^5	4.48	3.04	3.29	4.95	3.75	3.24	3.94	2.52	3.03
4.0×10^5	4.46	3.00	3.30	4.93	3.73	3.23	3.95	2.53	3.03
6.3×10^5	4.47	2.98	3.33	4.96	3.73	3.27	3.96	2.47	3.10
10^6	4.87	2.18	4.35	5.23	2.68	4.49	4.42	1.52	4.15

Table 2. Values of Z' , Z'' and Z^* over a frequency range of 1 to 106 Hz for graphite-electrode pairs 1d, 1e, and 1f, measured with one layer of filter paper saturated in 0.01 N NaCl.

Frequency (Hz)	Electrode pair 1d $C_E/A = 1.342 \times 10^{-4} \text{ F/cm}^2$ $\alpha_E = 0.197$ $r_D = 5.74 \text{ cm}$			Electrode pair 1e $C_E/A = 2.204 \times 10^{-4} \text{ F/cm}^2$ $\alpha_E = 0.200$ $r_D = 5.74 \text{ cm}$			Electrode pair 1f $C_E/A = 2.227 \times 10^{-4}$ $\alpha_E = 0.360$ $r_D = 5.74 \text{ cm}$		
	Z^* (Ω)	Z' (Ω)	Z'' (Ω)	Z^* (Ω)	Z' (Ω)	Z'' (Ω)	Z^* (Ω)	Z' (Ω)	Z'' (Ω)
	1	69.4	21.7	65.9	48.1	20.5	43.4	97.4	78.9
1.6	47.6	17.4	44.3	34.0	17.9	28.9	83.0	72.5	40.3
2.5	33.0	13.9	29.9	25.1	16.0	19.3	73.6	67.7	28.8
4.0	23.4	11.7	20.3	19.6	14.7	13.0	67.7	64.2	21.2
6.3	17.2	10.1	13.9	16.3	13.8	8.83	64.3	62.2	16.6
10	13.1	8.88	9.63	14.3	13.0	6.08	62.1	60.4	14.2
16	10.4	7.94	6.72	13.2	12.5	4.26	60.1	58.6	13.7
25	8.61	7.21	4.71	12.5	12.2	3.04	57.6	55.7	14.4
40	7.48	6.71	3.30	12.0	11.8	2.21	54.3	51.9	16.1
63	6.77	6.36	2.31	11.5	11.4	1.65	49.8	46.5	17.9
10^2	6.34	6.13	1.63	11.3	11.3	1.32	44.1	39.8	18.9
1.6×10^2	6.09	5.97	1.17	11.1	11.0	1.13	37.9	32.9	18.8
2.5×10^2	5.91	5.85	0.88	10.8	10.8	1.08	31.8	26.6	17.4
4.0×10^2	5.80	5.76	0.68	10.6	10.5	1.16	26.2	21.4	15.2
6.3×10^2	5.70	5.67	0.60	10.3	10.2	1.35	21.5	17.2	12.9
10^3	5.60	5.57	0.59	9.94	9.80	1.68	17.6	13.8	10.9
1.6×10^3	5.48	5.44	0.63	9.43	9.20	2.09	14.2	10.9	9.00
2.5×10^3	5.30	5.25	0.72	8.72	8.37	2.46	11.2	8.69	7.09
4.0×10^3	5.05	4.98	0.79	7.76	7.32	2.59	8.86	7.12	5.28
6.3×10^3	4.73	4.66	0.80	6.71	6.26	2.39	7.20	6.11	3.81
10^4	4.39	4.33	0.71	5.76	5.43	1.93	6.10	5.49	2.67
1.6×10^4	4.09	4.06	0.52	5.05	4.86	1.37	5.40	5.10	1.79
2.5×10^4	3.87	3.86	0.26	4.60	4.52	0.83	4.97	4.85	1.11
4.0×10^4	3.75	3.75	0.06	4.35	4.34	0.30	4.72	4.69	0.52
6.3×10^4	3.73	3.70	0.42	4.26	4.25	0.21	4.60	4.60	0.03
10^5	6.26	1.23	6.14	6.54	1.87	6.26	6.57	2.08	6.24
1.6×10^5	6.28	1.25	6.16	6.53	1.88	6.26	6.60	2.11	6.25
2.5×10^5	6.34	1.24	6.22	6.59	1.88	6.31	6.65	2.08	6.31
4.0×10^5	6.39	1.25	6.26	6.63	1.89	6.35	6.69	2.10	6.36
6.3×10^5	6.57	1.20	6.46	6.97	1.65	6.77	6.85	2.04	6.54
10^6	10.7	2.12	10.5	11.3	1.83	11.2	10.9	1.37	10.8

Table 3. Values of Z' , Z'' and Z^* over a frequency range of 1 to 106 Hz for graphite-electrode pairs 2a, 2b, and 2c, measured with one layer of filter paper saturated in 0.01 N NaCl.

Frequency (Hz)	Electrode pair 2a $C_E/A = 1.721 \times 10^{-4} \text{ F/cm}^2$ $\alpha_E = 0.235$ $r_D = 3.77 \text{ cm}$			Electrode pair 2b $C_E/A = 3.110 \times 10^{-4} \text{ F/cm}^2$ $\alpha_E = 0.251$ $r_D = 3.77 \text{ cm}$			Electrode pair 2c $C_E/A = 3.173 \times 10^{-4}$ $\alpha_E = 0.190$ $r_D = 3.77 \text{ cm}$		
	$Z^* (\Omega)$	$Z' (\Omega)$	$Z'' (\Omega)$	$Z^* (\Omega)$	$Z' (\Omega)$	$Z'' (\Omega)$	$Z^* (\Omega)$	$Z' (\Omega)$	$Z'' (\Omega)$
1	141.3	43.8	134.0	102.7	72.5	72.8	74.9	32.6	67.5
1.6	96.7	35.9	89.8	83.8	67.1	50.2	53.5	28.5	45.2
2.5	67.4	30.0	60.3	72.0	63.0	34.8	39.6	25.4	30.4
4.0	48.5	26.0	40.9	64.9	60.1	24.5	31.1	23.4	20.5
6.3	36.3	23.0	28.1	60.5	57.9	17.5	25.9	21.9	14.0
10	28.4	20.6	19.5	57.7	56.3	13.0	22.9	20.8	9.58
16	22.2	18.8	13.7	56.0	55.1	10.1	21.0	20.0	6.65
25	19.9	17.3	9.70	54.8	54.1	8.52	19.9	19.4	4.68
40	17.7	16.2	6.93	53.8	53.2	8.02	19.2	18.9	3.35
63	16.2	15.4	4.99	52.7	52.0	8.43	18.7	18.5	2.45
10 ²	15.2	14.8	3.62	51.2	50.3	9.68	18.3	18.2	1.86
1.6x10 ²	14.5	14.3	2.65	49.2	47.8	11.6	18.1	18.0	1.49
2.5x10 ²	14.0	13.9	1.95	46.2	44.1	13.9	17.8	17.8	1.29
4.0x10 ²	13.7	13.6	1.44	42.1	39.1	15.7	17.7	17.6	1.24
6.3x10 ²	13.5	13.4	1.08	37.2	33.3	16.6	17.5	17.4	1.33
10 ³	13.3	13.3	0.82	31.8	27.3	16.2	17.2	17.1	1.59
1.6x10 ³	13.1	13.1	0.65	26.1	21.7	14.6	16.8	16.7	1.98
2.5x10 ³	13.0	13.0	0.52	20.9	17.2	11.9	16.1	16.0	2.39
4.0x10 ³	12.9	12.9	0.44	16.7	14.1	9.03	15.2	15.0	2.63
6.3x10 ³	12.8	12.8	0.38	13.9	12.3	6.46	14.1	13.9	2.49
10 ⁴	12.7	12.7	0.33	12.0	11.2	4.48	13.1	13.0	2.05
1.6x10 ⁴	12.6	12.6	0.25	11.0	10.6	3.02	12.4	12.4	1.48
2.5x10 ⁴	12.5	12.4	0.12	10.3	10.2	1.95	12.0	12.0	0.92
4.0x10 ⁴	12.3	12.3	0.11	9.98	9.92	1.11	11.8	11.8	0.38
6.3x10 ⁴	12.2	12.2	0.41	9.77	9.76	0.41	11.6	11.6	0.15
10 ⁵	12.0	8.76	8.26	9.98	7.07	7.04	11.7	8.11	8.49
1.6x10 ⁵	12.0	8.77	8.24	9.99	7.07	7.05	11.7	8.10	8.45
2.5x10 ⁵	12.1	8.74	8.34	10.0	7.02	7.14	11.8	8.09	8.53
4.0x10 ⁵	12.1	8.76	8.30	10.0	6.98	7.19	11.7	8.07	8.52
6.3x10 ⁵	12.1	8.72	8.42	10.1	6.87	7.38	11.7	7.96	8.64
10 ⁶	13.2	6.44	11.5	11.5	4.80	10.5	12.8	5.95	11.3

Table 4. Values of Z' , Z'' and Z^* over a frequency range of 1 to 106 Hz for graphite-electrode pairs 2d, 2e, and 2f, measured with one layer of filter paper saturated in 0.01 N NaCl.

Frequency (Hz)	Electrode pair 2d $C_E/A = 1.560 \times 10^{-4} \text{ F/cm}^2$ $\alpha_E = 0.220$ $r_D = 3.77 \text{ cm}$			Electrode pair 2e $C_E/A = 4.069 \times 10^{-4} \text{ F/cm}^2$ $\alpha_E = 0.250$ $r_D = 3.77 \text{ cm}$			Electrode pair 2f $C_E/A = 2.823 \times 10^{-4}$ $\alpha_E = 0.238$ $r_D = 3.77 \text{ cm}$		
	$Z^* (\Omega)$	$Z' (\Omega)$	$Z'' (\Omega)$	$Z^* (\Omega)$	$Z' (\Omega)$	$Z'' (\Omega)$	$Z^* (\Omega)$	$Z' (\Omega)$	$Z'' (\Omega)$
1	155	60.1	142	66.7	31.2	59.0	86.1	35.4	78.4
1.6	109	48.8	97.0	48.2	26.0	40.6	61.0	29.2	53.6
2.5	77.6	40.6	66.2	35.7	22.2	28.0	44.5	24.8	36.9
4.0	57.3	35.1	45.3	27.5	19.5	19.4	33.4	21.5	25.6
6.3	44.1	31.2	31.2	22.1	17.5	13.5	26.1	19.1	17.8
10	35.7	28.3	21.6	18.7	16.1	9.46	21.3	17.2	12.6
16	30.3	26.2	15.1	16.5	15.1	6.65	18.2	15.9	8.88
25	27.0	24.7	10.7	15.1	14.4	4.69	16.1	14.8	6.31
40	24.8	23.6	7.66	14.2	13.8	3.33	14.8	14.1	4.50
63	23.5	22.8	5.63	13.6	13.4	2.38	13.9	13.6	3.23
10 ²	22.5	22.1	4.29	13.2	13.1	1.72	13.4	13.2	2.35
1.6x10 ²	21.8	21.6	3.46	13.0	12.9	1.25	13.0	12.9	1.75
2.5x10 ²	21.3	21.1	3.04	12.7	12.7	0.92	12.7	12.6	1.35
4.0x10 ²	20.8	20.6	2.97	12.6	12.6	0.67	12.5	12.5	1.10
6.3x10 ²	20.2	20.0	3.15	12.5	12.5	0.53	12.4	12.3	1.00
10 ³	19.4	19.1	3.50	12.4	12.4	0.42	12.2	12.2	1.01
1.6x10 ³	18.3	17.9	3.84	12.3	12.3	0.35	12.0	12.0	1.14
2.5x10 ³	17.0	16.5	3.94	12.2	12.2	0.30	11.7	11.7	1.35
4.0x10 ³	15.6	15.1	3.71	12.2	12.2	0.28	11.3	11.2	1.58
6.3x10 ³	14.4	14.0	3.28	12.1	12.1	0.27	10.7	10.5	1.68
10 ⁴	13.3	13.0	2.79	12.0	12.0	0.27	9.95	9.83	1.55
1.6x10 ⁴	12.5	12.3	2.28	11.8	11.8	0.24	9.36	9.27	1.23
2.5x10 ⁴	11.7	11.6	1.74	11.7	11.7	0.14	8.92	8.89	0.82
4.0x10 ⁴	11.2	11.1	1.15	11.5	11.5	0.07	8.66	8.66	0.37
6.3x10 ⁴	10.8	10.8	0.55	11.4	11.4	0.37	8.52	8.52	0.10
10 ⁵	10.3	7.05	7.47	11.4	7.69	8.38	9.04	5.30	7.32
1.6x10 ⁵	10.3	7.07	7.44	11.4	7.67	8.37	9.04	5.31	7.31
2.5x10 ⁵	10.3	7.02	7.49	11.3	7.58	8.43	9.06	5.27	7.37
4.0x10 ⁵	10.3	7.00	7.51	11.3	7.51	8.48	9.08	5.27	7.40
6.3x10 ⁵	10.4	6.99	7.64	11.4	7.51	8.59	9.18	5.25	7.53
10 ⁶	11.5	4.82	10.4	12.3	5.67	10.9	10.7	3.05	10.2

Table 5. Values of C_E/A and α_E , with mean and standard deviation, for the 12 sets of graphite electrodes measured with one layer of filter paper saturated in 0.01 N NaCl.

Graphite electrode pair no.	r_D (cm)	C_E/A ($\times 10^{-4}$ F/cm ²)	μ (C_E/A) ($\times 10^{-4}$ F/cm ²)	σ (C_E/A) ($\times 10^{-4}$ F/cm ²)	α_E	μ (α_E)	σ (α_E)
1a	5.74	1.06	1.61	0.496	0.230	0.225	0.069
1b	5.74	1.25			0.184		
1c	5.74	1.60			0.181		
1d	5.74	1.34			0.197		
1e	5.74	2.20			0.200		
1f	5.74	2.23			0.360		
2a	3.77	1.72	2.74	0.952	0.235	0.231	0.023
2b	3.77	3.11			0.251		
2c	3.77	3.17			0.190		
2d	3.77	1.56			0.220		
2e	3.77	4.07			0.250		
2f	3.77	2.82			0.238		

4.07×10^{-4} F/cm², with a μ of 2.74×10^{-4} F/cm² and a σ of 0.952×10^{-4} F/cm². The α_E values for these electrodes are in the range 0.190 to 0.251, with a μ of 0.231 and a σ of 0.023.

DISCUSSION AND CONCLUSIONS

The C_E/A and α_E (Table 5) determinations display a relatively wide range of values ($1.06 \pm 0.5 \times 10^{-4}$ to $4.07 \pm 0.93 \times 10^{-4}$ F/cm² for C_E/A , and 0.18 ± 0.02 to 0.36 ± 0.07 for α_E) for the pairs of electrodes with different diameters. The maximum and minimum C_E/A values of the range are in a similar order of magnitude, but the difference between them is too great to allow assignment of a single representative value to the graphite-electrode plates for use in the laboratory spectral-IP measurements. Although the error ranges ($\pm\sigma$), represented by the standard deviation (σ) values, for both diameters of electrode (5.74 and 3.77 cm) are less than 1, the C_E/A values for each specific pair of graphite electrodes must be known in order to accurately eliminate the electrode effect from the spectral-IP measurements. In comparison, the α_E values display a considerably smaller range of variation. Nevertheless, these values have a considerably greater effect on the spectral-IP measurements than the C_E/A values, implying that they also must be known for each specific pair of graphite electrodes, in order to eliminate the electrode effect from the spectral-IP measurements.

The imaginary impedance versus frequency (Z'' -f) curves for the graphite electrodes of different diameters (Fig. 3, 4) indicate that the linear sections have a frequency range wide enough at the lower frequency end of the curves to determine the C_E/A and α_E values with good accuracy. This implies that the C_E/A and α_E values can be considered to have good accuracy.

When these results (Table 5) are compared with those of the previous study (Katsube and Scromeda-Perez, 2003, Table 2), the C_E/A and α_E values for the same electrode sets are exactly the same. This is very surprising, considering that

three years have passed between the two sets of measurements and that each set of electrodes has been used for at least 30 to 40 measurements during that time. Initially, these electrode characteristics were expected to change slightly from measurement to measurement, due to wearing and contamination of the electrode surfaces by the chemical characteristics of the sample under test. The importance of this type of repeatability test arose from this concern. The results of this study suggest that the C_E/A and α_E values in Table 5 can be assigned to each set of graphite electrodes with confidence. Nonetheless, these repeatability tests and the statistical analysis should be carried out from time to time until more of the theoretical background of the wearing and contamination of the electrode surfaces is known.

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